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# Theoretical grounds of relativistic methods for calculation of spin – spin coupling constants in nuclear magnetic resonance spectra

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The theoretical grounds of the modern relativistic methods for quantum chemical calculation of spin – spin coupling constants in nuclear magnetic resonance spectra are considered. Examples and prospects of application of relativistic calculations of these constants in the structural studies of organic and heteroorganic compounds are discussed. Practical recommendations on relativistic calculations of spin – spin coupling constants using the available software are given. The bibliography includes 622 references.

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## I. Introduction

In our previous review,[1] we considered the theoretical grounds and the prospects of practical use of modern quantum chemical methods for calculation of spin – spin coupling constants (SSCCs) in the nuclear magnetic resonance (NMR) spectra at a non-relativistic level. However, for the molecular electron – nuclear systems involving one or several heavy nuclei, near which electrons have relativistic velocities, the description of the electronic structure at the non-relativistic level is inadequate. Hence, a different approach is needed, namely, the use of Einstein's special theory of relativity, which actually underlies all of the modern relativistic calculations of SSCCs. It is noteworthy that resorting to the general relativity theory is of no meaning in atomic/molecular mechanics and, particularly, in the case of relativistic calculations of SSCCs because of the negligibly small contribution of gravity forces.

Owing to the exceptionally high computational demands of relativistic calculations of SSCCs (the computational effort is incomparably greater than that involved in non-relativistic calculations), studies of this type are few and are restricted to consideration of small molecules, and the number of publications on the calculation of SSCCs within the full four-component relativistic Dirac approach is even smaller. Nevertheless, such papers appear and would appear more often with the development of computer hardware and software.

This brings about a reasonable question of what particular nuclei should be considered heavy enough, *i.e.*, where the SSCC calculation at the non-relativistic level becomes inadequate and relativistic approaches are needed. According to our many-year experience, taking account of relativistic effects already makes sense starting from elements of the third period, especially with a 'heavy' environment, and becomes absolutely obligatory for elements of the fourth and, the more so, the fifth period. For example, this refers in full measure to calculations of the $^{29}Si-{}^{13}C$, $^{31}P-{}^{13}C$, $^{77}Se-{}^{1}H$, $^{77}Se-{}^{13}C$, $^{125}Te-{}^{1}H$ and $^{125}Te-{}^{13}C$ coupling constants. Moreover, relativistic effects can be significant for calculation of the SSCCs between light nuclei (*e.g.*, $^{1}H-{}^{1}H$, $^{13}C-{}^{1}H$, $^{15}N-{}^{1}H$, $^{13}C-{}^{13}C$, $^{13}C-{}^{15}N$, $^{13}C-{}^{19}F$ and so on) if the molecule contains atoms of the fourth and higher periods that are not directly involved in the spin – spin coupling (secondary relativistic effects).

Considering the chemical diversity encountered by a research chemist, a review of modern relativistic methods for quantum chemical calculation of SSCCs seems highly topical, especially as the matters stand in Russia.

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This review surveys the foundations of the relativistic theory of nuclear spin coupling which is measured experimentally as SSCCs in the NMR spectra. We discuss the modern relativistic methods for quantum chemical calculation of SSCCs in terms of both full four-component relativistic Dirac equation and various approximate two-component procedures. A number of problems faced by SSCC relativistic calculations (first of all, fulfilment of kinetic balance conditions and the variational collapse) as well as the accuracy factors of relativistic calculations by various methods are analyzed. The software used in the world practice for the relativistic calculations of SSCCs are presented and practical recommendations for performing such calculations with the prospect of using them in structural studies are given.

The following mathematical designations are used in the review. Vectors are denoted by characters with arrows above them ($\vec{a}$). Matrices are typed in bold (**A**) and can be written as both lower- and upper-case Latin and Greek letters in accordance with the generally accepted international conventions applied for particular matrices pertaining to relativistic quantum mechanics. Hence, matrix vectors, *i.e.*, matrices consisting of several components are typed in bold and have an arrow above them ($\vec{\mathbf{A}} = \{\mathbf{A}_1, \mathbf{A}_2, ...\}$). The circumflex accent sign above the character ($\hat{a}$) implies an operator, in particular, this sign marks the matrix, vector and vector matrix operators ($\hat{\mathbf{A}}$, $\hat{\vec{a}}$ and $\hat{\vec{\mathbf{A}}}$).

The abbreviations used in the text are expanded below.

*Abbreviations derived from scientist's names*

BSS — Barysz – Sadlej – Snijders,
D — Dirac,
DC — Dirac – Coulomb,
DCB — Dirac – Coulomb – Breit,
DHF — Dirac – Hartree – Fock,
DHFR — Dirac – Hartree – Fock – Roothaan,
DKH1 — First-Order Douglas – Kroll – Hess,
DKH2 — Second-Order Douglas – Kroll – Hess,
DKS — Dirac – Kohn – Sham,
F — Fermi,
FW — Foldy – Wouthuysen,
HF — Hartree – Fock,
SH — Schrödinger,
VWN — Vosko – Wilk – Nusair.

*Other abbreviations*:

A2C — Approximate 2-Component,
ADC — Algebraic Diagrammatic Construction,
AMFI — Atomic Mean-Field Integral,
COSMO — Conductor-like Screening Model,
CC — Coupled Clusters,
CISD — Configuration Interaction Singles and Doubles,
CCSD — Coupled Clusters Singles and Doubles,
CI — Configuration Interaction,
CPDFT — Coupled-Perturbed Density Functional Theory,
DE — Dirac Exact,
DFT — Density Functional Theory,
DPT — Direct Perturbation Theory,
4-DPT — 4-Component Direct Perturbation Theory,
DMRG — Density Matrix Renormalization Group,
DSO — Diamagnetic Spin – Orbit,
DZ — Double-zeta,
EFW — Exact Foldy – Wouthuysen,
EOM — Equation of Motion,
EOM-CC — Equation of Motion Coupled Cluster Method,
ESC — Elimination of the Small Component,
FC — Fermi-Contact,
HCS — Homogeneously Charged Sphere,
fpFW — free particle FW,
IEF – PCM — Integral Equation Formalism Polarizable Continuum Model,
IP — Inner Projection,
GAS-CC — Generalized-Active-Space-Coupled Clusters,
GGA — Generalized Gradient Approximation,
LDA — Local Density Approximation,
LDBS — Locally Dense Basis Set,
FORA — First-Order Regular Approximation,
IOTS — Infinite-Order Two-Component,
IORA — Infinite-Order Regular Approximation,
IORAmm — Infinite-Order Regular Approximation with modified metric,
KR-MCSCF — Kramers-Restricted MCSCF,
mDKS-RMB — matrix Dirac – Kohn – Sham Restricted Magnetic Balance,
MFA — Mean Field Approximation,
MFSSO — Mean Field Spin-Same-Orbit,
MRCC — Multi Reference CC,
MCSFC — Multi-Configurational Self-Consistent,
MPE — Multiple-Expansion Method,
MRCC — Multi-Reference CC,
NESC — Normalized ESC,
NVPA — No Virtual-Pair Approximation,
OPM — Optimal Potential Method,
ODA — Orbital Decomposition Approach,
PCE — Picture Change Error,
PCM — Polarizable Continuum Model,
PSO — Paramagnetic Spin-Orbit,
RA — Regular Approximation,
RDFT — Relativistic DFT,
relECP — Relativistic Effective Core Potential,
RESC — Relativistic Scheme by Eliminating Small Components,
RFM — Reaction Field Method,
RFW — Regular FW,
RKB — Restricted Kinetic Balance,
RLDA — Relativistic LDA,
RMB — Restricted Magnetic Balance,
RPA — Random Phase Approximation,
RPF — Relativistic Prolapse-Free,
RI — Resolution of Identity,
SCF — Self-Consistent Field,
SD — Spin-Dipolar,
SO — Spin – Orbit,
SORA — Second-Order Regular Approximation,
SOO — Spin-Other-Orbit,
SS — State Selective Ansatz,
SSCC — Spin–Spin Coupling Constant,
SSO — Spin-Same-Orbit,
TD-DHF — Time-Dependent DHF,
TD-RDFT — Time-Dependent RDFT,
TZ — Triple-zeta,
UKB/EKB — Unrestricted/Extended Kinetic Balance,
UESC — Unnormalized ESC,
QZ — Quadruple-zeta,
QM/MM — Quantum Mechanics/Molecular Mechanics,

X2C — Exact 2-Component,
X2Cmmf — X2C with molecular-mean-field,
ZFC — ZORA FC,
ZSD — ZORA SD,
ZORA — Zeroth Order Regular Approximation.

## II. Structural applications of spin–spin coupling constants for heavy atoms

The spin–spin coupling constants for the nuclei of spin-1/2 isotopes of heavy elements, starting from elements of the fourth period, are most often determined quite easily from the NMR spectra of samples with natural isotope abundances and provide unique information, first of all, about the stereoelectronic structure of heteroorganic compounds. However, quantum chemical calculation of such SSCCs is highly resource-consuming and contains quite a number of pitfalls even for a skilled professional. This is largely due to strong relativistic effects that have to be taken into account for correct comparison of the computational and experimental results.

The stereospecificity of SSCCs, which is most clear-cut for heavy atoms (such as $^{77}$Se, $^{119}$Sn, $^{125}$Te, $^{199}$Hg and $^{209}$Pb) and somewhat less pronounced for light atoms (such as $^{1}$H, $^{13}$C, $^{15}$N, $^{19}$F, $^{29}$Si and $^{31}$P), is related, first of all, to the lone pair (LP) effect. According to our many-year research, selenium[2] and tellurium[3] atoms have a very

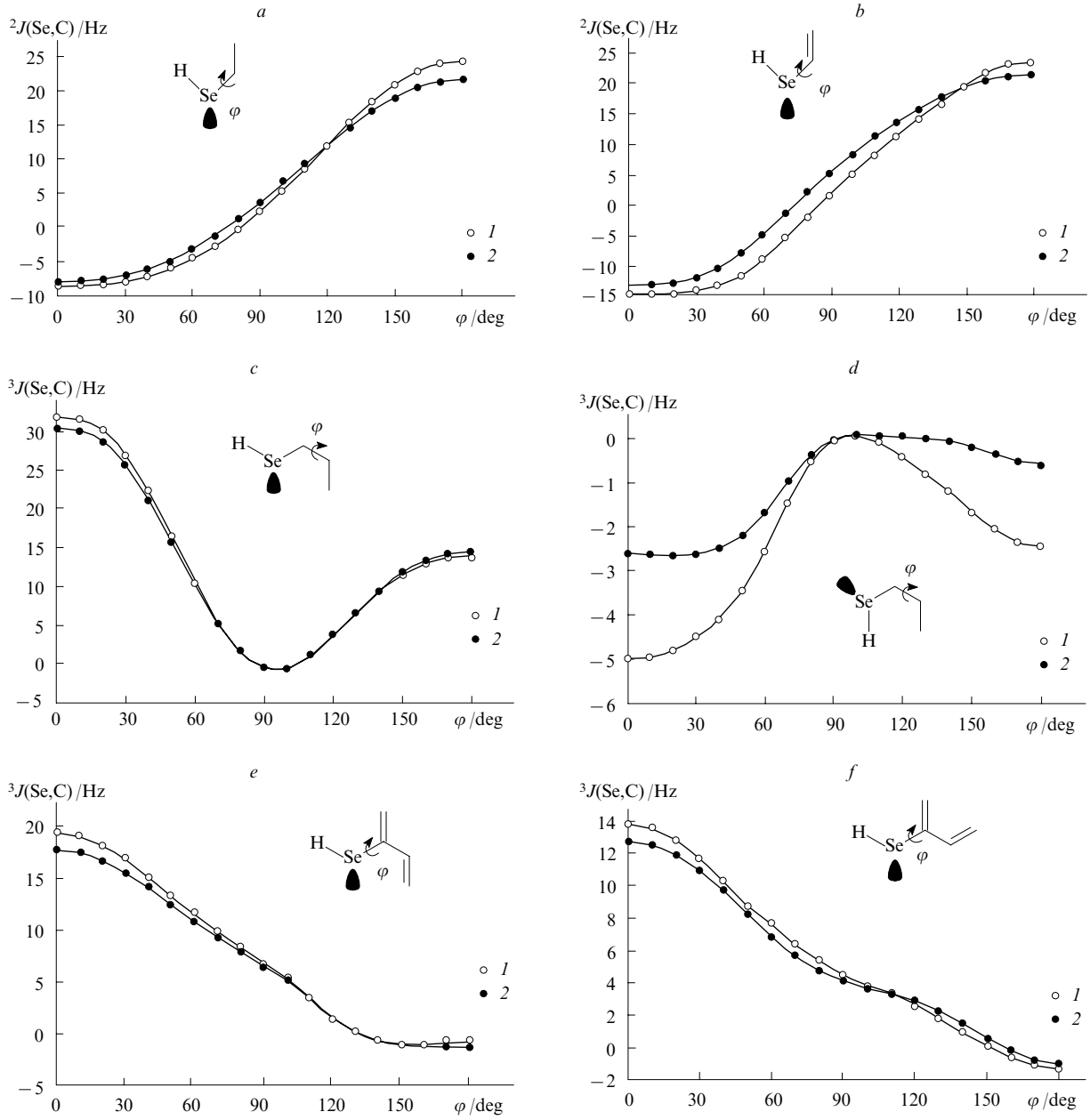



**Figure 1.** Angular dependences of the geminal and vicinal $^{77}$Se–$^{13}$C coupling constants in various molecules (*a*–*f*) calculated considering relativistic effects in the full four-component relativistic DFT scheme (*1*) and non-relativistic calculation results (*2*) (from the data of Ref. 4).

strong LP effect, which can be described correctly only taking account of relativistic effects.

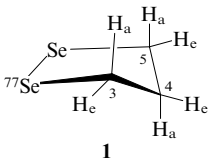
Rusakov and Krivdin [4] considered the stereochemical behaviour of the $^2J(^{77}Se,^{13}C)$ and $^3J(^{77}Se,^{13}C)$ constants taking into account the relativistic effects in terms of the full four-component relativistic DFT scheme. The dependences of the geminal and vicinal constants on the dihedral angle in open-chain alkyl and alkenyl selenide molecules determined in this study are shown in Fig. 1.

As can be seen, the stereochemical dependences of $^2J(^{77}Se,^{13}C)$ and $^3J(^{77}Se,^{13}C)$ calculated considering the relativistic effects largely resemble the non-relativistic analogues; however, in some cases, the classical Karplus curves [5] are determined to a considerable extent by particularly the relativistic component. The LP effect on the stereochemical behaviour of the $^2J(^{77}Se,^1H)$ and $^3J(^{77}Se,^1H)$ constants is also fairly pronounced. In particular, this was confirmed by calculations performed using non-relativistic second-order polarization propagator methods for unsaturated selenium-containing heterocycles,[6–8] selanylallenes,[9] diselenanes and diselenolanes [10] as well as for selenium-modified natural sugars and glycosides.[11, 12]

As can be seen from the several examples of the use of quantum chemical calculations of the $^{77}Se-^1H$ and $^{125}Te-^1H$ coupling constants in structural studies of organoselenium and -tellurium compounds, which are given below, the clear-cut stereospecificity of SSCCs for heavy nuclei to the LP orientation effect can serve for solving unique stereochemical problems.

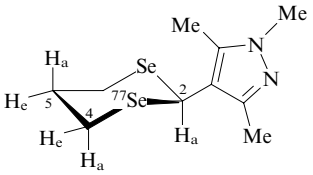
Rusakov *et al.*[10] investigated the stereochemical behaviour of the geminal and vicinal $^{77}Se-^1H$ constants in the pyrazolyl-1,3-diselenane and 1,2-diselenolane series at the level of second-order polarization propagator approximation and established a pronounced stereospecificity of both types of SSCCs to the LP orientation effect of selenium. This stereospecificity results in a substantial (up to 30 Hz!) difference between the geminal and vicinal constants between selenium and axial or equatorial protons, which is illustrated below in relation to unsubstituted 1,2-diselenolane (**1**) and 2-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)-1,3-diselenane (**2** ). The calculated $^2J(^{77}Se,^1H)$ and $^3J(^{77}Se,^1H)$ constants were used to perform the conformational analysis of the 1,2-diselenolane and 1,3-diselenane rings.[10]

**Structures 1, 2**




**1**

$^2J(Se,H_{3a}) = 2.38$ Hz
$^2J(Se,H_{3e}) = 27.09$ Hz
$^3J(Se,H_{4a}) = 0.92$ Hz
$^3J(Se,H_{4e}) = 13.22$ Hz

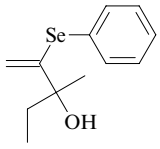



**2**

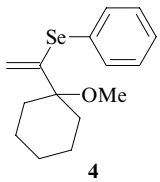
$^2J(Se,H_{4a}) = -1.32$ Hz
$^2J(Se,H_{4e}) = 27.38$ Hz
$^3J(Se,H_{5a}) = 4.05$ Hz
$^3J(Se,H_{5e}) = 12.81$ Hz

An interesting example of stereoelectronic effects is provided by sterically hindered phenylselanylalkenes **3** – **7** studied by Rusakov *et al.*[9]

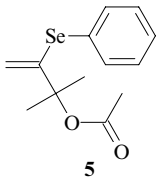
**Structures 3 – 7**



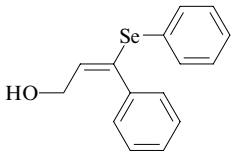

**3**



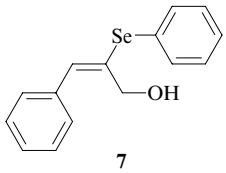

**4**




**5**



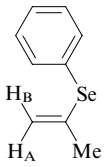

**6**




**7**

According to theoretical computational data and experimental measurement of the vicinal $^{77}Se-^1H$ coupling constants across a double bond, all compounds of this series, except for compound **6**, assume a *gauche-s-cis*-conformation at the $Se-C_{sp}^2$ bond. Meanwhile, compound **6** exists in a *trans*-conformation stabilized by a strong π-stacking interaction between two phenyl groups. The stereospecificity of vicinal $^{77}Se-^1H$ coupling constants across a double bond can be illustrated by the example of the simplest selanylalkene **8** for which two SSCCs with the cisoid and transoid spin – spin coupling constants were calculated and compared with the experiment (the experimental values are given in parentheses). The LP orientational effect manifested in the geminal and vicinal $^{77}Se-^1H$ constants, which is well reproduced in calculations, can serve for performing the stereochemical analysis of organoselenium compounds with free and hindered internal rotation around the Se – C bond.

**Structure 8**

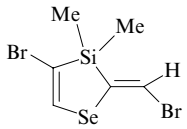



**8**

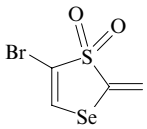
$^3J(Se,H_A) = 8.27$ (7.4) Hz
$^3J(Se,H_B) = 4.57$ (4.7) Hz

Yet another illustrative example of using high-level *ab initio* calculations of the $^{77}Se-^1H$ constants in structural studies is provided by conformational analysis and assignment of diastereotopic protons in the series of selenasilole **9**, thiaselenole **10**, thriaselenolane **11** and dihydrothiaselenine **12** derivatives.[6, 7]

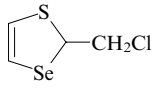
**Structures 9 – 12**



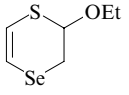

**9**




**11**



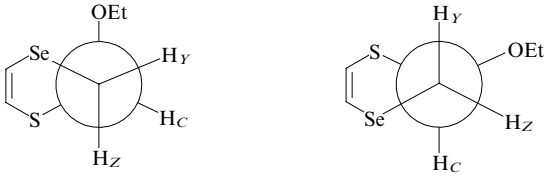

**10**




**12**

The calculations showed that in the preferred conformations of dihydrothiaselenine **12** (*A* and *B*), the geminal $^2J$(Se,H) constants involving coupling of the $H_Y$ and $H_Z$ diastereotopic protons differ by almost 20 Hz as a result of the LP orientational effect (26 and 8 Hz for the *cis*- and *trans*-orientations of the selenium LP, respectively); comparison with the experiment enables unambiguous assignment of this diastereotopic pair.

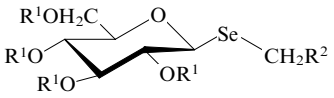
**Structures 12*A*,*B***




*A* *B*

A similar assignment of diastereotopic protons by the same procedure was carried out for much more complex biochemical objects — selenium-modified sugars, selenoglycosides **13**–**15**.[12]

**Structures 13–15**



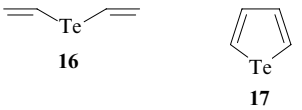

**13–15**

**13**: $R^2$ = H: $R^1$ = H (**a**), $R^1$ = Me, $R^2$ = H (**b**); $R^1$ = Ac, $R^2$ = H (**c**);
**14**: $R^1$ = H, $R^2$ = Me;
**15**: $R^1$ = Ac: $R^2$ = Me (**a**), Ph (**b**), *p*-CN–Ph (**c**), *p*-MeO–Ph (**d**), *p*-$NO_2$–Ph (**e**), *p*-Br–Ph (**f**), *m*-Cl–Ph (**g**), *o*-$CF_3$–Ph (**h**).

Calculations and experimental measurements of the geminal SSCCs between selenium and diastereomeric methylene protons allowed unambiguous diastereotopic assignment of the latter in the selenoglycoside **13**–**15** side chains, while the calculations of geminal SSCCs between selenium and the anomeric proton in the same series of compounds were used to establish the configuration of the anomeric centre and to determine the effective conformations of molecules **13**–**15** related to the internal rotation around the anomeric Se–C bond.[11,12]

A correlated calculation of the geminal and vicinal $^{125}$Te–$^1$H constants for divinyl telluride (**16**) and tellurophene (**17**) with allowance for relativistic effects, solvent effect and vibrational corrections has been reported.[3]

**Structures 16, 17**




**16** **17**

The LP orientational effect of tellurium in the geminal and vicinal $^{125}$Te–$^1$H coupling constants can be as high as 100 Hz (!) (Fig. 2); this makes this type of SSCCs exceptionally useful for stereochemical analysis of organotellurium compounds, in particular, for assignment of the configuration at the double bond in the molecules of tellurium alkyne derivatives.

Thus, a brief excursion to the structural applications of SSCCs involving heavy nuclei demonstrated how important

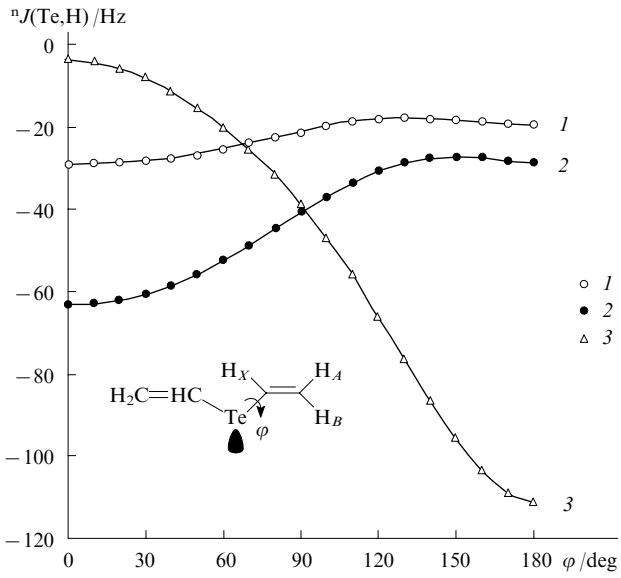



**Figure 2.** Angular dependences of the geminal and vicinal $^{125}$Te–$^1$H coupling constants for divinyl selenide calculated by DFT considering relativistic effects in terms of the quasirelativistic two-component zero order scheme (from the data of Ref. 3). (*1*) $^3J$(Te,$H_B$), (*2*) $^3J$(Te,$H_A$), (*3*) $^2J$(Te,$H_X$).

it is to take into account the relativistic effects in the quantum chemical calculations of these parameters for solving stereochemical problems of heteroorganic chemistry.

## III. Some aspects of the relativistic quantum theory

### III.1. Relativistic effects

The effects caused by the difference between relativistic and non-relativistic views of physical reality are called relativistic effects.

The most vivid idea of the categories of relativistic effects manifested in molecules containing heavy nuclei can be derived from analysis of additional terms of the quasirelativistic many-body Breit–Pauli Hamiltonian[13] that distinguish it from the Schrödinger Hamiltonian, which does not at all take into account the spin degrees of freedom. The Breit–Pauli Hamiltonian is obtained by the Foldy–Wouthuysen (FW) procedure of elimination of the small component (ESC),[14–17] has the accuracy $O(c^{-2})$ and contains all terms corresponding to the most significant relativistic effects, in particular, mass–velocity, Darwin and spin–orbit coupling effects.

The mass–velocity effect corresponds to the relativistic increase in the particle mass with increase in the particle velocity. One more relativistic effect corresponding to the Darwin correction is related to smearing (coordinate uncertainty) of a moving charge (in this case, an electron). It can be represented as an additional electrostatic nuclear potential that acts on the oscillating electron with a coordinate fluctuating at a distance about $\delta r \approx 1/m_e$ (Schrödinger zitterbewegung) around the mean value.

The mass–velocity effect together with the Darwin effect form the scalar relativity, the former being regarded as the relativistic correction to the kinetic energy of an electron, while the latter is the correction to its potential

energy. These corrections have different signs; therefore for some orbitals they counterbalance each other and the overall scalar relativistic effect is almost absent for such orbitals.

Yet another, equally important effect, called spin – orbit coupling, results in splitting of spin orbitals with the orbital angular momentum $l > 0$ into two types: those with the spin parallel and antiparallel to the orbital angular momentum. In this case, the orbitals are defined by the principal angular momentum, which is the vectorial sum of the orbital angular momentum and the spin

$$\vec{J} = \vec{L} + \vec{S}$$

In this case, the usual quantum numbers are supplemented by the principal angular momentum quantum number $j$; thus, for the same angular momentum $l > 0$, there is a set of states with the quantum numbers ($j$, $m_j$).

In particular, the spin – orbit coupling eliminates the p-shell degeneracy *via* additional splitting into two degenerate $p_{1/2}$-orbitals ($j = 1/2$, the spin and the angular momentum are antiparallel) and four degenerate $p_{3/2}$-orbitals ($j = 3/2$, the spin and the angular momentum are parallel). The energies of $p_{1/2}$ and $p_{3/2}$ type orbitals are different, although the orbital quantum number is the same ($l = 1$). Similarly, the degeneracy is eliminated for other shells (Table 1).

The one-electron relativistic perturbations comprising scalar relativity and spin – orbit coupling are manifested as so-called direct relativistic effects, whereas all other (two-electron) terms give rise to some relativistic corrections to the effective electron – electron interaction potential and serve as a source of so-called indirect relativistic effects.

The scalar relativity is manifested to the highest extent as the contraction of $ns_{1/2}$ and $np_{1/2}$ type orbitals providing a non-zero probability for electrons to be located on the nucleus or in the near vicinity of the nucleus. For these orbitals, the order of relativistic effects is determined by the factor $Z_{ef}^2/c^2$, where $Z_{ef}$ is the effective nuclear charge,[19] and in this case, a strong direct relativistic effect is observed due to the fact that the effective nuclear charge for electrons that occupy the $ns_{1/2}$ and $np_{1/2}$ orbitals is comparable with the real nuclear charge ($Z$), *i.e.*, $Z_{ef} \approx Z$.

The electrons located in the inner (core) shells have a greater tangential component of velocity than the outer-shell electrons. Correspondingly, the Lorentz factor

$$\gamma = \left(\frac{1 - v^2}{c^2}\right)^{-1/2}$$

**Table 1**. Relativistic shells according to the notation of Swirles.[18]

| Shell | $s_{1/2}$ | $p_{1/2}$ | $p_{3/2}$ | $d_{3/2}$ | $d_{5/2}$ | $f_{5/2}$ | $f_{7/2}$ | $g_{7/2}$ | $g_{9/2}$ |
|---|---|---|---|---|---|---|---|---|---|
| Designation | s | $\bar{p}$ | p | $\bar{d}$ | d | $\bar{f}$ | f | $\bar{g}$ | g |
| Orbital quantum number $l$ | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| Principal orbital quantum number $j$ | 1/2 | 1/2 | 3/2 | 3/2 | 5/2 | 5/2 | 7/2 | 7/2 | 9/2 |
| Degree of degeneracy $(2j+1)$ | 2 | 2 | 4 | 4 | 6 | 6 | 8 | 8 | 10 |

will be much higher for these electrons, and the same is true for the effective mass ($m_0$ is the rest mass)[20]

$$m_{ef} = m_0 \gamma$$

Since the effective Bohr radius ($a_0$) is inversely proportional to the effective mass

$$a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{m_{ef} e^2}$$

and the radial maximum of orbits $R_n = a_0 n^2$ is directly proportional to $a_0$, then it is evident that the higher the effective mass of the electron in this shell, the more pronounced the relativistic displacement toward the nucleus. The degree of appearance of relativity is directly dependent on the nuclear charge. Indeed, for the hydrogen atom, the relativistic orbital contraction is scarcely observed, whereas it is quite noticeable for mercury. In particular, the 1s shell of mercury ($Z_{Hg} = 80$) is contracted by 23% because of the direct relativistic effects in comparison with the non-relativistic consideration.[20]

It is noteworthy that s and $p_{1/2}$ type valence orbitals are subject to some scalar relativistic effect, despite the fact that the radial maximum of these orbitals is far beyond the near-nuclear region and the shielding of the nucleus is substantial in remote points. The reason is that the probability for these electrons to be located near the nucleus is non-zero. Moreover, the dependence of the relativistic contraction of the s type atomic valence orbitals on the full (non-shielded) nuclear charge was shown [21] to be quadratic, which means that the direct relativity would affect these orbitals as strongly as it affects the inner orbitals of the same type.

The direct spin – orbit effect becomes less significant with increasing orbital quantum number $l$. From the mathematical standpoint, this is explained in the following way: the atomic integrals of the angular component of the spin – orbit operator increase with increasing $l$; however, the radial integrals decrease much faster than the angular integrals increase because the probability for atomic orbitals with large $l$ to be located near the nucleus is too low.

Thus, direct relativistic effects are quite significant in the near-nuclear region and play the primary role in the energy stabilization and contraction of orbitals with non-zero electron density on or near the nucleus, namely, the $ns_{1/2}$- and $np_{1/2}$-orbitals. However, this does not at all mean the lack of influence of the direct relativity on the outer orbitals, for example, d or f type orbitals. This influence is present but it is very low as compared with the effect on the s- and $p_{1/2}$-orbitals. Moreover, it is well known that contraction of inner orbitals enhances the already strong shielding of the nucleus for valence orbitals, which results, on the one hand, in a noticeable weakening of the direct relativistic effect and, on the other hand, in expansion and energy destabilization of these orbitals.

From the above, it could follow that the effect of relativity on the valence orbitals having zero or negligibly low electron density on or near the nucleus should be insignificant as the direct effect is highly suppressed in this case by considerable shielding of the nucleus: $Z_{ef} \ll Z$. However, as shown by relativistic quantum chemical calculations,[22] this assumption is quite misleading. Moreover, it was found [22] that for a hydrogen-like atom, the extent of

influence of relativistic effects on the valence orbital $\mu$ is determined by the relativistic correction

$$\delta a_\mu = \frac{c^a_{l,j} Z^2}{c^2}$$

to the average value of the one-electron operator of some physical quantity $\hat{a}$ in this orbital; $Z$ is the full unshielded nuclear charge; the coefficients $c^a_{l,j}$ are determined by the pair of quantum numbers which characterize this orbital $\mu$; in some cases, they exceed the same coefficients for inner orbitals. The quadratic dependence of $\delta a_\mu$ on the total nuclear charge is attributable to an indirect relativistic effect.

From the physical standpoint, the indirect relativistic effect is caused by the direct relativistic effect on each electron; in total, this leads to a change in the potential energy of interaction of each electron with all other electrons and gives rise to some additional (induced) shielding of the nucleus. In its mathematical essence, the indirect relativistic effect is based on the requirement of mutual orthogonality of molecular orbitals that result from the self-consistency procedure. As a result of an arbitrarily small direct relativistic effect on at least one inner orbital that passes through the nucleus, all other molecular orbitals should be redistributed according to the mutual orthogonality requirement. From this it follows that indirect relativistic effects have relevance to all types of orbitals, unlike the direct relativistic effects, the maximum appearance of which is restricted by the subset of orbitals that are located near the nucleus or pass through the nucleus.

The contraction of s and $p_{1/2}$ type orbitals penetrating into the near-nuclear region does not induce a pronounced energy destabilization of both s and $p_{1/2}$ valence orbitals as well as d- and f-orbitals. Meanwhile, the direct relativistic contraction of orbitals having a radial maximum in the close vicinity of the radial maxima of d and f valence orbitals has a considerable destabilizing indirect relativistic effect on the latter. As a rule, these orbitals comprise s and $p_{1/2}$ type valence orbitals,[22] which, on the one hand, have a radial maximum located far beyond the inner region in the neighbourhood of the radial maxima of the d and f valence orbitals, and, on the other hand, they affect the neighbourhood of the nucleus, which exposes them to the influence of direct relativity, which is capable of inducing relativistic contraction and the subsequent indirect relativistic effects on the other part of the molecular orbital set. In a study devoted to the effect of relativity on the electronic configuration of neutral atoms of d- and f-elements, Autschbach *et al.*[23] analyzed the relativistic changes in the inner and valence orbitals. It was shown that in neutral many-electron atoms, s- and p-orbitals undergo relativistic contraction and are stabilized,[24] whereas the d- and f-orbitals experience the indirect relativistic expansion effect, which is a consequence of the contraction of s- and p-orbitals of the same atomic shell and shells with greater principal quantum numbers.

The direct and indirect relativistic effects produce together the total relativistic effect, which can prove to be much lower than its components as a result of mutual exclusion. For example, s-orbitals are mainly affected by direct relativity; therefore, virtually no mutual exclusion with the indirect effects takes place in this case. This gives rise to clear-cut relativistic contraction of s-orbitals and energy stabilization. The p-type orbitals are much less affected by the relativity than the s-orbitals, as direct and indirect effects are nearly equivalent, which results in the almost complete mutual exclusion. The d and f type orbitals are affected to the greatest extent by indirect relativity, while the role of direct relativity is minor; therefore, as for the s-orbitals, the total relativistic effect is significant in this case. Unlike the stabilizing action of the total relativistic effect on s-orbitals, in the case of d- and f-orbitals, this leads to spatial expansion and energy destabilization.[25]

A very important issue related to the relativistic change in the 3D shape of orbitals is the effect of relativity on intramolecular bonds. This issue is considered in a number of publications[26–33] reporting the results of many-year theoretical research. It is evident that factors such as the relativistic contraction (or expansion) of atomic and molecular orbitals, change in the *s*-character and bond lengths and relativistic change in the geometry and electronic configuration also substantially affect the SSCC values.

### III.2. Dirac formalism

A detailed account of the theoretical grounds of relativistic quantum chemistry methods is given in a number of monographs[34–47] and reviews.[19,48–52] We will dwell on some issues that are important for relativistic calculations of molecular properties, in particular, SSCCs.

Consider a free fermion, because all common designations and the mathematical apparatus proceed from this simple case, while the extension to a many-body state and taking account of the presence of an external electromagnetic field do not go far beyond this apparatus.

The time evolution of a free quantum particle in the non-relativistic representation is described by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \widehat{H}_{SH} \psi(\vec{r}, t) \quad (1)$$

where $\widehat{H}_{SH} = \widehat{T}$ is a simple quantum-mechanical kinetic energy operator $\widehat{T} = \hat{\vec{p}}^{\,2}/2m$, while the momentum operator in the coordinate representation has the form $\hat{\vec{p}} = -i\hbar\hat{\vec{\nabla}}$. This equation is not Lorentz-covariant, its left- and right-hand parts being transformed in different ways. Therefore, this is not a satisfactory equation for the relativistic representation. Moreover, Eqn (1) does not contain a spin operator.

In order to pass to the relativistic analogue, it is necessary to assign a particular quantum mechanical operator to the Einstein relativistic energy[53,54] of a free moving particle. Thus, the square root is initially taken as a free relativistic Hamiltonian; the expression under the radical includes the second derivatives with respect to coordinates

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \sqrt{-\hbar^2 c^2 \hat{\nabla}^2 + m^2 c^4}\, \psi(\vec{r}, t) \quad (2)$$

A series expansion of the square root contains an infinite number of terms with different powers of the differentiation operator with respect to spatial coordinates. The time evolution operator in the left-hand side always appears in the 1st power. Thus, the space coordinates and time appear in the equation in an unsymmetric fashion, the theory itself being non-local. Moreover, this description does not consider the spin degree of freedom.

The search for a proper quantum equation requires a different approach. One of such equations is the Klein – Gordon equation, which has been obtained by the repeated action of the time differentiation operator on the Eqn (2) using the commutation relation between differentiation operators with respect to time and spacial coordinates. As a result, the Klein – Gordon equation

$$-\hbar^2 X \frac{\partial^2}{\partial t^2}\psi(\vec{r},t) = (-\hbar^2\hat{\nabla}^2 c^2 + m^2c^4)\,\psi(\vec{r},t) \tag{3}$$

is represented as a classical wave equation, which is not free from drawbacks either. First, there are the negative energy solutions, which represent the antiparticles and give rise to extra problems in the practical relativistic calculations. Second, the probability density derived from Eqn (3) is not positively defined and, therefore, the probability interpretation is inadmissible in this case. Third, Eqn (3) does not contain a spin operator.

Dirac proposed that the square root be linearized, so that the differentiation operators with respect to space coordinates are of the first order, *i.e.*, of the same order as the time differentiation operator in the left-hand side of Eqn (2).[55–57] The general form of this equation is as follows:

$$\mathrm{i}\hbar\frac{\hat{\partial}\boldsymbol{\psi}(\vec{r},t)}{\partial t} = \left(c\,\vec{\boldsymbol{\alpha}}\,\hat{\vec{p}} + mc^2\boldsymbol{\beta}\right)\boldsymbol{\psi}(\vec{r},t) \tag{4}$$

Equation (4) is the Dirac equation for a free particle. In order to determine the unknowns $\boldsymbol{\beta}$ and $\vec{\boldsymbol{\alpha}}$, it is necessary to quadrate Eqn (4) and compare it with the Klein – Gordon equation (3). This results in equations for $\boldsymbol{\beta}$ and $\vec{\boldsymbol{\alpha}}$, from which one can see that they are matrices (called the Dirac matrices), which obey the following algebra:

$$\{\boldsymbol{\alpha}_i, \boldsymbol{\alpha}_k\} = 2\delta_{ik}\mathbf{I} \tag{5}$$

$$\{\boldsymbol{\alpha}_i, \boldsymbol{\beta}\} = \mathbf{0} \tag{6}$$

$$\boldsymbol{\alpha}_i^2 = \boldsymbol{\beta}^2 = \mathbf{I} \tag{7}$$

In order to establish the general form of Dirac matrices, it is necessary to consider the following circumstances: first, for the Hamiltonian in Eqn (4) to remain Hermitian, it is necessary that $\boldsymbol{\beta}$ and $\vec{\boldsymbol{\alpha}}$ be also Hermitian; second, from the last condition (7), it follows that the eigenvalues of these matrices should be $\pm 1$; third, from anticommutation relations (5) and (6), it follows that these matrices should be traceless and, hence, they should have an even dimension. The minimal even dimension of the $\boldsymbol{\beta}$ and $\vec{\boldsymbol{\alpha}}$ that meets all of these conditions is 4 (this establishes the minimal dimension for one-particle approximations of various relativistic approaches for the calculation of SSCCs).

The Dirac matrices in the block form are expressed as

$$\vec{\boldsymbol{\alpha}} = \begin{pmatrix} \mathbf{0}_{2\times 2} & \vec{\boldsymbol{\sigma}}_{2\times 2} \\ \vec{\boldsymbol{\sigma}}_{2\times 2} & \mathbf{0}_{2\times 2} \end{pmatrix} \tag{8}$$

$$\boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & -\mathbf{I}_{2\times 2} \end{pmatrix} \tag{9}$$

where $\vec{\boldsymbol{\sigma}}$ are the Pauli matrices related to the spin operator $\hat{\vec{\mathbf{S}}} = (\hbar/2)\vec{\boldsymbol{\sigma}}$

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{10}$$

$$\boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{11}$$

$$\boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{12}$$

For the Pauli matrices the following relations can be established:

$$\{\boldsymbol{\sigma}_i, \boldsymbol{\sigma}_j\} = \delta_{ij}\mathbf{I} \tag{13}$$

$$\boldsymbol{\sigma}_i^2 = \mathbf{I} \tag{14}$$

$$\boldsymbol{\sigma}_i\boldsymbol{\sigma}_j = \delta_{ij}\mathbf{I} + \mathrm{i}\varepsilon_{lij}\boldsymbol{\sigma}_l \tag{15}$$

Equation (15) uses the Einstein notation, which implies summation over the repeating indices.

The Pauli spin matrices $\vec{\boldsymbol{\sigma}} = (2/\hbar)\hat{\vec{\mathbf{S}}}$ appear naturally upon the root linearization, *i.e.*, the notion of spin follows from the specific form of the expression for the Einstein relativistic energy.

On the other hand that artificial inclusion of spin into consideration *via* the Pauli matrices leads to a system of two-component equations; they can be gathered into a four-component Dirac equation from which one can derive the Einstein formula for energy.[58] Therefore, it is difficult to determine what is the cause and what is the consequence.

The Dirac equation in the form (4) is completely defined and meets all of the requirements; in particular, it is Lorentz-covariant, it ensures a positively defined probability density, thus permitting the probability interpretation, and, furthermore, the notion of spin appears here as an additional degree of freedom.

The appearance of spin in the Dirac equation implies the possibility of interpreting spin as only a relativistic additional degree of freedom. However, it is noteworthy that, although neither the Schrödinger equation nor the Klein – Gordon equation contain spin operators in an explicit form, the particle spin still cannot be regarded as pertaining only to the relativistic theory. Formally, it can be demonstrated that in the construction of the correct four-component non-relativistic limit proposed by Lèvy-Leblond,[59] the spin operator is retained, although mathematically this scheme is equivalent to the Schrödinger one. Thus, it should not be deemed that spin has an exclusively relativistic nature.

After separation of the temporal part, the stationary Dirac equation can be written in a convenient block form (since our subsequent consideration would concern bound particles, it is expedient to add a potential at this stage)

$$\hat{\mathbf{h}}^{\mathrm{D}}_{4\times 4}\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1} = \left(c\,\vec{\boldsymbol{\alpha}}\,\hat{\vec{p}} + mc^2(\boldsymbol{\beta} - \mathbf{I}) + \hat{V}\mathbf{I}\right)_{4\times 4}\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1} = \tag{16}$$

$$= \begin{pmatrix} \hat{V}\mathbf{I}_{2\times 2} & c\vec{\boldsymbol{\sigma}}_{2\times 2}\hat{\vec{p}} \\ c\vec{\boldsymbol{\sigma}}_{2\times 2}\hat{\vec{p}} & (\hat{V} - 2mc^2)\,\mathbf{I}_{2\times 2} \end{pmatrix}\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1} = E\,\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1}$$

The energy scale of Eqn (16) is shifted in such a way that the $+mc^2$ level corresponds to zero. The solutions of this equation $\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1}$ are stationary 4-spinors, which, in accordance with the general block structure of Eqn (16), can be

represented as two components, namely, the large (subscript $L$) $\boldsymbol{\psi}_L$ and small (subscript $S$) components $\boldsymbol{\psi}_S$:

$$\boldsymbol{\psi}^{\mathrm{D}}_{4\times 1} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \boldsymbol{\psi}_{L_{2\times 1}} \\ \boldsymbol{\psi}_{S_{2\times 1}} \end{pmatrix} \tag{17}$$

The normalization condition expressed in terms of these components is as follows:

$$1 = \int \boldsymbol{\psi}^{\mathrm{D}+}\boldsymbol{\psi}^{\mathrm{D}}\,\mathrm{d}V = \int \left(\boldsymbol{\psi}^{+}_{L}\boldsymbol{\psi}_{L} + \boldsymbol{\psi}^{+}_{S}\,\boldsymbol{\psi}^{+}_{S}\right)\mathrm{d}V \tag{18}$$

The Dirac equation (16) has two types of solutions, those with positive $(0;\ +\infty)$ and negative $(-\infty;\ -2\,m_{\mathrm{e}}\,c^2)$ energies. Positive energy solutions correspond to an electron continuum not bounded from above, while negative energy solutions correspond to a positron continuum not bounded from below. Dirac assumed that the solutions corresponding to the positron continuum are most stable because of large negative energies, and all electrons tend to fall into the positron continuum with release of a large amount of energy $h\nu > 2\,m_{\mathrm{e}}c^2$ ($10^8$ kJ mol$^{-1}$) and to occupy all possible energetically more favourable states, thus forming the 'Dirac sea'.

It is presumed that electrons appear in the electron continuum from the 'Dirac sea' *via* excitation from some positron level to an electron level. This results in a vacancy, *i.e.*, a 'hole', in the positron level; this vacancy can be regarded as a positively charged particle with the same mass as the mass of electron, *i.e.*, a positron. Any one-electron problem cannot be considered separately from the 'Dirac sea', which contains an infinite number of fermions, so that the description of this 'sea' in terms of a many-body theory involves insurmountable complexity. This concept has acquired the name of the Dirac hole theory [60] and was proposed only a few years before Anderson discovered the positron experimentally.[61]

Substitution of 4-spinor (17) into Dirac equation (16) gives a system of matrix equations for the large and small components

$$\begin{cases} \widehat{\mathbf{V}}\,\boldsymbol{\psi}_L + c\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\boldsymbol{\psi}_S = E\,\boldsymbol{\psi}_L \\ c\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\boldsymbol{\psi}_L + (\widehat{\mathbf{V}} - 2mc^2)\,\boldsymbol{\psi}_S = E\,\boldsymbol{\psi}_S \end{cases} \tag{19}$$

Elimination of the small component

$$\boldsymbol{\psi}_S = \frac{1}{2mc}\,\widehat{\mathbf{B}}\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}\,\boldsymbol{\psi}_L = \widehat{\mathbf{X}}\boldsymbol{\psi}_L$$

where

$$\widehat{\mathbf{B}} = \left(\mathbf{I} + \frac{E - \widehat{\mathbf{V}}}{2mc^2}\right)^{-1} \tag{19a}$$

from set (19) results in the following equation for the large component $\boldsymbol{\psi}_L$:

$$\hat{\mathbf{h}}^{\mathrm{ESC}}\boldsymbol{\psi}_L = \left(\widehat{\mathbf{V}} + \frac{1}{2m}\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}\,\widehat{\mathbf{B}}\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}\right)\boldsymbol{\psi}_L = E\,\boldsymbol{\psi}_L \tag{20}$$

Thus, the four-component Dirac equation (16) is reduced to an accurate two-component equation, *i.e.*, to an equation for the 4-spinor large component, which, in its turn, comprises two components. This procedure is referred to as the elimination of the small component (ESC). The 2-spinor $\boldsymbol{\psi}_S$ has a suppression factor of 1/2c with respect to $\boldsymbol{\psi}_L$, and therefore the former is called a small component and the latter one a large component. This procedure demonstrates a formal way to reduce the four-component Dirac equation to a simpler two-component form involving the large component. Then, if it were possible to determine exactly the large component from the equation, the small component would be exactly evaluated by applying the exact operator $\widehat{\mathbf{X}}$ to the exact large component, so that the problem would be solved exactly. Unfortunately, in practice, this is impossible without introducing some additional approximations, as operator (19a) is energy-dependent and application of this operator requires specific approximate approaches. They are mainly related to a specific choice of the expansion parameter in the operator $\widehat{\mathbf{B}}$. This provides a broad range of two-component methods, which are considered below.

An absolutely different approach to solving problem (19) is also possible: the energy parameter $E$ can be completely eliminated, which would give an equation for the operator $\widehat{\mathbf{X}}$

$$\widehat{\mathbf{X}} = \frac{1}{2mc^2}\left(c\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}} + [\widehat{\mathbf{V}}, \widehat{\mathbf{X}}] - \widehat{\mathbf{X}}\,c\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\widehat{\mathbf{X}}\right) \tag{21}$$

This equation can be solved only by the iterative method, while the operator $\widehat{\mathbf{X}}$ itself does not have a closed form except for a few cases for different potentials,[38,62] excluding the case for Coulombic one. The operator (19a) arising during the procedure of component elimination plays a key role in the formation of various approximate two-component Hamiltonians.

The simplest approximation for the operator $\widehat{\mathbf{B}}$ can serve as an example of obtaining the non-relativistic limit. In the point nucleus model, the operator $\widehat{\mathbf{B}}$ is transformed into the Blinder factor

$$B(r) = \left(1 + \frac{E}{2mc^2} + \frac{r_0}{r}\right)^{-1}$$

where $r_0 = Z\,\mathrm{e}^2/2\,mc^2$. The $r_0$ value is about the size of an atomic nucleus; therefore, for electrons that are not located in the vicinity of the nucleus ($r_0/r \ll 1$), $E/2\,mc^2 \to 0$ for $c \to \infty$ (transition to the non-relativistic limit). Thus, for the electrons which are located in close vicinity to the nucleus, the Blinder operator, in the non-relativistic limit, approximately equals to the identity operator, $\widehat{\mathbf{B}} \approx \widehat{\mathbf{I}}$ In that case, the two-component Hamiltonian reduces to the following operator:

$$\hat{\mathbf{h}}^{\mathrm{ESC}}_{\mathrm{nr}} \approx \widehat{\mathbf{V}} + \frac{1}{2m}\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}} \tag{22}$$

By making use of a property of the Pauli matrices (15), one can readily demonstrate that expression (22) can be written as a non-relativistic (two-component) Hamiltonian

$$\hat{\mathbf{h}}^{\mathrm{ESC}}_{\mathrm{nr}} \approx \widehat{\mathbf{V}} + \frac{1}{2m}\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}} = \widehat{\mathbf{V}} + \frac{1}{2m}\,\boldsymbol{\sigma}_i\,\hat{p}_i\,\hat{p}_j = \tag{23}$$

$$= \widehat{\mathbf{V}} + \frac{1}{2m}\left(\delta_{ij}\mathbf{I} + \mathrm{i}\varepsilon_{lij}\boldsymbol{\sigma}_l\right)\hat{p}_i\,\hat{p}_j = \left(\widehat{V} + \frac{\hat{p}^2}{2m}\right)\mathbf{I}_{2\times 2}$$

The problem based on the Hamiltonian $\hat{\mathbf{h}}^{\mathrm{ESC}}_{\mathrm{nr}}$

$$\left(\hat{V}+\frac{\hat{p}^2}{2m}\right)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=E\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \quad (24)$$

is equivalent to the Schrödinger equation; however, unlike the latter, Eqn (24) retains the two-component structure, which implies a spin nature of these components. As the spin part of the components, one can choose the eigenvectors of the matrix $\boldsymbol{\sigma}_z$ or any other linear combination of the Pauli matrices.

The extension of the one-particle Dirac equation to the many-particle relativistic case is more complicated than that in the non-relativistic case. This is due to the fact that the relativistic approach uses matrix operators and 4-spinors. For example, in the non-relativistic case in the simplest single-determinant approximation, the $N_e$-electron wave function can be obtained by the anti-symmetrization of the simple product of one-particle states. The relativistic version requires a tensor (direct, Cartesian) product of one-particle 4-spinors rather than the simple product of one-particle states.

Strictly speaking, the Hilbertian space of an $N_e$-electron system ($^{N_e}H$) is the tensor product of $N_e$ one-particle Hilbertian spaces $^1H(i)$, $i = 1 \ldots N_e$

$$^{N_e}H=\prod_{i=1}^{N_e\,\otimes}{}^1H(i)={}^1H(1)\otimes\ldots\otimes{}^1H(N_e) \quad (25)$$

Since the dimension of the one-body problem is $(4\times4)$, then as it follows from (25), the dimension of the $N_e$-body problem is $(4^{N_e}\times4^{N_e})$.

One more specific feature of the construction of the relativistic many-body Hamiltonian is the modified description of electron – electron interaction, which will be considered below, and now we can confine ourselves to the Coulomb approximation. In the rest the construction of the many-electron Hamiltonian does not differ from this procedure for the non-relativistic analogue. Thus, in the Born – Oppenheimer approximation,[63] the many-electron Dirac – Coulomb Hamiltonian has the form

$$\widehat{\mathbf{H}}_{DC}=\sum_{n=1}^{N_e}\hat{\mathbf{h}}^D(n)+\sum_{n>m}^{N_e}\widehat{\mathbf{V}}_C(n,m)+\sum_{N>M}^{N_{nuc}}\frac{Z_NZ_M}{r_{NM}}\mathbf{I} \quad (26)$$

where $N_e$ and $N_{nuc}$ are the numbers of electrons and nuclei in the system, respectively. In relation (26) and below, the system of Hartree atomic units is used in which $m_e = e = \hbar = 4\pi\varepsilon_0 = 1$. The speed of light expressed in the atomic units is the inverse fine structure constant $c = \alpha^{-1} \approx 137.036$. The first term in relation (26) is the sum of one-electron Dirac operators $\hat{\mathbf{h}}^D(n)$, each of them for any $n$th electron being represented as

$$\hat{\mathbf{h}}^D_{4^{N_e}\times4^{N_e}}(n)=\prod_{i=1}^{n-1\,\otimes}\mathbf{I}_{4\times4}(i)\otimes\hat{\mathbf{h}}^{1e}_{4\times4}(n)\otimes\prod_{i=n+1}^{N_e\,\otimes}\mathbf{I}_{4\times4}(i) \quad (27)$$

where $\hat{\mathbf{h}}^{1e}_{4\times4}(n)$ represents the sum of the one-electron Dirac Hamiltonian and the potential energy operator of the $n$th electron interaction with the nuclei

$$\hat{\mathbf{h}}^{1e}_{4\times4}(n)=c\,\vec{\boldsymbol{\alpha}}_{4\times4}\hat{\vec{p}}_n+c^2(\boldsymbol{\beta}_{4\times4}-\mathbf{I}_{4\times4})-\sum_{M}^{N_{nuc}}\frac{Z_M}{r_{nM}}\mathbf{I}_{4\times4} \quad (28)$$

The first term in this expression is called kinetic, the second term is related to the rest energy, while the third one is the interaction potential of the electron with the nuclei.

The second term in (26) is the electron – electron interaction energy, which is zeroth order in hyperfine coupling constant (Coulomb approximation)

$$\widehat{\mathbf{V}}_C(n,m)=\frac{1}{r_{nm}}\prod_{i=1}^{N_e\,\otimes}\mathbf{I}_{4\times4}(i) \quad (29)$$

The last term in (26) is the common Coulomb energy of nuclear interaction and, as a rule, it is not considered from the relativistic standpoint.

The analogue of the Slater determinant for the relativistic problem is the many-electron wave function of dimension $4^{N_e}$. It is constructed as an anti-symmetrized tensor product of one-particle 4-spinors

$$\boldsymbol{\Psi}=\frac{1}{\sqrt{N!}}\sum_{P=1}^{N_e!}(-1)^{v_P}\widehat{P}\left[\prod_{i=1}^{N_e\,\otimes}\boldsymbol{\psi}_{A_i}(i)\right] \quad (30)$$

The summation in expression (30) involves all the possible permutations in the series $\{A_1, A_2, \ldots, A_{N_e}\}$, the total number of which is $N_e!$; $v_P$ is the number of pair permutations (transpositions); $(-1)^{v_P}$ gives $+1$ in the case of an even number of pair permutations and $-1$ in the case of an odd number of pair permutations, while $\widehat{P}$ is the permutation operator.

Relations (25) – (30) are exact as regards the dimensions, and they represent the foundation for various relativistic quantum chemical approaches to solving the electron problem. However, within the framework of standard relativistic methods, tensor structures of this type are not used because the many-electron problem is, most often, reformulated at the 'singe-particle' approximation level; otherwise, solution of the problem would not be physically acceptable in the sense of computational demands. The only exception is the DMRG method.[64 – 68]

The two-electron part of (26) describes the electron – electron interaction, which is expected to be Lorentz-invariant. Nevertheless, the common Coulomb interaction expressed as relation (29) does not take into account the finite propagation of electromagnetic fields (*i.e.* the fact that the speed of light is not infinite) which results in violation of the Lorentz invariance condition. The correct representation of this part, unfortunately, does not have a simple closed form,[69] which brings about the necessity of resorting to the perturbation theory.

A more accurate potential energy operator describing the interaction between two moving electrons is based on the Lienard – Wiechert retarded potentials,[54] which actually describe the scalar and vector potentials in time moment $t$ at the point $\vec{r}_1$ as charge and current density functionals in the preceding moment $t' = t - R/c$

$$\phi(\vec{r}_1,t)=\int_V\frac{\rho_{t-R/c}}{R}\mathrm{d}V \quad (31)$$

$$\vec{A}(\vec{r}_1, t) = \frac{1}{c}\int_V \frac{\vec{j}_{t-R/c}}{R}\mathrm{d}V \tag{32}$$

where $R = |\vec{r}_1 - \vec{r}(t')| = c(t - t')$ is the distance between the point $\vec{r}_1$ and an arbitrary point of the continuous distribution of electrons in space in the time moment $t'$. The relativistic energy of the system calculated using potentials (31) and (32) is expanded in a power series of $c^{-1}$. This gives the Hamiltonian operator in which terms corresponding to the potential energy of interaction between the electrons are distinguished; these terms include a zero approximation (non-relativistic Coulomb potential) and the relativistic counterpart starting from the second order in the reciprocal of the speed of light $c^{-1}$.

In practice, corrections of only the second order with respect to $c^{-1}$ are usually left. This leads to so-called Coulomb–Breit interaction.[70–77]

$$\hat{\mathbf{g}}_{ij}^{\mathrm{CB}} = \frac{\mathbf{I}}{r_{ij}} - \frac{1}{2}\left(\frac{\vec{\boldsymbol{\alpha}}_i\vec{\boldsymbol{\alpha}}_j}{r_{ij}} + \frac{(\vec{\boldsymbol{\alpha}}_i\vec{r}_{ij})(\vec{\boldsymbol{\alpha}}_j\vec{r}_{ij})}{r_{ij}^3}\right) + O(c^{-4}) \tag{33}$$

The first term of this expression is zeroth order in the hyperfine coupling constant and is the common non-relativistic Coulomb operator. The second term (in parentheses) is the Breit interaction,[70] which consists of two parts, one being direct interaction between electron spins called Gaunt interaction [78] and the other being a gauge-dependent term determined by the chosen gauge of the vector potential for electromagnetic field quantization.

A discussion of the choice of the most appropriate description of the two-electron operator in the relativistic approach from the standpoint of using the most popular Coulomb and Feynman gauges is presented in a paper of Sucher.[79] In a number of publications,[15–17,80] particular attention is paid to the transformation of the term corresponding to the Coulomb–Breit interaction on going to two-component Hamiltonians.

The expression for the Breit interaction having a closed form does not ensure the Lorentz covariance, but in combination with the Coulomb interaction, it represents the electron – electron interaction more correctly than the Coulomb interaction alone. The scope of its applicability is rather broad, although there is a certain limitation: in Breit's paper,[70] the perturbative expansion of the electron–electron interaction energy is performed, strictly speaking, in terms of the parameter $\alpha Z$, where $Z$ is the charge of the nucleus in the field of which the two electrons move. Meanwhile, the expansion parameter should obey the condition $\alpha Z \ll 1$, so this approach is inapplicable for heavy nuclei for which $\alpha Z$ is close to 1.

In practice, the addition of the Gaunt operator to the Dirac–Coulomb Hamiltonian leads to the dramatic increase in the computational cost. Therefore, the necessity of the inclusion of such additional operators should be thoroughly evaluated. In particular, in order to provide the accurate electronic structure calculation or to take into account the spin–orbit interaction at the electron correlation level, one should at least include the Gaunt term into the Dirac–Coulomb Hamiltonian.

### III.3. The major problems associated with relativistic calculations

The first relativistic four-component calculations were associated with multiple problems that were not encountered previously in non-relativistic procedures.[81–86] One of them, the 'continuum dissolution' problem, or Brown–Ravenholl disease arises upon the attempt to consider the electron–electron interaction within the framework of the relativistic theory.[81] This problem arises because solutions of the Dirac equation form two continuums: the electron and positron ones. When the correlated electron movement is taken into account even at the simplest level, any two electrons in the system can be coupled in such a way that one electron can be excited to any level of the electron continuum, while the other one can pass to the corresponding level of the positron continuum, the total system energy being retained. Since the positron continuum is not bounded from below, while the electron one is not bounded from above, the number of such electron–positron states for an electron pair is infinite. In other words, any energy level of the system of the bound electron pair system is infinitely degenerate.

However, transitions to the positron continuum are forbidden because all the states of the positron continuum are already occupied and the electrons located in these states form the infinite set — the 'Dirac sea'.

The complexity is in the fact that all theories starting out from the Dirac equation would involve the Brown–Ravenholl disease in one or another form unless transitions to the positron continuum are artificially restricted. This is done using special projection operators $\boldsymbol{\Lambda}_n^+$ (see Refs 50, 87–89) composed of electron states,

$$\boldsymbol{\Lambda}_n^+ = |\boldsymbol{\psi}_n(\vec{r})\rangle\langle\boldsymbol{\psi}_n(\vec{r})| \tag{34}$$

which transform the single-electron and two-electron parts of the many-body Dirac Hamiltonian into the electron continuum space

$$\sum_{n=1}^{N_e}\hat{\mathbf{h}}^{\mathrm{D}}(n) \longrightarrow \sum_{n=1}^{N_e}\boldsymbol{\Lambda}_n^+\hat{\mathbf{h}}^{\mathrm{D}}(n)\boldsymbol{\Lambda}_n^+ \tag{35}$$

$$\sum_{n<m=1}^{N_e}\hat{\mathbf{g}}(n,m) \longrightarrow \sum_{n<m=1}^{N_e}\boldsymbol{\Lambda}_n^+\boldsymbol{\Lambda}_m^+\hat{\mathbf{g}}(n,m)\boldsymbol{\Lambda}_m^+\boldsymbol{\Lambda}_n^+ \tag{36}$$

Projection of the problem to the electron continuum space gives a no-pair Hamiltonian, which correctly describes the system by automatically eliminating the positron continuum, the electron energy spectrum being restricted only to the upper part (electron continuum).

There are several methods for choosing the projection operators $\boldsymbol{\Lambda}_n^+$. First, they can be constructed from the Dirac equation solutions for a free particle that form the electron continuum (or, as they are also called, free positive-energy solutions). This forms the 'free' representation. Second, projection operators can be constructed from 'bound' positive-energy solutions, which are electron continuum solutions of the Dirac equation with inclusion of the external field. This forms the Furry representation.[90] In quantum chemical applications, the nuclear field is, most often, taken as the external field. The third iterative method for the construction of the projection operators from positive-energy solutions of the Dirac–Fock equations was proposed by Mittleman.[51] The representation formed by these projection operators was called fuzzy.[87] A more detailed consideration of these issues can be found in the

paper of Kutzelnigg.[91] Note that neglecting the projection procedure brings about convergence problems in real quantum chemical calculations.[92]

Yet another topical problem in relativistic quantum chemical calculations is the variational collapse problem,[82] or, as it is also called, the finite basis set problem.[83] This problem arises in the expansion of wave functions in a specified finite-size basis set and switching to the matrix representation of various quantum mechanical operators.[93] This problem is manifested to a higher extent when optimized basis sets are used without any additional restrictions imposed on the basis functions.[85, 86, 94] The symptoms of the variational collapse are the following:[93]

— excessive unphysical solutions with zero or vanishingly small kinetic energy appear and are mixed with physical solutions; this may result in degeneration, so that it becomes difficult to separate the physical eigenvalues from unphysical ones;[82, 86]

— upon increase in the dimension of the basis set, the energy eigenvalues located much lower on the energy scale do not show systematic convergence but vary arbitrarily from one basis set to another;[85, 86, 95] moreover, the eigenenergies become hypersensitive to details of the particular basis set.

These problems, related to the variational collapse category, have been described in detail by Kutzelnigg,[93] who proposed ~20 methods for solving them; many of these methods have been later successfully implemented.

Unlike the Brown – Ravenholl disease,[81] which appears only in many-body cases, the variational collapse can appear even in the one-particle case, which markedly simplifies the search for ways of overcoming it.

In practice, solving the one-particle Dirac equation (16) (without shift of the energy scale) with expansion of the 4-spinor $\boldsymbol{\psi}$ in a finite basis set is reduced to the Hamiltonian matrix eigenvalue problem

$$\mathbf{H}_{\mathrm{D}} = (c\,\vec{\boldsymbol{\alpha}}\vec{\mathbf{p}} + c^2\boldsymbol{\beta} + \mathbf{V}) \tag{37}$$

This is accompanied by the appearance of obstacles caused by unboundedness of the Dirac Hamiltonian from below (as opposed to the Schrödinger Hamiltonian). The Schrödinger Hamiltonian

$$\widehat{H}_{\mathrm{SH}} = \widehat{T} + \widehat{V}$$

consists of the sum of the positively defined kinetic energy operator and the unbounded potential energy operator $\widehat{V}$, which is still indirectly bounded *via* the connection to the operator $\widehat{T}$ (see Ref. 96). This means that some matrix element $\langle\psi|\,\widehat{V}\,|\psi\rangle$ can take any negative value, but the sum $\langle\psi|\,\widehat{V}\,|\psi\rangle + \langle\psi|\,\widehat{T}\,|\psi\rangle$ is never lower than the ground state energy $E_0$.

In the Dirac Hamiltonian, the kinetic energy operator is not positively defined, therefore, it cannot serve as the counterbalancing factor when $\widehat{V}$ tends to $-\infty$. Thus, the Dirac Hamiltonian is not bounded from below. The name 'variational collapse' comes exactly from this feature, because it is the limiting factor in the application of methods based on the variation principle.

When $c \to \infty$ the Dirac Hamiltonian should be equivalent to the non-relativistic Schrödinger Hamiltonian, which is bounded from below, and, hence, the variational collapse problem is expected to disappear. However, this does not take place: the spectrum of the non-relativistic limit of the Dirac operator does not at all reproduce the Schrödinger Hamiltonian spectrum.[82, 95] Also, all indications of the variational collapse described above appear in this case.

From the mathematical standpoint, the essence of the variational collapse is that the Dirac Hamiltonian is singular on going to the non-relativistic limit $c \to \infty$.[93] This serves as the starting point for the search for methods to solve this problem, which should evidently be related to the procedure of finding the correct non-relativistic limit. The non-relativistic limit will be obtained correctly if the ESC procedure by FW transformations is first carried out [14] and then the rest energy is subtracted. In this case, the question arises of whether the kinetic term is adequately described in the matrix representation, and this is the key issue for the variational collapse problem.

If the FW transformation is applied to the Dirac operator (not shifted by the rest energy), then

$$\widehat{\mathbf{H}}_{\mathrm{D}} \to \widetilde{\widehat{\mathbf{H}}}_{\mathrm{D}} = \widehat{\mathbf{U}}^{+}\widehat{\mathbf{H}}_{\mathrm{D}}\,\widehat{\mathbf{U}} \tag{38}$$

$$\widehat{\mathbf{U}} = \left(\frac{1-\widehat{\mathbf{Z}}}{1+\widehat{\mathbf{Z}}}\right)^{1/4},\ \widehat{\mathbf{Z}} = \frac{\boldsymbol{\beta}}{c}\vec{\boldsymbol{\alpha}}\,\hat{\vec{p}} \tag{39}$$

$$\widetilde{\widehat{\mathbf{H}}}_{\mathrm{D}} = \boldsymbol{\beta}c^2\left(1+\frac{\hat{\vec{p}}^{\,2}}{c^2}\right)^{1/2} + \widehat{\mathbf{U}}^{+}\widehat{\mathbf{V}}\,\widehat{\mathbf{U}} \tag{40}$$

Then, expansion of $\widetilde{\widehat{\mathbf{H}}}_{\mathrm{D}}$ in a power series of $1/c$ gives the following expression:

$$\widetilde{\widehat{\mathbf{H}}}_{\mathrm{D}} = \boldsymbol{\beta}c^2 + \boldsymbol{\beta}\,\widehat{\mathbf{H}} + \widehat{\mathbf{F}} + O(c^{-4}) \tag{41}$$

where

$$\widehat{\mathbf{H}} = \widehat{\mathbf{T}} + \boldsymbol{\beta}\widehat{\mathbf{V}} = \frac{\hat{\vec{p}}^{\,2}}{2}\mathbf{I} + \boldsymbol{\beta}\widehat{\mathbf{V}} \tag{42}$$

$$\widehat{\mathbf{F}} = -\frac{\boldsymbol{\beta}}{2c^2}\,\widehat{T}^2 - \frac{1}{8c^2}\left[\left[\widehat{\mathbf{V}}, \boldsymbol{\alpha}\hat{\vec{p}}\right], \boldsymbol{\alpha}\hat{\vec{p}}\right] \tag{43}$$

here

$$\widehat{\mathbf{H}} = \widehat{\mathbf{T}} + \boldsymbol{\beta}\widehat{V} = \begin{pmatrix} \widehat{\mathbf{T}} + \widehat{\mathbf{V}} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \widehat{\mathbf{T}} - \widehat{\mathbf{V}} \end{pmatrix}$$

is the non-relativistic Schrödinger Hamiltonian factorized as two parts: for electron (upper part) and positron (lower part) continuums. The operator $\widehat{\mathbf{F}}$ is the set of corrections in the Pauli Hamiltonian. It is evident that if all terms starting from $O(c^{-2})$ are omitted, the correct non-relativistic limit of the Dirac operator will be obtained.

In the matrix representation, the FW procedure is a usual unitary transformation, resulting in the following expressions:

$$\mathbf{H}_{\mathrm{D}} \to \widetilde{\mathbf{H}}_{\mathrm{D}} = \mathbf{U}^{+}\mathbf{H}_{\mathrm{D}}\mathbf{U} \tag{44}$$

$$\mathbf{U} = \left(\frac{\mathbf{I}-\mathbf{Z}}{\mathbf{I}+\mathbf{Z}}\right)^{1/4},\ \mathbf{Z} = \frac{\boldsymbol{\beta}}{c}\vec{\boldsymbol{\alpha}}\,\vec{\mathbf{p}} \tag{45}$$

$$\widetilde{\mathbf{H}}_{\mathrm{D}} = \boldsymbol{\beta}\, c^2 \left( \mathbf{I} + \frac{\vec{\mathbf{p}}^{\,2}}{c^2} \right)^{1/2} + \mathbf{U}^{+}\mathbf{V}\mathbf{U} \tag{46}$$

$$\widetilde{\mathbf{H}}_{\mathrm{D}} = \mathbf{U}^{+}\mathbf{H}_{\mathrm{D}}\mathbf{U} = \boldsymbol{\beta}\, c^2 + \boldsymbol{\beta}\,\mathbf{H}' + \mathbf{F} + O(c^{-4}) \tag{47}$$

where

$$\mathbf{H}' = \frac{\vec{\mathbf{p}}\,\vec{\mathbf{p}}}{2}\mathbf{I} + \boldsymbol{\beta}\,\mathbf{V} \tag{48}$$

$$\mathbf{F} = -\frac{\boldsymbol{\beta}}{2c^2}\left( \frac{\vec{\mathbf{p}}\,\vec{\mathbf{p}}}{2} \right)^2 - \frac{1}{8c^2}\left[ \left[ \mathbf{V}, \boldsymbol{\alpha}\,\vec{\mathbf{p}} \right], \boldsymbol{\alpha}\,\vec{\mathbf{p}} \right] \tag{49}$$

Relations (48) and (49) contain the sum of products of the matrices of the Cartesian components of the momentum operator

$$\| \vec{\mathbf{p}}\,\vec{\mathbf{p}} \|_{il} = \sum_j \| \vec{\mathbf{p}} \|_{ij} \, \| \vec{\mathbf{p}} \|_{jl} = \tag{49a}$$

$$= \sum_{k=1}^{3} \sum_j \langle \chi_i | \hat{p}_k | \chi_j \rangle \langle \chi_j | \hat{p}_k | \chi_l \rangle$$

which is not the same as the matrix form of the operator

$$\hat{\vec{p}}^{\,2} \rightarrow \| 2\mathbf{T} \|_{il} = \| \vec{\mathbf{p}}^{\,2} \|_{il} = \left\langle \chi_i \left| \sum_{k=1}^{3} \hat{p}_k^2 \right| \chi_l \right\rangle \tag{49b}$$

This is exactly the main cause of the variational collapse problem. Evidently, expression (49a) differs from equation (49b) by the presence of the projection operator to the chosen basis

$$\sum_j |\chi_j\rangle\langle\chi_j|$$

which is not an identity operator at a finite basis set; otherwise, both expressions would be equivalent (this is the source of the second name of the variational collapse problem, namely, the finite basis set problem).

Thus, proceeding from the matrix form (48) and basis set incompleteness, the non-relativistic limit of the Dirac operator can be written in the operator form as

$$\widehat{\mathbf{H}} = \frac{\hat{\vec{p}}\,\widehat{Q}\,\hat{\vec{p}}}{2}\mathbf{I} + \boldsymbol{\beta}\,\widehat{\mathbf{V}} \tag{50}$$

where $\widehat{Q}$ is the projection operator to the basis. It is clear that in this form, the kinetic part differs from the correct positively defined kinetic part of expression (42) and does not provide boundedness of the non-relativistic limit from below. The possibilities for solving this problem depend on the chosen concept. A variety of methods were reported by Kutzelnigg.[93]

In our opinion, the most efficient method for solving the variational collapse problem is a specific transformation of the Hamiltonian accompanied by renormalization of the 4-spinor. This transformation is called the Dyall–Kutzelnigg transformation.[97] Interestingly, the application of this transformation to the Dirac Hamiltonian results in splitting of the problem into two parts, spin-free and spin-dependent ones. However, the key meaning of this transformation is that this circumvents the variational collapse problem.

It was shown[93] that the Dyall–Kutzelnigg transformation reduces the Dirac equation to the generalized symmetric problem for the eigenvalues of symmetric matrix **A**

$$\mathbf{A}\boldsymbol{\Psi} = \omega\,\mathbf{B}\,\boldsymbol{\Psi} \tag{51}$$

of the transformed Dirac Hamiltonian $\widehat{\widetilde{\mathbf{H}}}_{\mathrm{D}}^{\mathrm{DK}}$

$$\widehat{\widetilde{\mathbf{H}}}_{\mathrm{D}}^{\mathrm{DK}} = \widehat{\mathbf{C}}\,\widehat{\mathbf{H}}_{\mathrm{D}}\,\widehat{\mathbf{C}} = \begin{pmatrix} \widehat{\mathbf{V}} & \widehat{\mathbf{T}} \\ \widehat{\mathbf{T}} & \dfrac{\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}\,\widehat{V}\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}}{4c^2} - \widehat{\mathbf{T}} \end{pmatrix} \tag{52}$$

$$\widehat{\mathbf{C}} = \begin{pmatrix} \mathbf{I}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \dfrac{\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}}}{2c}\mathbf{I}_{2\times 2} \end{pmatrix} \tag{53}$$

and symmetric positively defined matrix **B** of the metric modification operator $\widehat{\mathbf{B}}$

$$\widehat{\mathbf{B}} = \begin{pmatrix} \mathbf{I}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \dfrac{\widehat{\mathbf{T}}}{2c^2} \end{pmatrix} \tag{54}$$

The generalized problem for the eigenvalues (51) can be reduced to the classical symmetric problem by using the Cholesky decomposition[98] for the symmetric matrix $\mathbf{B} = \mathbf{B}^{1/2}\,\mathbf{B}^{1/2}$

$$\mathbf{M}\boldsymbol{\Phi} = \mathbf{B}^{-1/2}\mathbf{A}\mathbf{B}^{-1/2}\boldsymbol{\Phi} = \omega\,\boldsymbol{\Phi}\,, \quad \boldsymbol{\Phi} = \mathbf{B}^{1/2}\boldsymbol{\Psi} \tag{55}$$

In turn, problem (55) is split into blocks after a certain transformation proposed by Kutzelnigg.[93] The upper left block of the transformed matrix $\widetilde{\mathbf{M}}$ corresponds to the Pauli limit for the positive energy states

$$\widetilde{\mathbf{M}}_{++} = \mathbf{T} + \mathbf{V} + \frac{\mathbf{V}\mathbf{T} + \mathbf{T}\mathbf{V} + \vec{\boldsymbol{\sigma}}\,\vec{\mathbf{p}}\,\mathbf{V}\,\vec{\boldsymbol{\sigma}}\,\vec{\mathbf{p}}}{4c^2} + \frac{\mathbf{T}^2}{2c^2} + O(c^{-4}) \tag{56}$$

It can be seen from expression (56) that the transformations considered above give the correct two-component Schrödinger limit at $c^0$ and two-component Pauli Hamiltonian with well-known corrections at $c^{-2}$.

Thus, the Dyall–Kutzelnigg transformation leads to symmetric problem for the eigenvalues (55) of matrix **A** of transformed Hamiltonian (52), the upper left block of which provides the correct non-relativistic limit. This means that the application of this transformation solves the variational collapse problem. In practice, this scheme is equivalent to the application of kinetically balanced basis sets.

### III.4. Kinetic balance and relativistic basis sets

One way to solve the variational collapse problem considered above is the use of the special type of basis sets.

In the case of four-component relativistic many-electron variational methods, everything is finally reduced to single-electron equations such as the Dirac equation

$$\begin{pmatrix} \mathbf{V}(\vec{r}) & c\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}} \\ c\,\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}} & \mathbf{V}(\vec{r}) - 2c^2 \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_i^L(\vec{r}) \\ \boldsymbol{\psi}_i^S(\vec{r}) \end{pmatrix} = \varepsilon_i \begin{pmatrix} \boldsymbol{\psi}_i^L(\vec{r}) \\ \boldsymbol{\psi}_i^S(\vec{r}) \end{pmatrix} \tag{57}$$

Here $\mathbf{V}(\vec{r})$ is some effective potential. As follows from the general appearance of these one-particle equations, there is a clear relationship between the large and small components of molecular 4-spinors

$$\boldsymbol{\psi}_i^S(\vec{r}) = \left(1 + \frac{\varepsilon_i - \mathbf{V}(\vec{r})}{2c^2}\right)^{-1} \frac{\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{2c} \boldsymbol{\psi}_i^L(\vec{r}) \tag{58}$$

In the case of spherically symmetric potential $\mathbf{V}(r)$, for example, for an atom, the radial part of the atomic 4-spinors has the general form [99]

$$\boldsymbol{\Phi}_{k,m} = \begin{pmatrix} \dfrac{1}{r} P(r) \boldsymbol{\chi}_{k,m} & (\theta, \varphi) \\ \dfrac{\mathrm{i}}{r} Q(r) \boldsymbol{\chi}_{-k,m} & (\theta, \varphi) \end{pmatrix} \tag{59}$$

where $(P(r), Q(r))^{\mathrm{T}}$ is a radial two-component spinor, $\boldsymbol{\chi}_{k,m}(\theta, \varphi)$ are spherical bispinors centred on the atom and being the eigenfunctions of both the squared total angular momentum $\hat{\vec{j}}^2$ ($\hat{\vec{j}} = \hat{\vec{l}} + \hat{\vec{s}}$) and its projection $\hat{j}_z$ [eigenvalues $j(j+1)$ and $m$, respectively] with the angular quantum number

$$l = j + \frac{1}{2}\operatorname{sgn} k$$

where $j$ is the total angular momentum quantum number

$$j = |k| - \frac{1}{2}$$

$k$ is the relativistic azimuthal quantum number ($\mathbf{k} = \vec{\boldsymbol{\sigma}}\vec{l} + \mathbf{1}_{2\times 2}$, $k < 0$ corresponds to the large component and $k > 0$ corresponds to the small component).

The Dirac equation for a radial component takes the following form:

$$\begin{pmatrix} \mathbf{V}(r) & c\left(-\dfrac{\partial}{\partial r} + \dfrac{k}{r}\right) \\ c\left(\dfrac{\partial}{\partial r} + \dfrac{k}{r}\right) & \mathbf{V}(r) - 2c^2 \end{pmatrix} \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = \varepsilon \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \tag{60}$$

Correspondingly, for radial functions, the relationship between the components is expressed as

$$Q(r) = \left(1 + \frac{\varepsilon - \mathbf{V}(r)}{2c^2}\right) \frac{1}{2c} \left(\frac{\partial}{\partial r} + \frac{k}{r}\right) P(r) \tag{61}$$

Expressions (58) and (61) represent the so-called exact kinetic balance condition.[100] Expression (61) is also called exact kinetic balance for the radial components. However, the dependence of the exact kinetic balance operator on the energy eigenvalues $\varepsilon$ and the potential $\mathbf{V}(\vec{r})$ not defined beforehand presents a challenge. In many-electron calculations carried out by means of such approaches as the Dirac – Hartree – Fock (DHF) or four-component density functional theory (4DFT), $\mathbf{V}(\vec{r})$ is determined by solutions redefined in each step of the self-consistency procedure. This sharply complicates the concept of construction of the basis sets for small components, as the exact kinetic balance operator should also be redefined in every iteration step.

As a rule, relativistic calculations use various approximations for the exact kinetic balance operator. The simplest and the most popular is the operator $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}/2c$ corresponding to the exact non-relativistic limit. The use of this operator is not always justified, because one has to know in advance that the effective potential $\mathbf{V}(\vec{r})$ and the orbital energies are much smaller than $2c^2$. It was shown [101 – 103] that the use of kinetically balanced basis set

$$\{\boldsymbol{\chi}_\mu^S\} \supseteq \{\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\boldsymbol{\chi}_\mu^L\}$$

results in variational stability.

Stanton and Havriliak [104] introduced the term 'kinetic balance principle' for this type of choice of basis sets and demonstrated that the use of this principle eliminates catastrophic variational failure: orbital energies do not drop below the exact values by more than an amount of order $c^{-4}$. In the complete basis set limit, this error disappears, which also served as the starting point for some ideas in the construction of relativistic basis sets.

Note that the simplest kinetic balance operator $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}/2c$ is included in the operator $\widehat{\mathbf{C}}$ [see relation (53)]. Moreover, it can be easily demonstrated that the construction of a basis set according to the simple kinetic balance principle is finally equivalent to the application of the Dyall – Kutzelnigg transformation. From this it follows that a kinetically unbalanced basis set, if it is not infinite (which cannot be implemented in practice), will lead to variational collapse without some additional Hamiltonian transformations even in the non-relativistic limit.

In the relativistic molecular orbital theory, a many-electron wave function is expressed as anti-symmetrized Cartesian product of single-electron wave functions (molecular 4-spinors). The large and small components of the molecular 4-spinors are expanded in a separate series [105, 106]

$$\boldsymbol{\psi}(\vec{r}) = \begin{pmatrix} \boldsymbol{\psi}^L(\vec{r}) \\ \boldsymbol{\psi}^S(\vec{r}) \end{pmatrix} \approx \begin{pmatrix} \displaystyle\sum_{\mu=1}^{N} C_\mu^L \mathbf{M}[L, \mu, \vec{r}] \\ \mathrm{i} \displaystyle\sum_{\mu=1}^{N} C_\mu^S \mathbf{M}[S, \mu, \vec{r}] \end{pmatrix} \tag{62}$$

where $\{\mathbf{M}[L, \mu, \vec{r}]\}$ and $\{\mathbf{M}[S, \mu, \vec{r}]\}$ are the basis sets for large and small components, respectively

$$\mathbf{M}[L, \mu, \vec{r}_{A_\mu}] = N_\mu^L \frac{1}{r_{A_\mu}} g_\mu^L(r_{A_\mu}) \boldsymbol{\chi}_{k_\mu, m_\mu}(\theta_{A_\mu}, \varphi_{A_\mu}) \tag{63}$$

$$\mathbf{M}[S, \mu, \vec{r}_{A_\mu}] = N_\mu^S \frac{1}{r_{A_\mu}} g_\mu^S(r_{A_\mu}) \boldsymbol{\chi}_{-k_\mu, m_\mu}(\theta_{A_\mu}, \varphi_{A_\mu}) \tag{64}$$

In expressions (63) and (64), $\boldsymbol{\chi}_{k_\mu, m_\mu}(\theta_{A_\mu}, \varphi_{A_\mu})$ are two-component spherical spinors centred on the atom $A$ and having the angular and spin structures identical to the structure of atomic spherical bispinors, $C_\mu^{L/S}$ are the expansion coefficients, $g_\mu^{L/S}(r_{A_\mu})$ are radial amplitudes, $N_\mu^{L/S}$ are normalization factors, $\mu$ is the multi-index $\mu = \{A, k, j, m, \lambda\}$, the index $\lambda$ refers to the coefficient in the exponent of a specific case of the Gaussian basis functions

$$g_\mu^L(\vec{r}_A) = r_{A_\mu}^{l_\mu + 1} \exp(-\lambda_\mu r_{A_\mu}^2) \tag{64a}$$

The action of the simple kinetic balance operator $(\vec{\boldsymbol{\sigma}}\hat{\vec{p}})$ on the large component of the two-component basis spinor $\mathbf{M}[L, \mu, \vec{r}_{A_\mu}]$ written in the general form $(1/r)F(r)\boldsymbol{\chi}_{k,m}(\theta, \varphi)$,

where $F(r)$ is the radial function differentiable along the whole space, can be represented as follows:

$$\vec{\sigma}\hat{\vec{p}}\left(\frac{F(r)}{r}\chi_{k,m}(\theta,\varphi)\right)=\frac{\mathrm{i}}{r}\left(\frac{\partial F(r)}{\partial r}+k\frac{F(r)}{r}\right)\chi_{-k,m}(\theta,\varphi) \quad (65)$$

It can be seen that the operator $\vec{\sigma}\hat{\vec{p}}$ transfers the large components into the small component space. By using expression (65), one can determine the shape of the radial part of the small component generated in this way (for Gaussian functions as examples)

$$N_{\mu}^{S}g_{\mu}^{S}(r_{A_\mu})=\left(\frac{\partial}{\partial r_{A_\mu}}+\frac{k_\mu}{r_{A_\mu}}\right)N_{\mu}^{L}g_{\mu}^{L}(r_{A_\mu})= \quad (66)$$

$$=\left(\frac{\partial}{\partial r_{A_\mu}}+\frac{k_\mu}{r_{A_\mu}}\right)N_{\mu}^{L}r_{A_\mu}^{l_\mu+1}\exp(-\lambda_\mu r_{A_\mu}^{2})=$$

$$=N_{\mu}^{L}\left[(k_\mu+l_\mu+1)-2\lambda_\mu r_{A_\mu}^{2}\right]r_{A_\mu}^{l_\mu}\exp(-\lambda_\mu r_{A_\mu}^{2})$$

The normalization factors $N_{\mu}^{L/S}$ are chosen in such a way that for any $\mu$ and $\nu$ values, the overlap integrals

$$S_{\mu\nu}^{L/S}=N_{\mu}^{L/S}N_{\nu}^{L/S}\int_{0}^{\infty}g_{\mu}^{L/S^*}(r)g_{\nu}^{L/S}(r)\mathrm{d}^3\vec{r}$$

be normalized to unity. As can be seen from (66), the exponent remains invariable.

This G-spinor basis set (consisting of Gauss type spinors) is an example of the basis set constructed according to the restricted kinetic balance (RKB) principle.[105, 107, 108] This name is related to the exact projection of the large component space to the small component space

$$\mathbf{M}[S,\mu,\vec{r}\,]=\vec{\sigma}\hat{\vec{p}}\mathbf{M}[L,\mu,\vec{r}\,]$$

The G-spinor basis set in spherical coordinates is very convenient from the mathematical standpoint. Using this basis set eliminates many difficulties, as G-spinors have the same symmetry properties as the atomic 4-spinors. The principle of basis set construction in terms of RKB is also applicable to Gaussian functions in the Cartesian coordinates; however, the final expressions for small components are more sophisticated as they are linear combinations of the initial primitive Gaussian functions in the Cartesian coordinates and do not possess special symmetry properties.

The action of the RKB operator on one primitive Gaussian function from the large component basis space with a radial part (64a) results in a linear combination of primitive Gaussian functions. The coefficients in the exponents of these functions coincide with the initial $\lambda_\mu$, while the exponents $r$ are $l_\mu$ and $l_\mu + 2$. Thus, the orbital quantum numbers are shifted downwards and upwards, respectively, by unity with respect to the initial orbital quantum number ($l_\mu + 1$). As an example, consider one p-function from the large component basis space, which is transformed into one basis function of the small component space representing a linear combination of s- and d-functions.

This procedure for the basis set construction has some subtle details. For example, the Gaussian s-function from the large component basis set gives rise to one p-function in the small component basis set with the same exponent as the initial s-function. If among the basis functions for large components, there is a d-function with the same exponent as in the considered s-function, it, in turn, generates some linear combination of p- and f-functions in the small component basis set, which have the same exponent. This means that, on the one hand, the small component basis set contains some separate p-function, the exponent of which coincides with the exponent of the initial s-function, and, on the other hand, the same p-function is included, with some weight coefficient, into another basis function of the same small component basis set. Evidently, this state of things can lead to a linear dependence of the small component basis set, which increases with increasing basis set dimension; therefore, modern program packages stipulate special procedures that help to avoid this situation.

However, there are approaches that help to turn this disadvantage into an advantage. This is decreasing the dimension of the basis space, from which the small component basis set is constructed. Within the framework of these approaches, the basis functions for the large component basis space are selected in such a way that the exponents of functions with the orbital moments $l_\mu$ and $l_\mu+2$ be equal. Then the $(l-1)$ components that appear at a particular stage will exactly coincide with the $(l+1)$ components generated in the preceding stage, and only $(l+1)$ components will be new in each stage. These efficient basis sets are called dual and are widely used in the modern relativistic quantum chemistry. An even higher efficiency is achieved by making exponents of all basis functions equal, for example, as in the Huzinaga and Klobukowsky basis sets;[109] however, compactness is not the only criterion that must be met by a relativistic basis set.

Yet another difficulty in the construction of RKB-based relativistic basis sets is contraction. The outlined method for generation of small component basis sets according to the RKB principle from contracted large component basis sets is not entirely clear. Indeed, the non-trivial task — determination of contraction coefficients in the generation of basis sets for small components — has been the subject of numerous debates for a long time.[100] Direct application of the restricted kinetic balance operator $\vec{\sigma}\hat{\vec{p}}$ for the construction of small component basis set gives erroneous results, first of all, in the calculation of molecular integrals of the electron–nuclear interaction in the small component part.[100] As a rule, in most cases, kinetically balanced decontracted basis sets are used in four-component relativistic or quasirelativistic calculations.

In the general case, if the potential $\mathbf{V}(\vec{r})$ is not small as compared with $2c^2$ (region around heavy nuclei), the use of the non-relativistic restricted kinetic balance operator $\vec{\sigma}\hat{\vec{p}}$ is not quite correct. A solution to this problem that mimics going beyond the scope of RKB is some artificial saturation of the small component basis set.

Generally, any principle of construction of a balanced basis set, which is not based on the 'exact projection' rule or, even if relies on this rule, still leads to extension of the small component basis space by addition of special basis functions chosen according to the problem specification, is called the unrestricted/extended kinetic balance (UKB/EKB) principle.[105, 108]

In particular, when a small component basis set is constructed according to the UKB principle using the DIRAC software,[110] positron orbitals, also called unphys-

ical solutions, serve as these additional functions. The kinetic energies of the positron orbitals are zero. In this case, according to the uncertainty principle, they should be delocalized throughout the whole space; however, this is not an obstacle for using the positron orbitals as additional functions in constructing the small component basis set, as in essence, they possess some physically substantiated properties. The atomic structure is not reflected in the positron orbitals. Actually, for positrons the atom is either totally absent, if it is neutral, or looks like some point charge, if the atom is charged. A positively charged atom repels, while the negatively charged one attracts the positrons and thus transfers them in the bound state. In the most frequent case of a neutral atom, the positron wave functions are solutions of the free Dirac equation but have no projection to the electron continuum. Therefore, on the one hand, addition of positronic solutions to the small component basis set does not cause an additional linear dependence and, on the other hand, it turns out that unphysical solutions behave in a quite physical way.

One more convenient feature of the positronic solutions is that they can be easily separated from the electronic solutions, as their energy levels are located below $-2c^2$. The procedure of elimination of unphysical solutions from the molecular space at final calculation stages was reported.[111]

The differences between the RKB and UKB balances have been considered.[105] For better understanding of their origin, the characteristic one-particle Dirac equation should be represented in the matrix form.

If the restricted kinetic balance condition is fulfilled, the dimensions of the basis sets for the large and small components coincide (the exact projection scheme) and are equal to $N$. If the 4-spinors are substituted into the initial general type one-particle equation (57) in the form of expansion (62) in the sets of basis functions for large and small components (63) and (64), then this equation is represented in the matrix form as

$$\begin{bmatrix} \mathbf{V}^{LL} & \mathbf{\Pi}^{LS} \\ \mathbf{\Pi}^{SL} & \mathbf{V}^{SS} - 2c^2\mathbf{S}^{SS} \end{bmatrix} \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = \varepsilon \begin{pmatrix} \mathbf{S}^{LL} \\ \mathbf{S}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} \tag{67}$$

In this equation, the matrices have the dimension $N \times N$, $\mathbf{C}^{L/S}$ are the column vectors with the dimension $N \times 1$ of the coefficients of expansion of 4-spinor large and small components in the large and small component basis sets. Non-diagonal block kinetic matrices $\mathbf{\Pi}$ have the form

$$\| \mathbf{\Pi}^{LS} \|_{\mu\nu} = N_\mu^L N_\nu^S \int_0^\infty g_\mu^L(r)^* \left( -\frac{\partial}{\partial r} + \frac{k}{r} \right) g_\nu^S(r) \mathrm{d}r \tag{68}$$

$$\| \mathbf{\Pi}^{SL} \|_{\mu\nu} = N_\nu^S N_\mu^L \int_0^\infty g_\nu^S(r)^* \left( \frac{\partial}{\partial r} + \frac{k}{r} \right) g_\mu^L(r) \mathrm{d}r \tag{69}$$

The large and small blocks of the block-diagonal potential energy $\mathbf{V}$ and overlap $\mathbf{S}$ matrices can be expressed as

$$\mathbf{V}_{\mu\nu}^{LL/SS} = N_\mu^{L/S} N_\nu^{L/S} \int_0^\infty g_\mu^{L/S}(r)^* V(r) g_\nu^{L/S}(r) \mathrm{d}r \tag{70}$$

$$\mathbf{S}_{\mu\nu}^{LL/SS} = N_\mu^{L/S} N_\nu^{L/S} \int_0^\infty g_\mu^{L/S}(r)^* g_\nu^{L/S}(r) \mathrm{d}r \tag{71}$$

The first crucial difference between the RKB and UKB principles is the different descriptions of the kinetic energy matrix in the non-relativistic limit for each of these two schemes. In the case of RKB, the large block of the matrix of the kinetic energy operator $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}/2$ is expressed in terms of the kinetic matrix $\mathbf{\Pi}$ and overlap matrix $\mathbf{S}$ blocks[105]

$$2 \| \mathbf{T}^{LL} \|_{\mu\nu} = \| \mathbf{\Pi}^{LS} \left( \mathbf{S}^{SS} \right)^{-1} \mathbf{\Pi}^{SL} \|_{\mu\nu} \tag{72}$$

The fulfilment of the RKB principle ensures that the matrix identity (72) is strict even if the basis set used for large components is incomplete.[105] This fact ensures the correct non-relativistic limit in all cases (irrespective of basis set completeness)

$$\left\{ \frac{1}{2} \mathbf{\Pi}^{LS} \left( \mathbf{S}^{SS} \right)^{-1} \mathbf{\Pi}^{SL} + \left( \mathbf{V}^{LL} - \varepsilon \mathbf{S}^{LL} \right) \right\} \mathbf{C}^L = \mathbf{0} \tag{73}$$

In the case of UKB, some basis functions $N'$ are added to the basis set for small components, so that the dimensions of blocks of the Hamiltonian matrix will be different. The dimension of block $SS$ of the matrix $\mathbf{S}$ is $(N+N') \times (N+N')$, and the dimensions of blocks $LS$ and $SL$ of the kinetic matrix are $N \times (N+N')$ and $(N+N') \times N$, respectively; the matrix product $(1/2)\mathbf{\Pi}^{LS} \left( S^{SS} \right)^{-1} \mathbf{\Pi}^{SL}$ does not provide the exact matrix representation of the non-relativistic kinetic energy

$$\frac{1}{2} \mathbf{\Pi}^{LS} \left( \mathbf{S}^{SS} \right)^{-1} \mathbf{\Pi}^{SL} \neq \mathbf{T}^{LL}$$

only if the complete basis set limit is not considered. In practice, this results in an underestimated non-relativistic kinetic energy, an incorrect non-relativistic limit and a strongly underestimated (overestimated in magnitude) total relativistic energy.

One more difference between the RKB and UKB schemes does not attest in favour of the latter. The UKB scheme implies the appearance of additional $N'$ basis functions in the small component basis space. These functions are introduced artificially and, in some cases, they do not have a definite physical interpretation.[93] In addition, their presence increases the problem dimension, which substantially increases the computational cost and generates some other problems related to the increase in the small component basis set, in particular, the appearance of the linear dependence in this set.[112]

However, it should be borne in mind that, despite the drawbacks of the UKB principle, it should be preferred if one needs the most correct description of the electron density near heavy nuclei (*e.g.*, in the calculation of SSCCs for heavy nuclei). If the task is to calculate a property mainly confined to the valence region, RKB is a more reasonable choice, because the use of either UKB or RKB is almost equivalent in this case. In practice, it is most often quite sufficient to use a decontracted basis set, which has proved efficient for non-relativistic calculations of SSCCs, for large components in combination with the RKB principle for the construction of a small component basis set. Thus, the use of the UKB principle is rather desirable than necessary.

It is noteworthy that the types of kinetic balance considered above do not imply the presence of an external

magnetic field. For calculation of the NMR spectral parameters at the four-component level, this appears to be a considerable drawback. The concept of magnetically balanced basis set was first proposed by Kutzelnigg[113] and Aucar and co-workers,[114,115] and a discussion was reported by Pecul *et al.*[116] However, the practical application of the restricted magnetic balance (RMB) in the calculation of SSCCs and shielding constants was first reported by Malkin's team,[117,118] who used four-component DFT formalism. The approach was based on the restricted kinetic balance operator in which the momentum operator was extended to the magnetic field of the two nuclei involved in the spin–spin coupling of interest,

$$\hat{\mathbf{X}}^{(\vec{\mu}^M,\vec{\mu}^N)} = \frac{1}{2c}\left(\vec{\boldsymbol{\sigma}}\,\hat{\vec{p}} + \frac{1}{c}\vec{\boldsymbol{\sigma}}\,\vec{A}_{\vec{\mu}^M} + \frac{1}{c}\vec{\boldsymbol{\sigma}}\,\vec{A}_{\vec{\mu}^N}\right) \qquad (74)$$

Hence, the basis set for small components becomes dependent on the external magnetic field, that is, as applied to SSCCs, on the nuclear magnetic field. In a well-known paper of Repiský and co-workers,[118] RMB was demonstrated to ensure the variational stability at the same level as the usual RKB method.

About the same time, Xiao's team[119,120] proposed the orbital decomposition approach (ODA), which, like the RMB approach, took into account the effect of magnetic field, in particular, magnetic field of the nuclei. Both approaches — RMB and ODA — are applicable to the calculation of magnetic resonance parameters such as magnetic shielding constants and spin–spin coupling constants.

Komorovský *et al.*[118] compared these two approaches. Their common feature is that both go beyond the scope of the common restricted kinetic balance and consider the response of small components to magnetic perturbation, although in different ways. Unlike the RMB concept, the founders of the ODA method start from the operator form of the Dirac–Kohn–Sham (DKS) equations. In the ODA theory, the small component basis set cannot be introduced until the response equations are not formulated within the large component basis space. The resulting equations are fairly complex as they contain a specific type of operator that has single-electron potential and orbital energies in the denominator. Thus, the ODA method is based on expressing the small components in terms of the large components in the presence of a magnetic field (elimination of small components). An advantage of this approach is that only basis sets of large components are used in the ODA. However, this approach suffers from quite a few drawbacks, which have been discussed.[121] In particular, the resulting response equations are very cumbersome, and this considerably increases the computation time. This circumstance is inherent in the grounds of this method: the use of operator equations instead of the efficient matrix form.

The ODA method was implemented in the BDF program package,[122,123] and the first results refer only to the shielding tensor; however, the application of the ODA also to the calculation of SSCCs should also be anticipated.

The relativistic calculations of SSCCs require a specific approach to the choice of basis sets. They should possess properties suitable for correct description of the spin–spin interaction transfer mechanism, on the one hand, and the relativistic effects, on the other hand, and should also possess some universal features (in particular, those inherent also in non-relativistic basis sets). These features include, first of all, a high-quality approximation of the exact atomic wave functions with a minimal number of expansion terms, possibility of fast and efficient calculation of matrix elements and some other. In non-relativistic calculations, Gaussian basis sets are most popular, as they undoubtedly comply with the key universal requirements and, what is more important, are most efficient and convenient. The situation is similar for relativistic calculations: most basis sets are based in Gaussian type functions. A number of issues concerning ill-defined behaviour of Gaussian functions near nuclei (especially if the description of the near-nuclear region is of prime importance, for example, in the calculation of the SSCCs involving one or two heavy nuclei) are of little importance for relativistic calculations, as with any finite-size nuclear model, the problems of behaviour of Gaussian functions near the nucleus virtually disappear.

The simplest and the most natural version of a large component basis for the relativistic basis set is some non-relativistic basis set that has proved itself efficient for non-relativistic calculations. In most cases, exactly this approach is embodied in practice; furthermore, the chosen non-relativistic basis set should be used in the decontracted form. However, this position is not absolutely correct for the following reasons:[124]

— relativistic calculations require Gaussian functions with very high exponent values, so-called tight Gaussian functions, which describe in the best way the near-nuclear region; *e.g.*, the $2p_{1/2}$ orbital should give much higher density in the near-nuclear region than a non-relativistic 2p-orbital; furthermore, the latter, unlike the relativistic one, corresponds to a zero probability for the electron to be located at the centre of the nucleus;

— orbitals with the orbital moment $l > 0$ are split, in the relativistic case, into two components, which can have their radial maxima much more remote than the corresponding non-relativistic analogue; this makes the latter inapplicable for a relativistic problem.

During a long time, relativistic calculations have been performed using common basis sets optimized in terms of the Schrödinger equation formalism and some of their modifications taking into account the relativistic specific features. The non-relativistic basis sets used most often include Dunning's correlation-consistent basis sets,[125–133] Jensen polarization-consistent basis sets[134] and the Sauer basis sets,[135] which were specially modified for the calculation of SSCCs.

Upon some modifications, all of these basis sets in the decontracted form provide fairly accurate results also for relativistic systems, especially if they have been supplemented with special tight p-functions for improved description of spinors with the azimuthal quantum number $k = +1$ in the near-nuclear region. However, as the nuclear charge increases, the artificial measures undertaken for emulation of the correct structure of the wave function near the nucleus become insufficient, and it is evident that high-precision relativistic calculations of characteristics such as SSCCs require the use of relativistic basis sets optimized in terms of the four-component Dirac equation formalism.[136–179]

The first program for optimization of relativistic basis sets was proposed by Dyall and Faegri.[148] Initially, basis sets were optimized in this program by the DHF method using the Dirac–Coulomb (DC) Hamiltonian (without

considering the Breit interaction) and the finite-size nucleus model with a Gaussian charge density distribution. Then the program was extended to the possibility of obtaining correlation-consistent basis functions in terms of the configuration interaction method. This program initiated a series of relativistic Dyall basis sets,[166–177] which are currently most widely used in the relativistic quantum chemical calculations of SSCCs.

However, as a rule, relativistic basis sets result in so-called variational collapse,[158, 178–180] which arises upon neglecting the Talman variational principle [181] in exponent optimization. This principle leads, on the one hand, to the problem of finding the energy minimum from large orbital components, and, on the other hand, to the problem of finding the maximum in the variational space of small orbital components. This problem is related to the variational collapse, as in addition to the Talman variational principle, the kinetic balance condition should hold for large and small components, which is not always compatible. Often, in the construction of the basis sets, the Talman minimax principle is neglected and the basis functions are optimized for large components and then projected to the small component space using simple kinetic balance [104]

$$\{\psi^S\} \supseteq \{(\vec{\sigma}\hat{\vec{p}})\psi^L\}$$

In this case, the Dirac–Hartree–Fock–Roothaan total energy (DHFR) proves to be smaller (greater in magnitude) than the total energy obtained by the numerical solution of the DHFR equation with full-value application of the Talman principle. This problem was disclosed for the first time by Faegri [152] during the development of relativistic Gaussian basis sets in which the subset of s-, d- and g-functions have a common coefficient in the exponent, while the p-, f- and h-functions have a different coefficient.[148]

In practical calculations, this problem appears as an increase in the Dirac–Fock–Coulomb orbital energies in magnitude upon the addition of tight functions to the basis set [178, 182] and becomes more significant with increasing nuclear charge, especially starting from $Z \geqslant 80$.[161–163]

In the last decade, construction of relativistic basis sets free from the variational collapse has received considerable attention.[161–163] The most recent achievements in solving this problem were reported by Teodoro *et al.*,[178, 179] who proposed special relativistic basis sets of the QZ level for s-, p- and d-elements — RPF-4Z and aug-RPF-4Z of the RPF family. These basis sets allow one to avoid the variational collapse and are not inferior in the key characteristics to classical Dyall basis sets at the corresponding level.

Yet another important aspect concerns the specific character of the problem, *i.e.*, the effect of basis sets on the relativistic SSCC values. Enevoldsen *et al.*[183] investigated the dependences of the $^1J(^{13}C,^1H)$ and $^2J(^1H,^1H)$ coupling constants in methane on the number of tight s-functions added in the relativistic calculations by the DIRAC program [110] in terms of the four-component random phase approximation (4RPA) scheme (Table 2). The initial basis sets for the large components represented special decontracted relativistic Gaussian basis sets [184] optimized at the relativistic level using the modified GRASP software,[148, 185] and the basis functions of small components were constructed according to the RKB principle. The non-relativistic calculations were performed using the DALTON program [186] at the non-relativistic RPA level in the same relativistic basis sets as for large components.

As can be seen from the data presented in Table 2, the dependence of SSCCs calculated by four-component relativistic methods on the number and haracteristics of added s-functions is virtually the same as in the case of non-relativistic calculations (note that this conclusion concerns only those SSCCs in which the Fermi-contact interaction makes the predominant contribution). Enevoldsen *et al.*[183] explained this change in the SSCCs. First, the determination of the matrix elements of the relativistic operator of electron interaction with nuclear magnetic fields $\vec{\alpha}[\vec{\mathbf{I}}_N \times \vec{r}\,]/r^3$ in the molecular 4-spinor basis set gives rise to interconnection of the large and small components

$$\left(\langle \psi_p^L |, \langle \psi_p^S |\right) \begin{pmatrix} \mathbf{0} & \vec{\sigma} \\ \vec{\sigma} & \mathbf{0} \end{pmatrix} \frac{[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \begin{pmatrix} |\psi_q^L\rangle \\ |\psi_q^S\rangle \end{pmatrix} = \tag{75}$$

$$= \left\langle \psi_p^L \middle| \frac{\vec{\sigma}[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \middle| \psi_q^S \right\rangle + \left\langle \psi_p^S \middle| \frac{\vec{\sigma}[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \middle| \psi_q^L \right\rangle$$

Meanwhile, the large and small components are connected by the RKB condition

$$|\psi_p^S\rangle = \frac{1}{2c}\vec{\sigma}\hat{\vec{p}}\,|\psi_p^L\rangle$$

substitution of which into expression (75) affords the operator matrix element $\vec{\alpha}[\vec{\mathbf{I}}_N \times \vec{r}\,]/r^3$ in the molecular 4-spinor basis set as a matrix element in the large component basis set

$$\left\langle \psi_p \middle| \vec{\alpha} \frac{[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \middle| \psi_q \right\rangle = \tag{76}$$

$$= \left\langle \psi_p^L \middle| \vec{\sigma} \frac{[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \frac{\vec{\sigma}\hat{\vec{p}}}{2c} + \left(\frac{\vec{\sigma}\hat{\vec{p}}}{2c}\right)^+ \vec{\sigma} \frac{[\vec{\mathbf{I}}_N \times \vec{r}\,]}{r^3} \middle| \psi_q^L \right\rangle$$

In the non-relativistic limit, the matrix element (76) is reduced to the matrix element of the sum of contributions of the Fermi-contact and spin–dipole interactions in the same basis set of large components. Thus, the matrix element of the relativistic spin–spin interaction operator in the space of molecular 4-spinors is transformed under the RKB

**Table 2**. Changes in the $^1H-^1H$ and $^{13}C-^1H$ coupling constants (Hz) for the methane molecule calculated at the relativistic ($\Delta^1J_{rel}$) and non-relativistic ($\Delta^1J_{nr}$) levels upon successive addition of tight s-functions (from the data of Ref. 183).

| Exponential factor of the tight s-function | $\Delta^1J_{rel}(^{13}C,^1H)$ | $\Delta^1J_{nr}(^{13}C,^1H)$ | $\Delta^2J_{rel}(^1H,^1H)$ | $\Delta^2J_{nr}(^1H,^1H)$ |
|---|---|---|---|---|
| $1.3\times10^5$ | 10.894 | 10.820 | −2.4069 | −2.4091 |
| $1.4\times10^6$ | 2.4533 | 2.4380 | −0.6245 | −0.6251 |
| $1.6\times10^7$ | 1.1704 | 1.1707 | −0.2760 | −0.2765 |

conditions into a matrix element of the modified operator in the large component basis space, which coincides with the basis space of non-relativistic calculations. Hence, it follows that the qualitative behaviour of SSCCs depending on the basis set should not change on going from a non-relativistic to a relativistic scheme within the framework of the same method.

The dependence of SSCCs [exemplified by $^1J(^1\mathrm{H,X})$, X = $^{13}$C, $^{29}$Si, $^{73}$Ge, $^{119}$Sn] on the basis set has been studied for $XH_4$ molecules at the two-component calculation level using the Douglas–Kroll–Hess (DKH) method.[187] The initial basis set was the decontracted aug-cc-pVTZ Dunning's set [125–127] successively augmented by tight s-functions on the H and X atoms. As a result it was found that the convergence of the SSCCs calculated by the first-order DKH method (DKH1) is faster than the convergence of the SSCCs calculated by the second-order DKH scheme (DKH2) or the non-relativistic RPA scheme.

However, despite the fast SSCC convergence to the basis set, the DKH1 method gives overestimated relativistic corrections even for the SSCCs of light nuclei, while the DKH2 scheme, although provides a slower convergence of the property to the basis set, finally gives values that are closer to the values obtained using the four-component DHF scheme, which can be regarded as a calibration with respect to any two-component method within the same formalism.

In conclusion of this section, pay attention to the relativistic pseudopotentials (relECP).[188–192] In some cases, the relativistic description of properties within the all-electron basis set concept (*i.e.*, with inclusion of all single-particle electron wave functions into the calculation space) appears quite difficult because of very high expenditure of computer resources. A way to find a compromise between the computation accuracy and computation cost is the use of the relECP pseudopotentials proposed for the first time by Lee *et al.*[193] for calculating the electronic structures of some heavy elements.

The relECP concept is based on replacement of the representation of an electron system as a set of all constituent electrons by an effective analogue of this representation in which only the electrons of the valence subsystem, *i.e.*, the outer shell subset, are taken as separate particles. The presence of inner shell electrons, which are not considered as separate particles, is simulated as an additional effective spin-dependent single-electron potential for the interaction of each valence subsystem electron with all inner electrons

$$\widehat{H} = \sum_i \left(\widehat{T}_i + \widehat{U}_i\right) + \sum_{i>k} \frac{1}{r_{ik}} \tag{77}$$

All of the summations in this Hamiltonian are performed only over valence subsystem electrons, $\widehat{T}_i$ are non-relativistic kinetic energies of the electrons of this subsystem, $\widehat{U}_i$ is the spin-dependent pseudopotential which comprises interaction operators for the interaction of *i*th electron from the valence subsystem with the nuclear electric field and with the effective field of inner-shell electrons and bears all information about the relativistic effects and nuclear charge distribution.

This formalism at both relativistic and non-relativistic levels was developed, first of all, for calculating the molecular properties in which the key role is played by valence shell electrons. The application of this formalism to the calculation of SSCCs is not always justified, as the inner electrons are very important for SSCC calculations at any level of theory.

### III.5. Nuclear models

A significant aspect of relativistic quantum chemical calculations of SSCCs is the choice of a nuclear model.

The so-called point nucleus model is widely used in the non-relativistic theory;[194] according to this model, the charge density and the nuclear potential are determined by only one nuclear parameter — the charge $Z$. The charge density in this model has the form of Dirac $\delta$-function, while the potential is Coulombic

$$\rho^{\mathrm{p}}(R) = \mathrm{e}Z\delta(R) \tag{78}$$

$$V^{\mathrm{p}} = -\frac{\mathrm{e}Z}{r} \tag{79}$$

$R$, $r$ are the nuclear and electron radial coordinates.

This model is well suited for either non-relativistic or relativistic calculations of properties in which the valence shells of atoms play the predominant role. In the non-relativistic case, basis functions close to solutions of the Schrödinger equation for hydrogen-like atoms are usually most appropriate. If the point nucleus model is used, the basis functions have the same form for every type of atom and their radial parts can be expressed by the Slater functions $r^n \exp(-\lambda r)$. Nevertheless, Gaussian functions $r^n \exp(-\alpha r^2)$ are used most often in practice, which is related to the simplified calculation of the multicentre atomic integrals.[195] Functions of both types contain $r$ raised to an integer power, and for $r \to 0$ the singularity is absent. In the relativistic problem, the basis functions are so selected that they reproduce the solutions of the single-electron Dirac equation. In the relativistic case, the asymptotic behaviour of the radial functions at infinity ($r \to \infty$) is described, as shown by Grant and Quiney,[99] by the exponent $\exp(-\lambda r)$, where $\lambda$ is a real-valued positive parameter. The asymptotic behaviour at zero for these functions is determined, first of all, by the nuclear model used. According to the point nucleus model, their radial parts $R(r)$ contain the relativistic root. For example, for the $1s_{1/2}$ shell, $R(r)$ has the form

$$R(r) \sim r^{\sqrt{1-Z^2/c^2}-1} \exp(-\lambda r)$$

In the relativistic case, the modulus of the radius vector $r$ has no integer power because the velocity of light is finite. For $r \to 0$, the radial parts of the $s_{1/2}$- and $p_{1/2}$-shells have weak singularity,[99] so that the asymptotic behaviour of these functions near zero is difficult to describe. If the point nucleus model is still used in the relativistic quantum chemical calculations, to attain the same accuracy as in non-relativistic calculations (with the same parameters and nuclear model), very large basis sets, capable of providing the convergence of the calculated properties, are used.

Thus, the point nucleus model is not recommended for relativistic calculations, especially as applied to SSCCs, because this property is determined in the vast majority of cases by the inner electrons.

Relativistic calculations are better performed with other nuclear models that imply a finite size of a nucleus, not only for the reason of mitigating the mathematical difficulties (see above) but also for mere physical reasons associated, for example, with the large size of heavy nuclei.

A popular non-point nucleus models is the model proposed in Refs 194 and 196. This model uses the Gaussian function for nuclear charge distribution

$$\rho^{\mathrm{G}}(R) = \mathrm{e}Z\left(\frac{\lambda}{\pi}\right)^{3/2}\exp\left(-\lambda R^2\right) \tag{80}$$

and the nuclear potential is expressed in terms of the error function

$$V^{\mathrm{G}}(r) = -\frac{\mathrm{e}Z}{r}\mathrm{erf}(\sqrt{\lambda}r) \tag{81}$$

where

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp\left(-t^2\right)\mathrm{d}t \tag{82}$$

The use of the Gaussian nuclear model results in the change of boundary conditions in the nuclear region and, as a result, the atomic 4-spinors take the Gaussian form,[146] which is very beneficial when the Gaussian basis sets are used. This nuclear charge distribution makes it possible to avoid the singularity at zero and physically incorrect discontinuity of the nuclear charge distribution function at the boundary of the nucleus, which is the case for some other nuclear models with a finite-size nucleus.

A simpler model is representing a nucleus as a homogeneously charged sphere (HCS),[194] the charge density function of which is

$$\rho^{\mathrm{HCS}}(R) = \rho_0^{\mathrm{HCS}},\ R \leqslant R_0 \tag{83}$$

$$\rho^{\mathrm{HCS}}(R) = 0,\ R > R_0$$

$$\rho_0^{\mathrm{HCS}} = \frac{3\mathrm{e}Z}{4\pi R_0^3}$$

where $R_0$ is the nuclear radius. The potential at $r \leqslant R_0$ has the form

$$V^{\mathrm{HCS}}(r) = -\frac{\mathrm{e}Z}{2R_0}\left[3 - \left(\frac{r}{R_0}\right)^2\right]$$

and at $r > R_0$, it is given by

$$V^{\mathrm{HCS}}(r) = -\frac{\mathrm{e}Z}{r} \tag{84}$$

The HCS model is in essence quite simple. The potential inside the sphere is harmonic, which ensures the Gaussian shape of exact atomic 4-spinors, and this provides the possibility of using the efficient mechanism of calculation of atomic integrals while using the Gaussian basis sets.[146, 197 – 199] As can be seen from the potential form (84), its second derivative with respect to the electron radial coordinate has a discontinuity at the sphere boundary, which of course can bring some complications to numerical integration unless it is not specially envisaged.

The Fermi nuclear model[194, 200] is believed to correspond most closely to the real nuclear charge distribution; however, in this model it is impossible to represent the nuclear potential in an analytical form. The nuclear charge density function in the Fermi model has the form

$$\rho^{\mathrm{F}}(R) = \rho_0^{\mathrm{F}}(R)\left\{1 + \exp\left[4\ln\frac{3(R-C)}{T}\right]\right\} \tag{85}$$

The parameter $C$ is called the half-charge radius, because it determines the radial distance from the nucleus centre to the point in which the charge density is half its maximum value

$$\rho^{\mathrm{F}}(C) = 0.5\,\rho_0^{\max}$$

The parameter $T$ is defined as the thickness of the spherical layer in which $\rho^{\mathrm{F}}(R)$ falls from $0.9\,\rho_0^{\max}$ to $0.1\,\rho_0^{\max}$.

For all nuclear models, the nuclear parameters are either determined experimentally or calculated using empirical relations. For example, Visscher and Dyall[194] reported parameters of nuclear models for 109 elements.

In the relativistic quantum chemical calculations of SSCCs, the Gaussian nuclear model is used most frequently. Autschbach[47, 201] reported a detailed discussion of the effect of the type of nuclear model on the SSCC values. In particular, he considered the spherical Gaussian nuclear model[194, 196] in comparison with the point charge nuclear model[194] at the level of the two-component ZORA method[47] in terms of DFT (the complete version and scalar approximation) as applied to various types of SSCCs.[202 – 205]

Description of a nucleus as a finite-size object results in a considerable decrease (in magnitude) of the SSCCs for heavy nuclei such as $^{183}$W, $^{195}$Pt, $^{199}$Hg, $^{203}$Tl and $^{207}$Pb nuclei as compared with the values obtained using the point nucleus model. The magnitude of this effect is 10% – 15%, and for the SSCCs between two heavy nuclei it is even larger. The reduced $^1K$(Tl,Br) and $^1K$(Tl,I) constants for the compounds TlBr and TlI calculated using the ZORA – DFT(PBE0) method[206] with the point and Gaussian models of the nucleus are summarized in Table 3.

All calculations of the authors of that paper were performed using the ADF program package.[209 – 211] Typically, all of the basis sets are relativistic Slater sets optimized at the ZORA level.[201] In the presented SSCCs, the Fermi-contact interaction does not make a predominant contribution and, hence, they can be tested for convergence as functions of the basis sets, without being restricted to consideration of SSCCs with predominant Fermi-contact interaction.

Of note is the fact that the mechanisms of spin – spin interaction arising in the ZORA formalism somewhat differ from those derived from the Ramsey formalism.[212] Indeed, in the case of ZORA the following mechanisms can be distinguished: ZSO, ZSO – ZSO, ZPSO and ZDSO (ZSO stands for the ZORA spin – orbit and ZPSO stands for ZORA paramagnetic spin – orbit),[204] while in the Ramsey formalism there are Fermi contact (FC), spin – dipole (SD), paramagnetic spin – orbit (PSO) and diamagnetic spin – orbit (DSO) mechanisms. In the non-relativistic limit, the ZDSO contribution is transformed into DSO, ZPSO is

**Table 3**. Isotropic reduced $^1K$(Tl,Br) and $^1K$(Tl,I) coupling constants (data of Ref. 201).

| Basis set | $^1K$(Tl,Br) | | | $^1K$(Tl,I) | | |
|---|---|---|---|---|---|---|
| | point model | Gaussian model | difference (%) | point model | Gaussian model | difference (%) |
| TZ2P | −324.0 | −323.3 | 0.2 | −421.9 | −421.8 | 0.0 |
| JCPL | −399.3 | −384.9 | 3.7 | −521.4 | −505.2 | 3.2 |
| TZ2P0 | −356.5 | −361.8 | −1.5 | −395.4 | −396.7 | −0.3 |
| TZ2P1 | −354.1 | −353.3 | 0.2 | −468.1 | −467.9 | 0.0 |
| TZ2P2 | −391.6 | −384.8 | 1.8 | −516.8 | −507.1 | 1.9 |
| TZ2P3 | −424.1 | −401.6 | 5.6 | −546.3 | −522.2 | 4.6 |
| TZ2P4 | −471.5 | −440.6 | 7.0 | −579.0 | −548.3 | 5.6 |
| TZ2P5 | −486.3 | −454.6 | 7.0 | −585.7 | −555.2 | 5.5 |
| Experiment | | −361 | | | −474 | |

**Note**. The SSCC values are given in $10^{20}$ $T^2 J^{-1}$. The experimental data were taken from the date of Refs 207 and 208.

converted to PSO, ZSO turns into the sum FC + SD, and the ZSO – ZSO cross-contribution disappears. In the TlBr and TlI molecules, the ZSO mechanism makes a positive contribution, ZPSO makes a negative contribution, and the ZSO – ZSO cross-mechanism makes a great negative contribution.[201]

The accuracy of description of each mechanism is determined by specific features of the basis set used; therefore, the basis set starting from which the relative change in the SSCC is small (at a specified accuracy) can be regarded as sufficient for the description of not only SSCC as a whole but also each separate contribution. It can be seen from the data presented in Table 3 for the largest TZ2P4 and TZ2P5 basis sets, the result can be considered convergent to some accuracy and the relative difference between the results obtained using the two considered models of the nucleus is 5.5% for $^1K$(Tl,I) and 7% for $^1K$(Tl,Br). The results obtained by the Gaussian model were closer to the experimental values. This proves once again that for quantum chemical calculations of SSCCs using various relativistic and quasirelativistic methods, a finite-size nucleus model is always preferred.

## IV. Relativistic theory of the spin – spin coupling constants

### IV.1. Four-component representation of spin – spin coupling constants

The relativistic SSCC theory is based on the Dirac equation taking into account the electromagnetic field. The initial Dirac equation (with energy scale shift) for an electron in an external electromagnetic field has the form

$$\left[c^2(\boldsymbol{\beta}-\mathbf{I})+c\,\vec{\boldsymbol{\alpha}}\left(\hat{\vec{p}}-\frac{1}{c}\vec{A}(\vec{r},t)\right)+\phi(\vec{r},t)\,\mathbf{I}\right]\boldsymbol{\psi}(\vec{r},t)= \\ =\widehat{\mathbf{H}}_{\mathrm{D}}\boldsymbol{\psi}(\vec{r},t)=\mathrm{i}\frac{\partial\boldsymbol{\psi}(\vec{r},t)}{\partial t} \tag{86}$$

where $\vec{A}(\vec{r},t)$, $\phi(\vec{r},t)$ are the vector and scalar potentials, respectively, $\boldsymbol{\psi}(\vec{r},t)$ is the four-component complex wave function (4-spinor).

Using the four-dimensional momentum $\hat{p}^{\mu}$

$$\hat{p}^{\mu}=\mathrm{i}\frac{\partial}{\partial x_{\mu}}=\mathrm{i}\left\{\frac{1}{c}\frac{\partial}{\partial t};\,-\hat{\vec{\nabla}}\right\}=\left\{\frac{\widehat{E}}{c};\,-\mathrm{i}\hat{\vec{\nabla}}\right\} \tag{87}$$

the four-dimensional potential $A^{\mu}$

$$A^{\mu}=\left\{\phi,\vec{A}\right\} \tag{88}$$

and the elongated (by the magnetic field) four-dimensional momentum $\hat{\pi},^{\mu}$

$$\hat{\pi}^{\mu}=\hat{p}^{\mu}-\frac{1}{c}A^{\mu}=\left\{\hat{\pi}^0,\,\hat{\vec{\pi}}\right\} \tag{89}$$

where

$$\hat{\pi}^0=\frac{1}{c}\left(\mathrm{i}\frac{\partial}{\partial t}-\phi(\vec{x},t)\right) \tag{90}$$

$$\hat{\vec{\pi}}=\left(-\mathrm{i}\hat{\vec{\nabla}}-\frac{1}{c}\vec{A}(\vec{x},t)\right) \tag{91}$$

equation (86) can be represented in a more compact form

$$\left[c\hat{\pi}^0\,\mathbf{I}-c^2(\boldsymbol{\beta}-\mathbf{I})-c\,\vec{\boldsymbol{\alpha}}\hat{\vec{\pi}}\right]\boldsymbol{\psi}(\vec{r},t)=0 \tag{92}$$

or in the form [53]

$$\left[\hat{\mathbf{h}}_{\mathrm{D}}^0+\widehat{\mathbf{H}}_{\mathrm{mag}}\right]\boldsymbol{\psi}(\vec{r},t)=\mathrm{i}\frac{\partial\boldsymbol{\psi}(\vec{r},t)}{\partial t}=\widehat{E}\,\boldsymbol{\psi}(\vec{r},t) \tag{93}$$

Here $\hat{\mathbf{h}}_{\mathrm{D}}^0=\phi\,\mathbf{I}+c^2(\boldsymbol{\beta}-\mathbf{I})+c\,\vec{\boldsymbol{\alpha}}\hat{\vec{p}}$ is the Dirac operator free from the external magnetic field and $\widehat{\mathbf{H}}_{\mathrm{mag}}=-\vec{\boldsymbol{\alpha}}\vec{A}$ is the electron – magnetic field interaction operator.

When Eqn (93) is extended to a many-electron system occurring in the electromagnetic field of nuclei at rest, the operators $\hat{\mathbf{h}}_{\mathrm{D}}^0$ for each electron form the single-electron part of the Hamiltonian, while the exact electron – electron interaction not representable in the closed form can be expressed, in a zero approximation, by a Coulomb term. The one-particle operator $\widehat{\mathbf{H}}_{\mathrm{mag}}$ taking into account the interaction of electrons with the nuclear magnetic field, is transformed into the sum of operators $\widehat{\mathbf{H}}_N$ over all nuclei, that is

$$\widehat{\mathbf{H}}_{\mathrm{mag}}=\sum_{N=1}^{N_{\mathrm{nuc}}}\widehat{\mathbf{H}}_N \tag{94}$$

$$\widehat{\mathbf{H}}_N=-\sum_{n=1}^{N_{\mathrm{e}}}\prod_{i=1}^{n-1}{}^{\otimes}\,\mathbf{1}_{4\times4}(i)\otimes\vec{\boldsymbol{\alpha}}_n\vec{A}_N(\vec{r}_{nN})\otimes\prod_{i=n+1}^{N_{\mathrm{e}}}{}^{\otimes}\,\mathbf{1}_{4\times4}(i) \tag{95}$$

The 4-spinor $\psi(\vec{r}, t)$ is transformed into the wave function of the $N_e$-electron system $\Psi(\zeta_1, \zeta_2, ..., \zeta_e; t)$, where $\zeta_n$ is the set of degrees of freedom of an $n$th electron. The dimension of $\Psi(\zeta_1, \zeta_2, ..., \zeta_e; t)$ is $4^{N_e}$. The vector $\vec{r}_{nN} = \vec{r}_n - \vec{R}_N$ is the difference between the radius vector of the $n$th electron and the $N$th nucleus,

$$\vec{A}_N(\vec{r}_{nN}) = \left[\vec{\mu}_N \times \frac{\vec{r}_{nN}}{r_{nN}^3}\right]$$

is the vector potential of the magnetic field of the $N$th nucleus in the point of location of the $n$th electron, and $\vec{\mu}_N$ is the magnetic moment of the $N$th nucleus.

Thus, if the complex matrix structure in expression (95) is omitted, the operator $\hat{\mathbf{H}}_N$ can be expressed as

$$\hat{\mathbf{H}}_N = -\sum_n^{N_e} \boldsymbol{\alpha}_n \left[\vec{\mu}_N \times \frac{\vec{r}_{nN}}{r_{nN}^3}\right] = \sum_{\alpha=\{x,y,z\}} \mu_{N\alpha} \hat{\mathbf{Z}}_{N\alpha} \tag{96}$$

In expression (96), the Cartesian components of the operator $\hat{\mathbf{Z}}_N$ can be expressed in the context of tensor analysis using the Levi – Civita tensor $\varepsilon_{\alpha\beta\delta}$

$$\hat{\mathbf{Z}}_{N\alpha} = \sum_n^{N_e} \varepsilon_{\alpha\beta\delta}\, \boldsymbol{\alpha}_{n\beta} \frac{r_{nN\delta}}{r_{nN}^3} \tag{97}$$

In order to obtain an expression for the spin – spin coupling constant, it is necessary to resort to its classical definition according to which a SSCC is the fourth-rank tensor (for both nuclear and space variables) included in the energy correction $\Delta E$, which is bilinear in the nuclear spins $\vec{I}_N$

$$\Delta E = \sum_{\alpha,\beta=\{x,y,z\}} h J_{MN\alpha\beta}\, I_{N\alpha}\, I_{M\beta} \tag{98}$$

Often the SSCC appearing in expression (98) is expressed *via* the reduced SSCC $K_{MN\alpha\beta}$

$$J_{MN;\alpha\beta} = h \frac{\gamma_M \gamma_N}{4\pi^2} K_{MN\alpha\beta} \tag{99}$$

In view of expression (99) and the relationship between the magnetic nuclear moment and the spin moment of the $N$th nucleus $\vec{I}_N$ *via* the gyromagnetic ratio $\gamma_N$ according to the relation

$$\vec{\mu}_N = \hbar \gamma_N \vec{I}_N$$

the reduced SSCC is the second derivative of the total energy with respect to the nuclear magnetic moments

$$K_{MN;\alpha\beta} = \left[\frac{\partial^2 E(\vec{\mu}_N, \vec{\mu}_M)}{\partial\mu_{N\alpha}\partial\mu_{M\beta}}\right]_{\mu_{N\alpha}=\mu_{M\beta}=0} \tag{100}$$

The value $K_{MN\alpha\beta}$ depends only on the electronic environment and does not depend on the gyromagnetic ratios of the nuclei $\gamma_{M/N}$.

In order to find the energy correction bilinear in the nuclear magnetic moments according to relation (98), it is necessary to pass to the static many-body equation and construct the perturbation theory in which the unperturbed Hamiltonian is considered as a many-body Dirac – Coulomb Hamiltonian $\hat{\mathbf{H}}_0^{DC}$ [see relation (26)], and perturbation is the magnetic interaction

$$\hat{\mathbf{H}}^{pert} = \hat{\mathbf{H}}_{mag} = \sum_{N=1}^{N_{nuc}} \hat{\mathbf{H}}_N$$

given by expressions (94) and (95).

The many-electron wave function and energy are expanded in the Taylor series in perturbing parameters, which are represented in this case by the nuclear magnetic moments

$$\Psi(\mu_N) = \Psi^{(0)} + \sum_N \Psi_{N\alpha}^{(1)} \mu_{N\alpha} + \tag{101}$$

$$+ \sum_{NM} \Psi_{NM\alpha\beta}^{(2)} \mu_{N\alpha}\, \mu_{M\beta} + ... = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + ...$$

$$E(\mu_N) = E^{(0)} + \sum_N E_{N\alpha}^{(1)} \mu_{N\alpha} + \sum_{NM} E_{NM\alpha\beta}^{(2)} \mu_{N\alpha}\, \mu_{M\beta} + ... \tag{102}$$

$$... = E^{(0)} + E^{(1)} + E^{(2)} + ...$$

According to the standard perturbation theory, the energy correction up to the second order is expressed as

$$\Delta E = \left\langle \Psi^{(0)} \middle| \hat{\mathbf{H}}^{pert} \middle| \Psi^{(0)} \right\rangle + \tag{103}$$

$$+ 2\,\mathrm{Re} \sum_{n\neq 0} \frac{\left\langle \Psi^{(0)} \middle| \hat{\mathbf{H}}^{pert} \middle| \Phi^{(n)} \right\rangle \left\langle \Phi^{(n)} \middle| \hat{\mathbf{H}}^{pert} \middle| \Psi^{(0)} \right\rangle}{E^{(0)} - E^{(n)}}$$

In further a consideration, the higher orders are insignificant, as the smallest next order of the nuclear magnetic moments is the third one; meanwhile, according the initial definition (100), all terms remaining after two differentiations that contain, as a minimum, the first power of the nuclear magnetic moments go to zero. In expression (103), the first term is the average value of the operator $\hat{\mathbf{H}}^{pert}$ for the ground state of the unperturbed system $|\Psi^{(0)}\rangle$ with the energy $E^{(0)}$, while the second term is the sum over states where summation is performed over all excited states of the unperturbed system $|\Phi^{(n)}\rangle$ with the energies $E^{(n)}$.

The general form for SSCCs can be obtained from comparison of the second term of expression (103) with expression (98)

$$J_{NM\alpha\beta} = N_0 \mathrm{Re} \langle\langle \hat{\mathbf{Z}}_{N\alpha}; \hat{\mathbf{Z}}_{M\beta} \rangle\rangle_{\omega=0} \tag{104}$$

$$\hat{\mathbf{Z}}_{N\alpha} = \sum_n^{N_e} \varepsilon_{\alpha\beta\delta}\, \boldsymbol{\alpha}_{n\beta} \frac{r_{nN;\delta}}{r_{nN}^3} \tag{105}$$

In formula (104), there is a designation for the sum over states, $\langle\langle \hat{\mathbf{Z}}_{N\alpha}; \hat{\mathbf{Z}}_{M\beta} \rangle\rangle_{\omega=0}$, which is equivalent to the real part of the static limit of the linear response or the retarded polarization propagator function [213 – 218] in the energy form

$$\langle\langle \hat{\mathbf{Z}}_{N\alpha}; \hat{\mathbf{Z}}_{M\beta} \rangle\rangle_{\omega=0} = \sum_{n\neq 0} \frac{\left\langle \Psi^{(0)} | \hat{\mathbf{Z}}_{N\alpha} | \Phi^{(n)} \right\rangle \left\langle \Phi^{(n)} | \hat{\mathbf{Z}}_{M\beta} | \Psi^{(0)} \right\rangle}{E^{(n)} - E^{(0)}} \tag{106}$$

Typically, the excited many-body wave functions $|\mathbf{\Phi}^{(n)}\rangle$ included in the sum over states (106) are column vectors with the dimension $4^{N_e} \times 1$, while $\langle\mathbf{\Psi}(0)|$ are row vectors with the dimension $1 \times 4^{N_e}$, and the proper operators $\widehat{\mathbf{Z}}$ are the matrix vector operators with the dimension $4^{N_e} \times 4^{N_e}$. Thus, apart from the common product of the bra vector and the ket vector from the single-component quantum mechanics, which is reduced to integration over the whole coordinate space of the system of electrons, formula (106) also implies the row vector × matrix × column vector matrix product, which reflects the many-component nature of the relativistic approach.

Relativistic expression (104) for SSCCs, unlike the nonrelativistic Ramsey consideration, is not split into any separate contributions corresponding to the particular mechanisms of transfer of the spin–spin interaction between the nuclei.

Note also that, according to Ramsey,[212] the SSCC tensor $J_{NM\alpha\beta}$ can be split into two components — direct $J^{\mathrm{D}}_{N\alpha M\beta}$ and indirect $J^{\mathrm{ID}}_{NM}$ ones. The tensor $J^{\mathrm{D}}_{N\alpha M\beta}$ is a traceless dyadic responsible for the direct through-space mechanism of transfer of the interaction between nuclear spins, which was established experimentally for solids with clear-cut crystal lattice anisotropy; $J^{\mathrm{ID}}_{NM}$ is one-third of the trace of full tensor (104)

$$J^{\mathrm{ID}}_{NM} = \frac{1}{3}\sum_{\alpha=\{x,y,z\}} J_{N\alpha M\alpha} = \frac{1}{3}\mathrm{Sp}\,\mathbf{J} \tag{107}$$

An indirect SSCC is observed mainly in liquids and gases and corresponds to the tranmission of the spin–spin interaction between the nuclei by the electron environment (indirect spin–spin coupling); for these physical states of matter, $J^{\mathrm{D}}_{N\alpha M\beta}$ goes to zero upon space averaging. In what follows, we consider only the indirect spin–spin coupling constants transmitted through chemical bond electrons.

### IV.2. Two-component representation of spin–spin coupling constants

Two-component theory of SSCCs is highly significant for practical calculations. It clearly demonstrates the physics of nuclear spin–spin interaction and gives the idea of the origin of non-relativistic Ramsey formulae.[212]

The non-stationary Dirac equation (92) is equivalent to the system of equations

$$\begin{cases} c\,\hat{\pi}^0\boldsymbol{\psi}_L - c\,\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\boldsymbol{\psi}_S = 0 \\ -c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\boldsymbol{\psi}_L + \left(c\,\hat{\pi}_0 + 2c^2\right)\boldsymbol{\psi}_S = 0 \end{cases} \tag{108}$$

The relationship between the large and small components follows from the second equation of set (108)

$$\boldsymbol{\Psi}_S = \frac{\widehat{\mathbf{B}}}{2c}\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\boldsymbol{\Psi}_L \tag{109}$$

The operator $\widehat{\mathbf{B}}$ is given by

$$\widehat{\mathbf{B}} = \left(\widehat{\mathbf{I}} + \frac{\hat{\pi}^0}{2c}\right)^{-1} \tag{110}$$

The procedure of elimination of small components from expression (108) results in an equation for the large component

$$\left(c\hat{\pi}^0 - \vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\frac{\widehat{\mathbf{B}}}{2}\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\right)\boldsymbol{\psi}_L = \mathbf{0} \tag{111}$$

which, with the use of the properties of the Pauli matrices $\boldsymbol{\sigma}_i\,\boldsymbol{\sigma}_j = \delta_{ij} + \mathrm{i}\varepsilon_{ijk}\boldsymbol{\sigma}_k$, gives the following expression:

$$\left(\widehat{E} - \phi - \frac{1}{2}\hat{\vec{\pi}}\widehat{\mathbf{B}}\hat{\vec{\pi}} - \frac{\mathrm{i}}{2}\vec{\boldsymbol{\sigma}}\left[\hat{\vec{\pi}}\widehat{\mathbf{B}}\times\hat{\vec{\pi}}\right]\right)\boldsymbol{\psi}_L = 0 \tag{112}$$

For expansion of expression (112), it is necessary to use the following commutators:

$$\left[\hat{\vec{\pi}},\,\hat{\pi}^0\right] = -\frac{\mathrm{i}}{c}\vec{E} \tag{113}$$

$$\left[\hat{\vec{\pi}},\widehat{\mathbf{B}}\right] = \frac{\mathrm{i}}{2c^2}\,\widehat{\mathbf{B}}\,\vec{E}\,\widehat{\mathbf{B}} \tag{114}$$

which can be easily determined provided that the electric field strength is expressed in terms of the vector and scalar potentials of the electromagnetic field as

$$\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} - \hat{\vec{\nabla}}\varphi$$

and the operator $\widehat{\mathbf{B}}$ can be expanded in the series

$$\widehat{\mathbf{B}} = \left(\widehat{\mathbf{I}} + \frac{\hat{\pi}^0}{2c}\right)^{-1} = \sum_{n=0}^{+\infty}\left(\frac{-\widehat{\mathbf{I}}}{2c}\right)^n\left(\hat{\pi}^0\right)^n$$

and then all commutators $\left[\hat{\vec{\pi}},\,\left(\hat{\pi}^0\right)^n\right]$ can be successively found by the method of mathematical induction starting from expression (113) as the first step. It should also be taken into account that the vector product of the extended momentum operators is expressed in terms of the magnetic field strength

$$\left[\hat{\vec{\pi}}\times\hat{\vec{\pi}}\right] = \frac{\mathrm{i}}{c}\mathrm{rot}\,\vec{A} = \frac{\mathrm{i}}{c}\vec{B} \tag{115}$$

Thus, Eqn (112) can be transformed into the following fundamental equation (see p. 16 in Ref. 219):

$$\left(\widehat{E} - \phi - \frac{1}{2}\widehat{\mathbf{B}}\hat{\vec{\pi}}^2 - \frac{\mathrm{i}}{(2c)^2}\,\widehat{\mathbf{B}}\,\vec{E}\,\widehat{\mathbf{B}}\,\hat{\vec{\pi}} + \frac{1}{c}\hat{\vec{\mathbf{S}}}\,\widehat{\mathbf{B}}\,\vec{B} + \right. \tag{116}$$

$$\left. + \frac{1}{2c^2}\hat{\vec{\mathbf{S}}}\left[\widehat{\mathbf{B}}\,\vec{E}\,\widehat{\mathbf{B}}\times\hat{\vec{\pi}}\right]\right)\boldsymbol{\psi}_L = 0$$

where

$$\widehat{\mathbf{B}} = \left(\widehat{\mathbf{I}} + \frac{\widehat{E-\varphi}}{2c^2}\right)^{-1} = \left(\widehat{\mathbf{I}} + \frac{\hat{\pi}^0}{2c}\right)^{-1},\quad \hat{\vec{\mathbf{S}}} = \frac{1}{2}\vec{\boldsymbol{\sigma}}$$

($\hat{\vec{\mathbf{S}}}$ is the electron spin in the $\hbar$ units).

If we consider an electron moving in the overall electromagnetic field of point nuclei, then the scalar and vector potentials assume a definite mathematical form

$$\phi_{\mathrm{nuc}}(\vec{r}) = \sum_{N=1}^{N_{\mathrm{nuc}}}\phi(\vec{r}) = -\sum_{N=1}^{N_{\mathrm{nuc}}}\frac{Z_N}{|\vec{r}-\vec{r}_N|} = -\sum_{N=1}^{N_{\mathrm{nuc}}}\frac{Z_N}{r_{\mathrm{e}N}} \tag{117}$$

$$\vec{A}_{\mathrm{nuc}} = \sum_{N=1}^{N_{\mathrm{nuc}}}\vec{A}_{N_{\mathrm{nuc}}} = \sum_{N=1}^{N_{\mathrm{nuc}}}\frac{[\vec{\mu}_N\times\vec{r}_{\mathrm{e}N}]}{r^3_{\mathrm{e}N}} \tag{118}$$

where $\vec{\mu}_n$ is the magnetic moment of an $N$th nucleus, $\vec{r}_{eN} = \vec{r}_e - \vec{r}_N$ is the difference between the radius vectors of the electron and the $N$th nucleus.

This consideration initially implies the use of the Born – Oppenheimer approximation,[63] so that the derivatives of the nuclear field factors with respect to time just go to zero; hence, the field commutators with the energy operator $\hat{E}$ and, as a consequence, with the operator $\hat{\mathbf{B}}$ also become equal to zero. All this markedly simplifies the end elements of the Hamiltonian.

Note that the third term in the fundamental expression (116) is split into three characteristic components

$$-\frac{1}{2}\hat{\mathbf{B}}\hat{\vec{\pi}}^2 = -\frac{1}{2}\left\{\hat{\mathbf{B}}\hat{\vec{p}}^2 - \frac{1}{c}\left\{\hat{\vec{p}}\vec{A}_{\text{nuc}} + \vec{A}_{\text{nuc}}\hat{\vec{p}}\right\} + \frac{1}{c^2}\vec{A}^2_{\text{nuc}}\right\} \quad (119)$$

The first one

$$\hat{\mathbf{T}} = -\frac{1}{2}\hat{\mathbf{B}}\hat{\vec{p}}^2$$

corresponds to the kinetic energy with the opposite sign, while the second term is called the orbital magnetism operator, because it describes the interaction of the electron orbital moment with the nuclear magnetic moments

$$\hat{\mathbf{H}}_{\text{orb-mag}} = \frac{1}{2c}\hat{\mathbf{B}}\left\{\hat{\vec{p}}\vec{A}_{\text{nuc}} + \vec{A}_{\text{nuc}}\hat{\vec{p}}\right\} = \quad (120)$$

$$= \frac{1}{c}\hat{\mathbf{B}}\sum_{N}^{N_{\text{nuc}}}\frac{\vec{\mu}_N[\vec{r}_{eN}\times\hat{\vec{p}}]}{r^3_{eN}} = \frac{1}{c}\hat{\mathbf{B}}\sum_{N}^{N_{\text{nuc}}}\frac{\vec{\mu}_N\hat{\vec{L}}_{eN}}{r^3_{eN}}$$

Expression (120) was derived taking into account the fact that $\hat{\vec{p}}\vec{A}_{\text{nuc}} \sim \text{div}\vec{A}_{\text{nuc}} = 0$, as $\text{div}\vec{A}_{\text{nuc}}$ is reduced to the contraction of the symmetric and antisymmetric tensors

$$\text{div}\vec{A}_{\text{nuc}} = \sum_{N=1}^{N_{\text{nuc}}}\hat{\vec{\nabla}}_{\vec{r}}\frac{[\vec{\mu}_N\times\vec{r}_{eN}]}{r^3_{eN}} = \quad (121)$$

$$= \sum_{N=1}^{N_{\text{nuc}}}\sum_{ijk=1}^{3}\varepsilon_{ijk}\,\mu^j_N\frac{\partial}{\partial r^i_{eN}}\frac{r^k_{eN}}{r^3_{eN}} =$$

$$= \sum_{N=1}^{N_{\text{nuc}}}\mu^j_N\left(\varepsilon_{jki}\frac{\delta^{ik}r^2_{eN} - 3r^i_{eN}r^k_{eN}}{r^5_{eN}}\right) = 0$$

The condition $\text{div}\vec{A}_{\text{nuc}} = 0$ is called the Coulomb calibration. The vector potential of the magnetic field $\vec{A}_{\text{nuc}}$ (118) is defined in such a way that the Coulomb calibration condition is fulfilled, although the choice of the vector potential is known to be ambiguous, in particular, it can be defined to an accuracy of the gradient of an arbitrary scalar function $f$, which does not induce a change in the magnetic field strength, as $\vec{B} = \text{rot}\,\vec{A}$ and $\text{rotgrad}\,f = 0$.

Thus, Coulomb calibration is the simplest particular case. Generally, the arbitrary choice of the calibration of the magnetic field vector potential in real quantum chemical calculations with finite basis sets brings about problems associated with the dependence of some magnetic resonance parameters on the choice of the centre of the coordinate system.

The last term of expression (119)

$$\hat{\mathbf{H}}_{\text{diamag}} = -\frac{1}{2c^2}\hat{\mathbf{B}}\vec{A}^2_{\text{nuc}}$$

is bilinear in the field and is called diamagnetic

$$\hat{\mathbf{H}}_{\text{diamag}} = -\frac{1}{2c^2}\hat{\mathbf{B}}\sum_{NM}^{N_{\text{nuc}}}\frac{[\vec{\mu}_N\times\vec{r}_{eN}][\vec{\mu}_M\times\vec{r}_{eM}]}{r^3_{eN}r^3_{eM}} \quad (122)$$

This expression can be presented in a more convenient form using the known vector analysis relation $[\vec{a}\times\vec{b}][\vec{c}\times\vec{d}] = (\vec{a}\vec{c})(\vec{b}\vec{d}) - (\vec{a}\vec{d})(\vec{c}\vec{b})$

$$\hat{\mathbf{H}}_{\text{diamag}} = \quad (123)$$

$$= -\frac{1}{2c^2}\hat{\mathbf{B}}\sum_{NM}^{N_{\text{nuc}}}\frac{(\vec{\mu}_N\vec{\mu}_M)(\vec{r}_{eN}\vec{r}_{eM}) - (\vec{\mu}_N\vec{r}_{eM})(\vec{\mu}_M\vec{r}_{eN})}{r^3_{eN}r^3_{eM}}$$

The fourth term of expression (116) can be split into two parts

$$-\frac{\mathrm{i}}{(2c)^2}\hat{\mathbf{B}}\vec{E}\hat{\mathbf{B}}\hat{\vec{\pi}} = -\frac{\mathrm{i}}{(2c)^2}\hat{\mathbf{B}}\vec{E}_{\text{nuc}}\hat{\mathbf{B}}\hat{\vec{p}} + \frac{\mathrm{i}}{4c^3}\hat{\mathbf{B}}\vec{E}_{\text{nuc}}\hat{\mathbf{B}}\vec{A}_{\text{nuc}} \quad (124)$$

By using the relation

$$\vec{E}_{\text{nuc}} = -\hat{\vec{\nabla}}\phi_{\text{nuc}} = -\sum_{N=1}^{N_{\text{nuc}}}\frac{Z_N\vec{r}_{eN}}{r^3_{eN}}$$

and $\vec{A}_{\text{nuc}}$ from (118), expression (124) can be transformed to

$$-\frac{\mathrm{i}}{(2c)^2}\hat{\mathbf{B}}\vec{E}_{\text{nuc}}\hat{\mathbf{B}}\hat{\vec{\pi}} = -\frac{\mathrm{i}}{(2c)^2}\sum_{N=1}^{N_{\text{nuc}}}Z_N\hat{\mathbf{B}}\frac{\vec{r}_{eN}}{r^3_{eN}}\hat{\mathbf{B}}\hat{\vec{p}} + \quad (125)$$

$$+\frac{\mathrm{i}}{4c^3}\hat{\mathbf{B}}^2\sum_{NM=1}^{N_{\text{nuc}}}Z_N\frac{\vec{\mu}_M[\vec{r}_{eM}\times\vec{r}_{eN}]}{r^3_{eN}r^3_{eM}}$$

Since for deriving the expression for SSCC, only Hamiltonian terms that contain nuclear magnetic moments in some form are important, the first summand in relation (125) is of no value for the subsequent derivation and the second one is insignificant (see p. 20 in Ref. 219).

The fifth term in Hamiltonian (116) is the dipole – dipole interaction operator between the electronic and nuclear magnetic moments. This can be easily confirmed by substituting the nuclear magnetic field strength

$$\vec{B}_{\text{nuc}} = \text{rot}\,\vec{A}_{\text{nuc}} = \sum_{N=1}^{N_{\text{nuc}}}\frac{3\vec{r}_{eN}(\vec{\mu}_N\vec{r}_{eN}) - \vec{\mu}_N\vec{r}^2_{eN}}{r^5_{eN}} \quad (126)$$

Considering expression (126), the fifth term in the fundamental equation (116) corresponding to the dipole – dipole interaction of the electron spin and nuclear magnetic moments takes the following form:

$$\hat{\mathbf{H}}_{\text{dip}} = \frac{1}{c}\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\vec{B}_{\text{dip}} = \quad (127)$$

$$= \frac{1}{c}\hat{\mathbf{B}}\sum_{N=1}^{N_{\text{nuc}}}\frac{3(\hat{\vec{\mathbf{S}}}\vec{r}_{eN})(\vec{\mu}_N\vec{r}_{eN}) - (\hat{\vec{\mathbf{S}}}\vec{\mu}_N)\vec{r}^2_{eN}}{r^5_{eN}}$$

The sixth term in Eqn (116) is split into two summands

$$\frac{1}{2c^2}\hat{\vec{\mathbf{S}}}\left[\hat{\mathbf{B}}\vec{E}\hat{\mathbf{B}}\times\hat{\vec{\pi}}\right]= \tag{128}$$

$$=\frac{1}{2c^2}\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\left[\vec{E}_{\rm nuc}\times\hat{\mathbf{B}}\hat{\vec{p}}\right]-\frac{1}{2c^3}\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\left[\vec{E}_{\rm nuc}\times\hat{\mathbf{B}}\vec{A}_{\rm nuc}\right]$$

The first summand in expression (128) containing the nuclear electric field strength is a spin–orbit coupling operator, which in essence implies the interaction of an electron moving along an orbit with the magnetic field generated by this same electron,

$$\frac{1}{2c^2}\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\left[\vec{E}_{\rm nuc}\times\hat{\mathbf{B}}\hat{\vec{p}}\right]= \tag{129}$$

$$=\frac{1}{2c^2}\sum_{N=1}^{N_{\rm nuc}}Z_N\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\frac{\left[\vec{r}_{\rm eN}\times\hat{\mathbf{B}}\hat{\vec{p}}\right]}{r_{\rm eN}^3}\approx\frac{1}{2c^2}\hat{\mathbf{B}}^2\sum_{N=1}^{N_{\rm nuc}}Z_N\frac{\hat{\vec{\mathbf{S}}}\hat{\vec{L}}_{\rm eN}}{r_{\rm eN}^3}$$

This spin–orbit coupling is a very important relativistic effect, to which we will draw attention of the readers not once, but in this case, it does not play any role, as this is a closed electronic effect not including the magnetic field of the nuclei.

The second summand in expression (128) is the so-called contact interaction operator. It can be represented as follows:

$$-\frac{1}{2c^3}\hat{\vec{\mathbf{S}}}\hat{\mathbf{B}}\left[\vec{E}_{\rm nuc}\times\hat{\mathbf{B}}\vec{A}_{\rm nuc}\right]= \tag{130}$$

$$=-\frac{1}{2c^3}\hat{\mathbf{B}}^2\sum_{NM=1}^{N_{\rm nuc}}Z_N\hat{\vec{\mathbf{S}}}\frac{[\vec{r}_{\rm eN}\times[\vec{\mu}_M\times\vec{r}_{\rm eM}]]}{r_{\rm eN}^3r_{\rm eM}^3}$$

By means of the known vector analysis relation

$$[\vec{A}\times[\vec{B}\times\vec{C}]]=\vec{B}(\vec{A}\vec{C})-\vec{C}(\vec{A}\vec{B}) \tag{131}$$

expression (130) is simplified

$$\hat{\mathbf{H}}_{\rm cont}= \tag{132}$$

$$=-\frac{1}{2c^3}\hat{\mathbf{B}}^2\sum_{NM=1}^{N_{\rm nuc}}Z_N\frac{(\hat{\vec{\mathbf{S}}}\vec{\mu}_M)(\vec{r}_{\rm eN}\vec{r}_{\rm eM})-(\hat{\vec{\mathbf{S}}}\vec{r}_{\rm eM})(\vec{\mu}_M\vec{r}_{\rm eN})}{r_{\rm eN}^3r_{\rm eM}^3}$$

The contact term (132) is the isotropic hyperfine interaction. Analysis of its asymptotic behaviour with allowance made for $\hat{\mathbf{B}}^2$ leads to a three-dimensional Dirac $\delta$-function centred on this nucleus. Since the s and $p_{1/2}$ type functions differ from zero in the region of nucleus, only they give a non-zero contribution to this interaction. In the simplest case in the non-relativistic limit, expression (132) is replaced by the term containing the Dirac $\delta$-function,

$$\hat{\mathbf{H}}_{\rm cont}=-\frac{8\pi}{3c}\sum_{N=1}^{N_{\rm nuc}}Z_N\delta(\vec{r}_{\rm eN})\hat{\vec{\mathbf{S}}}\vec{\mu}_N \tag{133}$$

Hence, Eqn (116) can be written in the simplified form in which only the terms that form the unperturbed (*i.e.*, neglecting the nuclear magnetic field) Hamiltonian and the terms containing the nuclear magnetic fields in some form considered as perturbations are left. The other terms that were obtained during the transformation of the Hamiltonian terms from expression (116) are not related to the interactions of nuclear magnetic moments.

Thus, the fundamental equation (116) assumes the following form

$$\left(\mathrm{i}\frac{\partial}{\partial t}+\hat{\mathbf{T}}-\phi+\hat{\mathbf{H}}_{\rm orb-mag}+\hat{\mathbf{H}}_{\rm diamag}+\hat{\mathbf{H}}_{\rm dip}+\hat{\mathbf{H}}_{\rm cont}\right)\boldsymbol{\psi}_L=0 \tag{134}$$

Here

$$\hat{\mathbf{H}}_{\rm orb-mag}=N_{\rm orb-nuc}\hat{\mathbf{B}}\sum_{N}^{N_{\rm nuc}}\frac{\vec{\mu}_N\hat{\vec{L}}_{\rm eN}}{r_{eN}^3} \tag{135}$$

$$\hat{\mathbf{H}}_{\rm diamag}= \tag{136}$$

$$=N_{\rm diamag}\hat{\mathbf{B}}\sum_{NM}^{N_{\rm nuc}}\frac{(\vec{\mu}_N\vec{\mu}_M)(\vec{r}_{\rm eN}\vec{r}_{\rm eM})-(\vec{\mu}_N\vec{r}_{\rm eM})(\vec{\mu}_M\vec{r}_{\rm eN})}{r_{\rm eN}^3r_{\rm eM}^3}$$

$$\hat{\mathbf{H}}_{\rm dip}=N_{\rm dip}\hat{\mathbf{B}}\sum_{N=1}^{N_{\rm nuc}}\left(\frac{3(\hat{\vec{\mathbf{S}}}\vec{r}_{\rm eN})(\vec{\mu}_N\vec{r}_{\rm eN})}{r_{\rm eN}^5}-\frac{(\hat{\vec{\mathbf{S}}}\vec{\mu}_N)}{r_{\rm eN}^3}\right) \tag{137}$$

$$\hat{\mathbf{H}}_{\rm cont}= \tag{138}$$

$$=-\frac{1}{2c^3}\hat{\mathbf{B}}^2\sum_{NM=1}^{N_{\rm nuc}}Z_N\left[\frac{(\hat{\vec{\mathbf{S}}}\vec{\mu}_M)(\vec{r}_{\rm eN}\vec{r}_{\rm eM})-(\hat{\vec{\mathbf{S}}}\vec{r}_{\rm eM})(\vec{\mu}_N\vec{r}_{\rm eN})}{r_{\rm eN}^3r_{\rm eM}^3}\right]$$

The hyperfine magnetic perturbation terms (135)–(138) in the two-component approximation actually reproduce their non-relativistic analogues modified by means of so-called kinetic or kinematic relativistic factors $\hat{\mathbf{B}}$. Upon correct transition to the non-relativistic limit, these operators are transformed into Ramsey operators.[212]

To obtain expressions for SSCCs, this consideration has to be extended to a many-electron system. Then summation over all system electrons appears in the magnetic perturbation operators (135)–(138) and some two-electron operators, either linear or bilinear in the nuclear magnetic moments, are added (for the reason of non-trivial accompanying problems, the latter are not considered here). These operators are best reflected in the two-component magnetic Breit–Pauli Hamiltonian.[13]

Particular attention should be paid to the fact that on going to a many-electron system in the initial form, without any procedures applied to reduce a many-particle approximation to a single-particle one, the necessity appears not only to restore the correct dimension (obviously equal to $2^N\times2^N$) for the operators appearing in the two-component equation (134) but also to restore their correct matrix structure. An important issue in this extension is a correct approach to representation of many-body wave functions. For example, for the system ground state wave function, a good approximation is the relativistic analogue of the Slater determinant derived as the antisymmetrized tensor product of 2-spinors.

In order to obtain the energy correction bilinear in the nuclear magnetic moments, it is necessary to construct a perturbation theory in which the unperturbed Hamiltonian is considered as a part of Hamiltonian (134) extended to the many-particle case and consisting of characteristic terms of the non-magnetic part of the many-electron relativistic two-component Hamiltonian $\hat{\mathbf{H}}_0$, while terms (135)–(138) plus some two-electron operators are the perturbations.

The general form of the two-component many-electron Hamiltonian can be represented as

$$\widehat{\mathbf{H}} = \widehat{\mathbf{H}}_0 + \widehat{\mathbf{H}}^{\text{pert}} = \widehat{\mathbf{H}}_0 + \sum_i \widehat{\mathbf{H}}_i^{\text{pert}} \tag{139}$$

The first term $\widehat{\mathbf{H}}_0$ in this expression forms a relativistic two-component Hamiltonian of the 'free' electron subsystem, *i.e.*, the Hamiltonian devoid of the nuclear magnetic fields, which could be considered as external perturbations of the electron subsystem. The expression for such a Hamiltonian is the sum of kinetic energy and potential energy operators for electrons in the electrostatic field of nuclei, potential energy operators of electron – electron interaction and one- and two-electron operators reflecting various relativistic effects. The many-electron wave function and energy are expanded into Taylor series in perturbation parameters, which are represented by nuclear magnetic moments in this case, according to expressions (101) and (102). In expression (139), the sum

$$\sum_i \widehat{\mathbf{H}}_i^{\text{pert}} = \widehat{\mathbf{H}}^{\text{pert}}$$

is the set of magnetic perturbations.

In order to find the SSCC tensor, which is the second derivative of energy with respect to nuclear magnetic moments defined by relations (99) and (100), it is necessary to distinguish all terms appearing in the equation for energy corrections (103) bilinear in nuclear magnetic moments.

Thus, in the two-component many-particle consideration, the SSCC is given by

$$J_{MN\alpha\beta} = \left\langle \mathbf{\Psi}^{(0)} \middle| \widehat{\mathbf{H}}^{\text{pert}}_{NM\,\alpha\beta} \middle| \mathbf{\Psi}^{(0)} \right\rangle + \tag{140}$$
$$+ 2\text{Re} \sum_{ij} \sum_{n \neq 0} \frac{\left\langle \mathbf{\Psi}^{(0)} \middle| \widehat{\mathbf{H}}^{\text{pert}}_{i\,N\alpha} \middle| \mathbf{\Phi}^{(n)} \right\rangle \left\langle \mathbf{\Phi}^{(n)} \middle| \widehat{\mathbf{H}}^{\text{pert}}_{j\,M\beta} \middle| \mathbf{\Psi}^{(0)} \right\rangle}{E^{(0)} - E^{(n)}}$$

In this formula, the operators appearing in the summation over states in the one-electron part are expressed *via* relativistic two-component operators (135) – (138) extended to the many-particle case

$$\widehat{\mathbf{H}}^{\text{1e-pert}}_{i\,N\alpha} = \frac{\partial \widehat{\mathbf{H}}_i^{\text{pert}}}{\partial \mu_{N\alpha}}, \quad \widehat{\mathbf{H}}^{\text{1e-pert}}_{NM\,\alpha\beta} = \frac{\partial^2 \widehat{\mathbf{H}}^{\text{pert}}_{\text{diamag}}}{\partial \mu_{N\alpha}\, \partial \mu_{M\beta}} \tag{141}$$

The subscripts $i$ and $j$ in formulae (140) and (141) imply the types of magnetic perturbations that correspond to the electron sums of one-electron two-component hyperfine coupling operators — orbital magnetism (135) and dipole – dipole (137) and contact (138) interactions.

The relativistic two-component representation of the SSCC tensor expressed by relation (140) is split into contributions in the same way as in the non-relativistic limit, the simplest structure of operators (135) – (138) appearing in the one-electron terms of expression (140) is similar to non-relativistic analogues.

### IV.3. One-component representation of the spin – spin coupling constants

The Ramsey relations [212] for the contributions to the SSCCs are obtained from (135) – (138) and (140) by extension to the many-body case and transition to the non-relativistic limit ($\widehat{\mathbf{B}} \to \widehat{\mathbf{I}}$)

$$\mathbf{J}^{\text{X}}_{MN} = N_{\text{X}} \gamma_M \gamma_N \frac{1}{2} \text{Re} \left\langle\!\!\left\langle \widehat{\mathbf{H}}^{\text{X}}_N; \left(\widehat{\mathbf{H}}^{\text{X}}_M\right)^{\text{T}} \right\rangle\!\!\right\rangle_{\omega = 0} \tag{142}$$

$$\text{X} = \text{PSO},\ \text{SD},\ \text{FC}$$

$$\widehat{\mathbf{H}}^{\text{PSO}}_N = \sum_n^{N_e} \frac{[\mathbf{r}_{nN} \times \hat{\mathbf{p}}_n]}{r^3_{nN}} \tag{143}$$

$$\widehat{\mathbf{H}}^{\text{SD}}_N = \sum_n^{N_e} \frac{3\mathbf{r}_{nN}\mathbf{r}^{\text{T}}_{nN} - r^2_{nN}\mathbf{I}}{r^5_{nN}} \hat{\mathbf{s}}_n \tag{144}$$

$$\widehat{\mathbf{H}}^{\text{FC}}_N = \sum_n^{N_e} \delta(\mathbf{r}_{nN}) \hat{\mathbf{s}}_n, \tag{145}$$

$$\mathbf{J}^{\text{DSO}}_{MN} = N_{\text{DSO}} \gamma_M \gamma_N \langle \mathbf{\Psi}_0 | \widehat{\mathbf{H}}^{\text{DSO}}_{MN} | \mathbf{\Psi}_0 \rangle \tag{146}$$

$$\widehat{\mathbf{H}}^{\text{DSO}}_{MN} = \sum_n^{N_e} \frac{\mathbf{r}^{\text{T}}_{nM}\mathbf{r}_{nN}\mathbf{I} - \mathbf{r}_{nM}\mathbf{r}^{\text{T}}_{nN}}{\mathbf{r}^3_{nM}\, r^3_{nN}} \tag{147}$$

In formulae (142) – (147), the characters typed in bold refer to tensor objects in the Cartesian space. Formula (142) contains the designation for the sum over states

$$\left\langle\!\!\left\langle \widehat{\mathbf{H}}^{\text{X}}_N; \left(\widehat{\mathbf{H}}^{\text{X}}_M\right)^{\text{T}} \right\rangle\!\!\right\rangle_{\omega = 0}$$

The vectors $\mathbf{r}_{nN} = \vec{r}_n - \vec{r}_N$ are differences between the radius vectors of the $n$th electron and the $N$th nucleus, $\hat{\mathbf{s}}_n$ is the electron spin operator for the $n$th electron, $\delta(\mathbf{r}_{nN}) = \delta(\vec{r} - \vec{r}_N)$ is the three-dimensional Dirac $\delta$-function. The $\mathbf{A}^{\text{T}}$ corresponds to the transposed vector or vector-operator $\mathbf{A}$. For example, $\mathbf{r}_{nN}\mathbf{r}^{\text{T}}_{nN}$ is a $3 \times 3$ matrix with elements $r_{nN\alpha}\, r_{nN\beta}$, where $\alpha, \beta = \{x, y, z\}$. The summation in (143) – (145) and (147) is performed over all of the electrons $n = 1 \ldots N_e$. The coefficients $\gamma_M$ imply the gyromagnetic ratios of the nuclei, while the factors $N_{\text{X}}$ depend on the system of units used and are partial for each contribution. All operators and functions appearing in formulae (142) – (147), unlike relativistic formulae, have a simple one-component structure (regarding the spinor components).

Each of the non-relativistic contributions to a SSCC corresponds to a particular mechanism of transfer of the nuclear spin – spin interaction. The first contribution (142) – (143) is derived from the two-component orbital magnetism operator (135) and is called the paramagnetic spin – orbit (PSO) contribution. In physical essence, it reflects the transfer of the nuclear spin – spin interaction by induction of orbital electronic currents, *i.e.*, the magnetic moment of one nucleus generates a magnetic field, which induceds the orbital electron currents, generating, in turn, an additional magnetic field around another nucleus.

The second contribution [see formulae (142) and (144)] originates from the relativistic two-component dipole – dipole interaction operator (137) and is called the spin dipole (SD) contribution. The transfer mechanism corresponding to this contribution is that the dipole interaction of the magnetic moment of one nucleus with electron spins gives rise to so-called electron spin polarization (spin density perturbation), which also induces additional magnetic field around another nucleus.

The third contribution [see formulae (142) – (145)] comes from the Fermi contact (FC) interaction. It is derived from the contact term (138) and, in the physical meaning, it is identical to the spin dipole contribution but involves only

those orbitals that cross the nuclei involved in the SSCC. This is related to a specific asymptotic behaviour of the contact term (138) on going to the non-relativistic limit having the form of the Dirac $\delta$-function with critical points at the centres of these nuclei. The fourth contribution [see formulae (146) and (147)] is called the diamagnetic spin–orbit contribution (DSO) and is derived from the relativistic two-component diamagnetic operator (136) bilinear in the nuclear magnetic moments. In physical essence, it corresponds to the interaction of nuclear magnetic moments *via* the induced diamagnetic currents of the electron cloud.

The Ramsey formulae (142)–(147) can also be obtained in a different way without resorting to the relativistic equation of electron movement in the external nuclear field. For this purpose, terms corresponding to interactions of the electron and nuclear spins of the system are artificially added to the full many-body Schrödinger Hamiltonian. On the basis of the 'spin Hamiltonian' thus obtained, the standard perturbation theory is used to find energy corrections bilinear in the nuclear magnetic moments. This method seems artificial from the beginning, as it implies the addition of magnetic perturbation operators the form of which has to be known in advance, whereas if the Ramsey formulae are obtained from the relativistic theory, expressions for these operators are explicitly derived.

Ramsey[212] also considered the cross-terms — contributions containing pairs of magnetic operators corresponding to different mechanisms of transfer of nuclear spin–spin interaction: $\widehat{\mathbf{H}}^{\mathrm{X}}_{M}$ and $\widehat{\mathbf{H}}^{\mathrm{Y}}_{N}$ ($\mathrm{X} \neq \mathrm{Y}$). It was shown that the only possible non-zero cross-term is FC–SD; however, for this term to be significant, a strong dependence of the electron spins on the spatial orientation of the molecule is required; otherwise, this cross-term is vanishingly small. The other cross-terms automatically vanish because the matrix elements of the triplet operators, including FC and SD, are zero at those excited states included in the sum over states for which the matrix elements of the single PSO operator differ from zero and *vice versa*.

The Ramsey formulae (142)–(147) underlie all modern quantum chemical non-relativistic methods for SSCC calculation. The critical factor for the accuracy of description of SSCCs in the framework of each method is the level of description of the wave functions of the ground and excited states and the excited state transition energies.

The approach to SSCC calculation using Ramsey formulae (142)–(147) is based on the theory of second quantization and the theory of molecular orbitals. An interesting issue related to the use of these theories is the consecutive explicit account of the electron correlation (which is indirectly present in the Ramsey formulae in the correlated many-electron wave functions and energies). The approach associated with account of the correlation in an explicit form, as any approximation of the formal theory, gives more definite formulae, which can be software-implemented or used for analysis of the geometric dependences of SSCCs in terms of the molecular orbital theory.[220] This consideration would require the addition of a residual electron–electron interaction operator to the perturbation theory and transition to the second quantization terms.[221]

The full Hamiltonian of the system can be represented in the form

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_I + \widehat{T} \tag{148}$$

where $\widehat{H}_0 + \widehat{H}_I$ is the Müller–Plesset splitting[222, 223] of the full electron Hamiltonian in the absence of nuclear magnetic perturbations, while $\widehat{H}_0$ is the diagonal part of the Hartree–Fock Hamiltonian and is specified by the sum of single-particle Fock operators. With second quantization, it has the form

$$\widehat{H}_0 = \sum_r \varepsilon_r \, \hat{c}_r^{+} \, \hat{c}_r \tag{149}$$

The operator $\widehat{H}_I$ is the residual electron – electron interaction operator consisting of the one-particle off-diagonal part of the Hartree–Fock Hamiltonian $\widehat{W}$ and the two-particle electron – electron interaction operator $\widehat{V}$

$$\widehat{H}_I = \widehat{W} + \widehat{V} = \sum_{rs} W_{rs} \, \hat{c}_r^{+} \, \hat{c}_s + \frac{1}{2} \sum_{rspq} V_{rsqp} \, \hat{c}_r^{+} \, \hat{c}_s^{+} \, \hat{c}_p \, \hat{c}_q \tag{150}$$

where $W_{rs}$ and $V_{rsqp}$ are the matrix elements of the corresponding operators in the molecular orbital basis set $\{\chi_r\}$

$$V_{rsqp} = \left\langle \chi_r(1)\chi_s(2) \left| \frac{1}{r_{12}} \right| \chi_q(1)\chi_p(2) \right\rangle \tag{151}$$

$$W_{rs} = -\sum_i V_{ri[si]} = -\sum_i ( V_{risi} - V_{riis} ) \tag{152}$$

Here and below the letters $a$, $b$, $c$, ... and $i$, $j$, $k$, ... correspond to vacant and occupied molecular orbitals, respectively, while $p$, $q$, $r$, $s$ are orbital indices for both types of molecular orbitals. The operators $\hat{c}_r^{+}/\hat{c}_r$ are second-quantized electron creation and annihilation operators in the orbital $r$. The operator $\widehat{T}$ is a set of single-particle PSO, SD, FC and DSO magnetic perturbation operators

$$\widehat{T} = \widehat{T}_{\mathrm{PSO}} + \widehat{T}_{\mathrm{SD}} + \widehat{T}_{\mathrm{FC}} + \widehat{T}_{\mathrm{DSO}} \tag{153}$$

According to the second quantization approach, the operators $\widehat{T}$ take the following form:

$$\widehat{T}_{\mathrm{PSO}} = N_{\mathrm{PSO}} \sum_N \sum_{pq} \sum_{v=0,\pm1} (-1)^v \bar{\boldsymbol{\kappa}}^{\mathrm{PSO}}_{Nvpq} \, \widehat{E}_{pq} \, \mu_N^{-v} \tag{154}$$

$$\widehat{T}_{\mathrm{SD}} = N_{\mathrm{SD}} \sum_N \sum_{pq} \sum_{\mu,v=0,\pm1} (-1)^{v+\mu} \bar{\boldsymbol{\kappa}}^{\mathrm{SD}}_{N\mu v pq} \, \hat{s}^{-\mu}_{pq} \, \mu_N^{-v} \tag{155}$$

$$\widehat{T}_{\mathrm{FC}} = N_{\mathrm{FC}} \sum_N \sum_{pq} \sum_{v=0,\pm1} (-1)^v \, \bar{\delta}_{Npq} \, \hat{s}^{v}_{pq} \, \mu_N^{-v} \tag{156}$$

$$\widehat{T}_{\mathrm{DSO}} = N_{\mathrm{DSO}} \sum_{NM} \sum_{pq} \sum_{\mu,v=0,\pm1} (-1)^{v+\mu} \bar{\boldsymbol{\kappa}}^{\mathrm{DSO}}_{NM\mu v pq} \, \widehat{E}_{pq} \, \mu_N^{-\mu} \, \mu_M^{-v} \tag{157}$$

The scalar products in formulae (154)–(157) are expressed in terms of contravariant cyclic coordinates

$$\vec{a}\,\vec{b} = \sum_{\mu=0,\pm1} (-1)^{\mu} a^{\mu} \, b^{-\mu}$$

In particular, the cyclic coordinates of nuclear magnetic moments are expressed in terms of their Cartesian coordinates as

$$\mu_N^{\pm 1} = \frac{\mp\left(\mu_N^x \pm \mathrm{i}\,\mu_N^y\right)}{\sqrt{2}}, \quad \mu_N^0 = \mu_N^z \tag{158}$$

The cyclic coordinates of the electron spin operator have the form

$$\hat{s}_{pq}^{+1} = \frac{-c_{p\alpha}^{+} c_{q\beta}}{\sqrt{2}} \tag{159}$$

$$\hat{s}_{pq}^{-1} = \frac{c_{p\beta}^{+} c_{q\alpha}}{\sqrt{2}} \tag{160}$$

$$\hat{s}_{pq}^{0} = \frac{c_{p\alpha}^{+} c_{q\alpha} - c_{p\beta}^{+} c_{q\beta}}{2} \tag{161}$$

The operator $\widehat{E}_{pq}$ in formulae (154) and (157) is the singlet excitation operator

$$\widehat{E}_{pq} = c_{p\alpha}^{+} c_{q\alpha} + c_{p\beta}^{+} c_{q\beta} \tag{162}$$

Note that the summation over the electrons in perturbation operators (143) – (145) and (147) in the second-quantized form is converted to the summation over the pair of orbital indices $p$, $q$. This issue is described in detail in a book:[221] every arbitrary one-electron operator in the first-quantized form

$$\sum_{n=1}^{N} \hat{f}(\vec{r}_n)$$

can be matched by a second-quantized operator

$$\sum_{pq} \langle \chi_p | \hat{f}(\vec{r}) | \chi_q \rangle \, \hat{c}_p^{+} \, \hat{c}_q$$

where summation over indices $p$, $q$ covers the full set of orthonormal spin – orbits.

In the matrix elements of the PSO, SD, FC and DSO operators appearing in expression (154) – (157), integration over the spin variables has already been done (this is reflected as the bar above the corresponding element). Thus, they can be represented as

$$\bar{\boldsymbol{\kappa}}_{N v pq}^{\mathrm{PSO}} = \left\langle \bar{\chi}_p \left| \frac{[(\vec{r} - \vec{r}_N) \times \hat{\vec{\nabla}}]_v}{|\vec{r} - \vec{r}_N|^3} \right| \bar{\chi}_q \right\rangle \tag{163}$$

$$\bar{\boldsymbol{\kappa}}_{N \mu v pq}^{\mathrm{SD}} = \left\langle \bar{\chi}_p \left| \frac{3\,(\vec{r} - \vec{r}_N)_\mu (\vec{r} - \vec{r}_N)_v - \delta_{\mu v}}{|\vec{r} - \vec{r}_N|^5} \right| \bar{\chi}_q \right\rangle \tag{164}$$

$$\bar{\boldsymbol{\delta}}_{N pq} = \langle \bar{\chi}_p | \delta(\vec{r} - \vec{r}_N) | \bar{\chi}_q \rangle \tag{165}$$

$$\bar{\boldsymbol{\kappa}}_{NM \mu v pq}^{\mathrm{DSO}} = \tag{166}$$

$$= \left\langle \bar{\chi}_p \left| \frac{\delta_{\mu v} (\vec{r} - \vec{r}_N)(\vec{r} - \vec{r}_M) - (\vec{r} - \vec{r}_N)_\mu (\vec{r} - \vec{r}_M)_v}{|\vec{r} - \vec{r}_N|^3 \, |\vec{r} - \vec{r}_M|^3} \right| \bar{\chi}_q \right\rangle$$

The full Hamiltonian (148) in the general form can be written in the following way:

$$\widehat{H} = \widehat{H}_0 + \sum_r \lambda_r \widehat{H}_r = \widehat{H}_0 + \widehat{H}_{\mathrm{pert}} \tag{167}$$

The exact wave function $\Psi(\boldsymbol{\lambda})$ of the system ground state and the corresponding energy $E(\boldsymbol{\lambda})$ can be represented as the infinite Taylor series

$$E(\boldsymbol{\lambda}) = E^{(0)} + \sum_r \lambda_r E_r^{(1)} + \tag{168}$$

$$+ \frac{1}{2!} \sum_{rs} \lambda_r \lambda_s E_{rs}^{(2)} + \frac{1}{3!} \sum_{rst} \lambda_r \lambda_s \lambda_t E_{rst}^{(3)} + \ldots$$

$$\Psi(\boldsymbol{\lambda}) = \Psi^{(0)} + \sum_r \lambda_r \Psi_r^{(1)} + \tag{169}$$

$$+ \frac{1}{2!} \sum_{rs} \lambda_r \lambda_s \Psi_{rs}^{(2)} + \frac{1}{3!} \sum_{rst} \lambda_r \lambda_s \lambda_t \Psi_{rst}^{(3)} + \ldots$$

The energy and wave function corrections in formulae (168) and (169) can be found from comparison of the left-hand and right-hand sides of the Schrödinger equation at the products of various parameters $\boldsymbol{\lambda}$ with the same powers. From expression (98) for the energy correction bilinear in the nuclear magnetic moments, it follows that the consideration should cover only the summands that are quadratic in the magnetic perturbation operators $\widehat{T}$. Thus, the terms quadratic in $\widehat{T}$ with a zero and first order in $\widehat{H}_I$ have the following form, respectively:

$$\Delta E\,[H_I^0] = \sum_{n \neq 0} T_{0n} T_{n0} \left( E_0^{(0)} - E_n^{(0)} \right)^{-1} \tag{170}$$

$$\Delta E\,[H_I^1] = \sum_{n,m \neq 0} \big( H_{I0n} T_{nm} T_{m0} + T_{0n} H_{Inm} T_{m0} + \tag{171}$$

$$+ T_{0n} T_{nm} H_{Im0} \big) \left( E_0^{(0)} - E_n^{(0)} \right)^{-1} \left( E_0^{(0)} - E_m^{(0)} \right)^{-1} -$$

$$- \sum_{n \neq 0} \big( H_{I0n} T_{n0} T_{00} + T_{0n} H_{In0} T_{00} +$$

$$+ T_{0n} T_{n0} H_{I00} \big) \left( E_0^{(0)} - E_n^{(0)} \right)^{-2}$$

In expressions (170) and (171), $A_{nm} = \langle \Phi_n^{(0)} | \widehat{A} | \Phi_m^{(0)} \rangle$ ($\widehat{A} = \widehat{T}, \widehat{H}_I$) is the operator $\widehat{A}$ in the basis set of eigenfunctions of the non-perturbed Hamiltonian $\widehat{H}_0$.

In most cases, the FC contribution to the SSCC prevails over other contributions; therefore, it makes sense to consider the particular type of magnetic perturbation operator $\widehat{T}_{\mathrm{FC}}$; for other operators appearing in $\widehat{T}$, the reasoning is similar. Substituting the operator $\widehat{T}_{\mathrm{FC}}$ as (156) into expressions (170) and (171) gives the following formulae:

$$E^{\mathrm{FC}}[H_I^0] = \tag{172}$$

$$= N_{\mathrm{FC}}^2 \sum_{NM} \sum_{\substack{pq \\ rs}} \sum_{\eta, v = 0, \pm 1} \sum_{n \neq 0} \delta_{N pq} \delta_{N' rs} (-1)^{v+\eta} \times$$

$$\times \; \mu_N^{-v} \mu_M^{-\eta} \hat{s}_{pq0n}^{v} \hat{s}_{rsn0}^{\eta} \left( E_0^{(0)} - E_n^{(0)} \right)^{-1}$$

$$E^{\mathrm{FC}}[H_I^1] = \tag{173}$$

$$= N_{\mathrm{FC}}^2 \sum_{NM} \sum_{\substack{pq \\ rs}} \sum_{\eta,\nu=0,\pm1} \delta_{Npq}\delta_{Mrs}(-1)^{\nu+\eta}\, \mu_N^{-\nu}\mu_M^{-\eta} \times$$

$$\times \Bigg[ \sum_{n,m\neq 0} \big(H_{I0n}\,\hat{\mathbf{s}}^{\nu}_{pqnm}\,\hat{\mathbf{s}}^{\eta}_{rsm0} + \hat{\mathbf{s}}^{\nu}_{pq0n}\,H_{Inm}\,\hat{\mathbf{s}}^{\eta}_{rsm0} +$$

$$+ \hat{\mathbf{s}}^{\nu}_{pq0n}\,\hat{\mathbf{s}}^{\eta}_{rsnm}\,H_{Im0}\big)\left(E_0^{(0)} - E_n^{(0)}\right)^{-1}\left(E_0^{(0)} - E_m^{(0)}\right)^{-1} -$$

$$- \sum_{n\neq 0} \big(H_{I0n}\,\hat{\mathbf{s}}^{\nu}_{pqn0}\,\hat{\mathbf{s}}^{\eta}_{rs00} + \hat{\mathbf{s}}^{\nu}_{pq0n}\,H_{In0}\,\hat{\mathbf{s}}^{\eta}_{rs00} +$$

$$+ \hat{\mathbf{s}}^{\nu}_{pq0n}\,\hat{\mathbf{s}}^{\eta}_{pqn0}\,H_{I00}\big)\left(E_0^{(0)} - E_n^{(0)}\right)^{-2} \Bigg]$$

In the approximation of a single excitation configuration space, the wave functions of singlet and triplet excited states are expressed as the action of singlet $\widehat{Q}^{0,0}_{pq}$ and triplet $\widehat{Q}^{1,\nu}_{pq}$ excitation operators, respectively, on the many-electron Hartree–Fock wave function of the ground state $|\Phi_0^0\rangle$

$$\left|\Phi^{(\mathrm{S})}_{ai}\right\rangle = \widehat{Q}^{0,0}_{ai}\left|\Phi_0^0\right\rangle \tag{174}$$

$$\left|\Phi^{(\mathrm{T})\,1,\nu}_{ai}\right\rangle = \widehat{Q}^{1,\nu}_{ai}\left|\Phi_0^0\right\rangle,\ \nu = 0,\pm1 \tag{175}$$

where

$$\widehat{Q}^{0,0}_{pq} = \frac{(c^{+}_{p\alpha}\,c_{q\alpha} + c^{+}_{p\beta}\,c_{q\beta})}{\sqrt{2}} \tag{176}$$

$$\widehat{Q}^{1,\nu}_{pq} = \sqrt{2}\,\hat{s}^{\nu}_{pq},\ \nu = 0,\pm1 \tag{177}$$

The substitution of excited states as (174) and (175) into sums over states (172) and (173) and comparison of this expression with the determination of the energy correction bilinear in the nuclear magnetic moments (98) gives relations for the FC contribution in the framework of the molecular orbital theory up to the first order in the residual electron–electron interaction

$$J^{\mathrm{FC}}_{NM}[H_I^0] = N_{\mathrm{FC}}^2 \sum_{ia} \delta_{Nia}\,\delta_{Mai}\,(\varepsilon_a - \varepsilon_i)^{-1} \tag{178}$$

$$J^{\mathrm{FC}}_{NM}[H_I^1] = \tag{179}$$

$$= -N_{\mathrm{FC}}^2 \sum_{ia;jb} \delta_{Nia}\,V_{jaib}\,\delta_{Mbj}\,(\varepsilon_a - \varepsilon_i)^{-1}(\varepsilon_b - \varepsilon_j)^{-1}$$

The terms of a higher order in the $\widehat{H}_I$ have a chain form:

$$J^{\mathrm{FC}}_{NM}[H_I^2] = N_{\mathrm{FC}}^2 \sum_{\substack{ia;jb; \\ kc}} \delta_{Nia}\,V_{jaib}\,V_{kbjc}\,\delta_{Mck} \times \tag{180}$$

$$\times\,(\varepsilon_a - \varepsilon_i)^{-1}(\varepsilon_b - \varepsilon_j)^{-1}(\varepsilon_c - \varepsilon_k)^{-1}$$

$$J^{\mathrm{FC}}_{NM}[H_I^3] = -N_{\mathrm{FC}}^2 \sum_{\substack{ia;jb; \\ kc;ld}} \delta_{Nia}V_{jaib}\,V_{kbjc}\,V_{lckd}\,\delta_{Mdl} \times \tag{181}$$

$$\times\,(\varepsilon_a - \varepsilon_i)^{-1}(\varepsilon_b - \varepsilon_j)^{-1}(\varepsilon_c - \varepsilon_k)^{-1}(\varepsilon_d - \varepsilon_l)^{-1}$$

Formula (178) is the Pople–Santry expression;[224] in the case where molecular orbitals are approximated by a linear combination of atomic orbitals

$$|\chi_p\rangle = \sum_{\mu} C_{p\mu}|\varphi_\mu\rangle$$

Pople and Santry[224] found that the orbitals providing the most considerable contribution are the valence atomic s type orbitals centred on atoms $N$ and $M$. The formulae of higher order in the residual electron–electron interactions (179)–(181) attest to the same type of atomic orbitals playing the predominant role in the transfer of the Fermi contact nuclear spin–spin interaction between atoms $N$ and $M$. It is noteworthy that in the case of relativistic theory, the $p_{1/2}$ type atomic spinors, which also cross the nucleus, are added to the s type orbitals.

To conclude this Section, we will present the general relations for the four contributions to SSCCs in the second-quantized form determined using the molecular orbital theory without any approximations or constraints

$$J^{\mathrm{FC}}_{NM} = N_{\mathrm{FC}}\,\gamma_N\,\gamma_M\,\big\langle\big\langle\hat{\delta}_N;\hat{\delta}_M\big\rangle\big\rangle_{\omega=0} \tag{182}$$

$$J^{\mathrm{SD}}_{NM\alpha\beta} = N_{\mathrm{SD}}\gamma_N\gamma_M \sum_{\delta=1}^{3} \big\langle\big\langle\hat{\tau}^{\mathrm{SD}}_{N\alpha\delta};\hat{\tau}^{\mathrm{SD}}_{M\beta\delta}\big\rangle\big\rangle_{\omega=0} \tag{183}$$

$$J^{\mathrm{PSO}}_{NM\alpha\beta} = N_{\mathrm{PSO}}\,\gamma_N\,\gamma_M\,\big\langle\big\langle\,\hat{\tau}^{\mathrm{PSO}}_{N\alpha};\,\hat{\tau}^{\mathrm{PSO}}_{M\beta}\big\rangle\big\rangle_{\omega=0} \tag{184}$$

$$J^{\mathrm{DSO}}_{NM\alpha\beta} = N_{\mathrm{DSO}}\,\gamma_N\,\gamma_M \sum_{pq} \left\langle \bar{\chi}_p \left| \hat{\tau}^{\mathrm{DSO}}_{NM\alpha\beta} \right| \bar{\chi}_q \right\rangle_{\omega=0} \rho_{pq} \tag{185}$$

The operators in formulae (182)–(185) are expressed in the following way:

$$\hat{\delta}_N = \sum_{pq} \langle\bar{\chi}_p|\,\delta(\vec{r}-\vec{r}_N)\,|\bar{\chi}_q\rangle\,\hat{s}^0_{pq} \tag{186}$$

$$\hat{\tau}^{\mathrm{SD}}_{N\alpha\delta} = \tag{187}$$

$$= \sum_{pq} \left\langle \bar{\chi}_p \left| \frac{3(x_\alpha - x_{N\alpha})(x_\delta - x_{N\delta})}{|\vec{r}-\vec{r}_N|^5} - \frac{\delta_{\alpha\delta}}{|\vec{r}-\vec{r}_N|^3} \right| \bar{\chi}_q \right\rangle \hat{s}^0_{pq}$$

$$\hat{\tau}^{\mathrm{PSO}}_{N\alpha} = \sum_{pq} \left\langle \bar{\chi}_p \left| \frac{\big[(\vec{r}-\vec{r}_N)\times\hat{\vec{\nabla}}\big]_\alpha}{|\vec{r}-\vec{r}_N|^3} \right| \bar{\chi}_q \right\rangle \widehat{E}_{pq} \tag{188}$$

$$\hat{\tau}^{\mathrm{DSO}}_{NM\alpha\beta} = \tag{189}$$

$$= \left\langle \bar{\chi}_p \left| \frac{(\vec{r}-\vec{r}_N)(\vec{r}-\vec{r}_M)\,\delta_{\alpha\beta} - (x_\alpha - x_{N\alpha})(x_\beta - x_{M\beta})}{|\vec{r}-\vec{r}_N|^3\,|\vec{r}-\vec{r}_M|^3} \right| \bar{\chi}_q \right\rangle$$

$\rho_{pq}$ is the one-electron density matrix

$$\rho_{pq} = \langle\Psi^0\,|\,\widehat{E}_{pq}\,|\,\Psi^0\rangle \tag{190}$$

The Ramsey formulae representing the non-relativistic limit of the relativistic representation of SSCC, expressed in terms of the molecular orbital theory, form the basis for all modern quantum chemical approaches to the calculation of SSCCs at the non-relativistic level.

# V. Methods for relativistic calculations of spin – spin coupling constants

## V.1. Hierarchy of relativistic calculations of spin – spin coupling constants

The accuracy of SSCC calculation in molecules containing heavy magnetic nuclei is determined, first of all, by the level of electronic structure description, *i.e.*, the level at which the ground and the excited states and transition energies between them are described, as follows from the universal four-component relativistic definition of SSCC *via* the sum over states (106). Practically, this means complete dependence on the level of approximations applied for the solution of the many-body Dirac equation.

First of all, it should be noted that in all relativistic quantum chemical methods, the Born – Oppenheimer[63] approximation is widely used. The latter is based on the model of fixed nucle. The concept proposed initially for a non-relativistic case is also extended to the relativistic problem. The corrections to spin – spin coupling constants associated with the vibrational and rotational nuclear degrees of freedom are, most often, applied separately. All other schemes for relativistic calculation of the electronic structure are considered within the Born – Oppenheimer approximation.

One more important approximation which is common to all relativistic methods is the quasiclassical description of electromagnetic fields. It is known that owing to a finite velocity of propagation of interactions, a field should be considered as a system with its own degrees of freedom in combination with the system of interacting charged particles. This fact is responsible for impossibility of the accurate description of a system of interacting charged particles using the Hamiltonian function depending only on the coordinates, velocities and internal degrees of freedom (*e.g.*, spin) of these particles and containing no field degrees of freedom. Therefore, the quasiclassical description of the electromagnetic field proceeding from the assumption that the particle velocity is low compared with the speed of light is commonly used.

The approximations noted above are common to both non-relativistic and relativistic quantum chemical methods. In the former case, approaches are classified in accordance with the combination of the electronic structure calculation method and the basis sets used, while in the latter case, the method for considering relativistic effects, *i.e.*, actually the Hamiltonian model used, is added to these two parameters. This can be regarded as the introduction of the additional Hamiltonian axis to the concept proposed by Pople,[225, 226] who depicted the integrated notion of approach as a method – basis set system of axes (Fig. 3).

The principal parameter for classifying the methods, namely, the dimension of one-electron operators in the model Hamiltonian is laid on the 'Hamiltonian' axis. The dimension of one-electron operators equal to 1 corresponds to non-relativistic Hamiltonians (based on the Schrödinger Hamiltonian); the dimension of 2 corresponds to two-component Hamiltonians originating from various procedures of separation of the small component (actually, freezing of positronic degrees of freedom). The dimension of 4 implies a set of four-component Hamiltonians with their own grading, determined, first of all, by the chosen type of relativistic effects that are to be taken into account in the particular problem, by the method of description of the two-electron part and some other details.

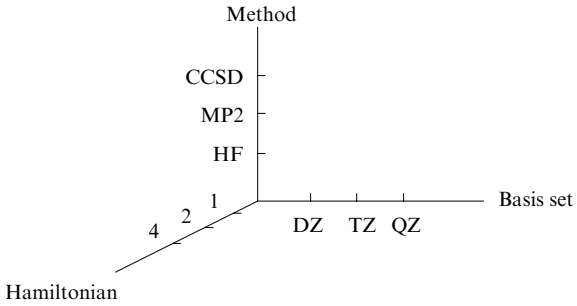



**Figure 3.** Three parameters of the relativistic (or quasirelativistic) method for calculation of the electronic structure.

To take into account various types of relativistic effects, it is necessary to use various classes of model Hamiltonians; this is related, first of all, to the spin degrees of freedom, as it is the spin that is responsible for many-component nature of the relativistic description. For example, spin-free operator describing the scalar relativistic effects (mass – velocity, Schrödinger zitterbewegung or Darwin effects) can be freely included in a non-relativistic program code. For inclusion of the spin – orbit coupling, at least a two-component scheme should be applied, while at the common non-relativistic level this is impossible. Currently, the most advanced versions of GAMESS[227] or DALTON[186] program packages, which are considered to be the customary non-relativistic ones, are suitable for taking account of the scalar relativistic effects and spin – orbit coupling effects within the two-component schemes at the level of electronic structure calculation and some first-order properties (which do not include SSCCs).

Most often, the names of relativistic approaches (methods) comprise not only the name of the electronic structure calculation technique but also the Hamiltonian model, *e.g.*, the Dirac – Hartree – Fock method stands for the Hartree – Fock relativistic approach using the four-component Dirac – Coulomb Hamiltonian or more complicated ones such as the Dirac – Coulomb – Gaunt or Dirac – Coulomb – Breit Hamiltonians.

Scaling of the computational cost for relativistic methods differs from scaling of the corresponding non-relativistic methods by the relativistic factor depending on the exponent of the basis set dimension used in the non-relativistic analogue.[228] This can be briefly expressed as

$$S = y(x)\, f(x)\, N^x$$

where $N$ is the basis set dimension; $x$ is the exponent characterizing growth of the computational cost of non-relativistic methods with increasing basis set dimension $N$; $f(x)$ is the non-relativistic scaling factor; $y(x)$ is the relativistic scaling factor. The difference between the computational scaling of relativistic and non-relativistic methods should be evaluated considering the factor $y(x)$. For example, in an arbitrary scheme of the coupled cluster (CC) theory,[229 – 236] this factor has the following form:[237]

$$y(x) \approx 4\sqrt{\pi\left(\frac{x}{2} - 1\right)}, \quad x \geqslant 4$$

In particular, in the non-relativistic CCSDT scheme scaled as $N^8$ (*i.e.*, $x = 8$),[238] the scaling relativistic factor $y(x) \approx 12$. This means that the relativistic CCSDT scheme is 12 times more costly than the non-relativistic analogue.

The development of relativistic approaches to the calculation of SSCCs is of a great importance. In the last decades, only a few independent relativistic approaches to SSCC calculation were developed. The best known four-component approaches are the Dirac–Hartree–Fock (DHF)[183,239,240] and Dirac–Kohn–Sham (DKS) methods.[117,241] A detailed description of relativistic four-component methods as applied to calculation of NMR parameters can be found in reviews of Xiao *et al.*[242] and Aucar *et al.*[243]

Currently, two-component approaches to SSCC calculation are more popular owing to the much lower computational cost as compared with four-component methods. A comprehensive review[244] devoted to two-component calculation methods of NMR parameters considers in detail various types of two-component Hamiltonians including both exact (*e.g.*, X2C) and approximate (*e.g.*, A2C) ones used in modern quantum chemical relativistic approaches to calculate NMR parameters, in particular, the SSCCs.

By the generally accepted notion of exact two-component methods is meant the fact that the eigensolutions of the two-component Hamiltonian used reproduce, with computer accuracy, the eigensolutions of its four-component analogue. Among exact two-component approaches, one can distinguish the X2C class, which is characterized by a specific feature: the components are decoupled in a single step, *i.e.*, by means of a single unitary transformation. However, as noted in the review of Peng and Reiher[245] devoted to the exact methods for Fock operator decoupling, this definition of X2C class from the formal standpoint appears ambiguous, because any unitary transformation can be represented as a product of an arbitrary number of transformations, so that the single-step procedure is transformed into a procedure with an arbitrary number of steps. In order to eliminate this ambiguity, Peng and Reiher[245] made a correction of the definition of X2C approaches according to which the mentioned single exact decoupling transformation can be algorithmically achieved in one step no matter how it was implemented in practice.

In a recent review, Autschbach[52] mentioned the initial definition of X2C as a combination of exact single-step component decoupling procedures. In the present review, we imply precisely this definition.

As a whole, the exact schemes are classified into three types: single-step (X2C)[120,245] and two-step[246–248] schemes and those comprising an infinite number of steps.[249] All other two-component approaches that are theoretically not equivalent to the initial four-component problem to an accuracy inherent in the theory of the scheme are called quasirelativistic, or approximate two-component schemes (A2C).

The following most well-known schemes correspond to the A2C class: direct perturbation theory (DPT) based approaches,[250–253] ZORA,[205,254–256] SORA–NESC,[257] different-order DKH approximations[258,259] (DKH2,[260,261] DKH3,[262,263] DKH4,[264] DKH5/6[265]) and IORA.[266,267] Direct perturbative methods are based on the Breit–Pauli Hamiltonian,[35] which includes the magnetic field of two considered nuclei and the external magnetic field[253,268] (in particular, for SSCC, the latter is set to zero). To date, the direct perturbation theory has been developed only to take into account the spin–orbit effects in SSCCs.[269–271]

The most-known exact decoupling schemes based on accurate two-component operators[58,107,272–276] are as follows: NESC,[277–284] infinite-order DKH,[248] BSS, or IOTC.[285–288]

### V.2. Four-component methods for the calculation of spin–spin coupling constants

For description of relativistic effects which are manifested in the molecular properties of systems with heavy nuclei and are mainly determined by valence electrons, it is quite sufficient to introduce effective charges and to use special modified operators at the one-component level. However, a reasonably accurate description of the relativistic effects in SSCC values determined, first of all, by inner electrons requires invoking of the four-component formalism of the relativistic Dirac theory extended to the many-electron case.

The four-component relativistic theory of SSCCs was discussed for the first time by Pyykkö,[289] and later by Aucar and Oddershede.[218] However, it is noteworthy that these studies do not consider the quantum electrodynamic effects (QEE).

Four-component methods are associated with very high computational expenses; therefore, currently, calculation of SSCCs at the four-component level is possible using either methods based on the four-component relativistic 4RPA approach without necessary application of Breit corrections[240] or the four-component DFT theory (4DFT)[290,291] as applied to SSCCs.[292–294] The former approach was tested on the calculations of the $^1J$(X,H) coupling constants for the series of compounds HX (X = $^{19}$F, $^{35}$Cl, $^{79}$Br, $^{127}$I),[240] $XH_4$ (X = $^{13}$C, $^{29}$Si, $^{119}$Sn, $^{207}$Pb) and $PbMe_3H$,[183] $XH_3$ (X = N, P, As, Sb, Bi) and $XH_2$ (X = O, S, Se, Te, Po),[295] as well as $^1J(^{129}Xe,^{19}F)$ and $^2J(^{19}F,^{19}F)$ constants for $XeF_n$ ($n$ = 2, 4, 6).[239] The accuracy of calculation of SSCCs using the uncorrelated four-component relativistic approach based on the RPA theory (TD-DHF) proved unsatisfactory. There are only few relativistic calculations of SSCCs for heavy nuclei in terms of the 4DFT formalism, as the theory and software implementation of this approach were presented quite recently. A theory of SSCCs in the 4DFT formalism using the restricted magnetic kinetic balance (mDKS–RMB) scheme suitable for practical implementation was first proposed by Repiský *et al.*[117] The proposed approach makes use of the restricted magnetic kinetic balance (RMB).[118] The paper cited presents the results of the first calculations of $^1J$(X,$^1$H) and $^2J(^1H,^1H)$ for the compounds $XH_4$ (X = $^{13}$C, $^{29}$Si, $^{73}$Ge, $^{119}$Sn, $^{207}$Pb) using this approach, which were performed using the ReSpect program.[296] The next study dealing with SSCC calculation according to the mDKS–RMB method was reported by Wodyński *et al.*[241] The authors analyzed the mDKS–RMB method for applicability of various basis sets and exchange-correlation functionals in the calculation of $^1J(^{199}Hg,^{13}C)$, $^2J(^{199}Hg,^{15}N)$ and $^1J(^{13}C,^{15}N)$ for the $Hg(CN)_2$ molecule. The relativistic calculations of the $^1J(^{29}Si,^1H)$, $^1J(^{29}Si,^{13}C)$, $^1J(^{77}Se,^{13}C)$ and $^1J(^{77}Se,X)$ constants (X = $^1$H, $^{13}$C, $^{15}$N, $^{19}$F, $^{29}$Si, $^{31}$P, $^{77}$Se) within the 4DFT and 4RPA formalism were also carried out[297–300] for a broad range of organosilicon and -selenium compounds using the DIRAC program.[110]

In general, it is expected that in the near future relativistic DFT-oriented approaches will be widely adopted in the

problems concerning investigation of NMR properties of realistic large molecules containing heavy atoms. This is due, most of all, to the balance between accuracy and computational cost which is potentially achievable by the DFT approach at any level, both relativistic or non-relativistic one.

**V.2.a. Four-component RPA method (4RPA)**

The many-body Dirac – Coulomb equation was solved using the Dirac – Hartree – Fock method [19, 38, 49] formulated by Swirles.[18] Proceeding from the Hartree formalism,[301, 302] she showed that the Dirac equation can be solved on the basis of the variational principle and that the relativistic single-particle DHF equations can be constructed using the same concept as the non-relativistic analogue.[303 – 309] The proposed method was tested in relation to Fe, W, Pt and Hg atoms and the singly charged mercury cation.[24, 310] Reformulation of this method in terms of the algebra of tensor operators markedly simplified this approach.[311, 312]

The theory of the RPA (TD-HF) method as applied to SSCCs has been described in detail.[218] Note that the RPA theory is universal in essence, so that it can be easily extended to the relativistic case, while retaining all general concepts formulated at the non-relativistic level. The RPA method is based on the linear response theory,[213] the key notion of which is the polarization propagator [213 – 218] describing this response.

In the spectral representation, the retarded polarization propagator has the form

$$\langle\langle \widehat{P}; \widehat{Q} \rangle\rangle^{r}_{E+i\varepsilon} = \sum_{n\neq 0} \left( \frac{\langle 0 | \widehat{P} | n \rangle \langle n | \widehat{Q} | 0 \rangle}{E - E_n + E_0 + i\varepsilon} - \frac{\langle 0 | \widehat{Q} | n \rangle \langle n | \widehat{P} | 0 \rangle}{E + E_n - E_0 + i\varepsilon} \right) \quad (191)$$

The physical interpretation of the propagator is determined by the set of operators, $\widehat{P}$ and $\widehat{Q}$. If interaction operators between nuclear magnetic moments and electron spin or orbital angular momentums are taken as $\widehat{P}$ and $\widehat{Q}$, this propagator will describe the response of the electron system to magnetic perturbation from nuclear spins, resulting in the change in the interaction energy between the nuclei, which discloses the meaning of SSCC as a propagator.

From expression (191), it can be seen that SSCC depends in an explicit form on exact excitation energies $E = \pm(E_n - E_0)$ and the transition moments for the corresponding magnetic operators, which are the real parts of the poles and the residues of the function $\langle\langle \widehat{P}; \widehat{Q} \rangle\rangle^{r}_{E+i\varepsilon}$, respectively.

The iterative solution of the equation of motion for the retarded polarization propagator (EOM),[243] which is an evolution equation in the energy form, allows the propagator to be expressed in a more compact form in terms of the superoperator formalism [313] using the inner projection (IP) technique [314]

$$\langle\langle \widehat{P}^{+}; \widehat{Q} \rangle\rangle^{r}_{E} = \left( \widehat{P}^{+} \middle| \frac{1}{E} \left[ \hat{I} + \sum_{n=1}^{\infty} \left( \frac{\widehat{H}_0}{E} \right)^{n} \right] \middle| \widehat{Q} \right) = (\widehat{P} | \hat{\tilde{\mathbf{h}}})(\hat{\mathbf{h}} | (E\hat{I} - \widehat{H}_0)^{-1} | \hat{\tilde{\mathbf{h}}})(\hat{\mathbf{h}} | \widehat{Q}) \quad (192)$$

In expression (192), it is assumed that

$$(\widehat{P} | \widehat{Q}) = \langle 0 | [\widehat{P}^{+}, \widehat{Q}] | 0 \rangle, \ [\widehat{H}_0, \widehat{Q}] \equiv \widehat{H}_0 \widehat{Q} \quad (193)$$

($(\hat{\mathbf{h}}|$ and $|\hat{\tilde{\mathbf{h}}})$ are the operator column-vector and row-vector, respectively.

The operator manifold $\{\hat{\mathbf{h}}\}$ is chosen to satisfy the practical needs of the problem under consideration. The non-perturbed ground state is the DHF wave function and $\{\hat{\mathbf{h}}\}$ is a set of elementary (spin-adopted) particle-number-preserving excitation operators:

$$\hat{\mathbf{h}} = \{\hat{\mathbf{h}}_2, \hat{\mathbf{h}}_4, \hat{\mathbf{h}}_6, ...\} \quad (194)$$

Here

$$\hat{\mathbf{h}}_2 = \{\hat{\mathbf{q}}^{+}, \hat{\mathbf{q}}\} = \{a_m^{+} a_a, \ a_a^{+} a_m\} \quad (195)$$

$$\hat{\mathbf{h}}_4 = \{\hat{\mathbf{q}}^{+}\hat{\mathbf{q}}^{+}, \ \hat{\mathbf{q}}\,\hat{\mathbf{q}}\} = \{a_m^{+} a_n^{+} a_a a_b, \ a_b^{+} a_a^{+} a_n a_m\} \text{ and so on} \quad (196)$$

Thus, since in the relativistic case, $\widehat{\mathbf{H}}_0 \equiv \widehat{\mathbf{H}}_{\mathrm{DCB}}$, the polarization propagator $\langle\langle \widehat{P}; \widehat{Q} \rangle\rangle^{r}_{E+i\varepsilon}$ has the following form:

$$\langle\langle \widehat{P}; \widehat{Q} \rangle\rangle^{r}_{E} = \widetilde{\mathbf{P}}\, \mathbf{M}^{-1} \mathbf{Q} \quad (197)$$

where $\widetilde{\mathbf{P}} = (\mathbf{P}_a, \mathbf{P}_b, ...)$ is a block row-vector, $\mathbf{Q} = (\mathbf{Q}_a, \mathbf{Q}_b, ...)^{\mathrm{T}}$ is a block column-vector and

$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{aa} & \mathbf{M}_{ab} & ... \\ \mathbf{M}_{ba} & \mathbf{M}_{bb} & ... \\ \vdots & \vdots & \ddots \end{pmatrix}^{-1}$ is a block matrix, the blocks of which correspond to various classes of excitation of the set $\hat{\mathbf{h}}$,

$$\mathbf{P}_a = (\widehat{P} | \hat{\tilde{\mathbf{h}}}_a), \ \mathbf{Q}_a = (\hat{\mathbf{h}}_a | \widehat{Q}) \quad (198)$$

$$\mathbf{M}_{ab} = (\hat{\mathbf{h}}_a | E\,\hat{\mathbf{I}} - \widehat{\mathbf{H}}_{\mathrm{DCB}} | \hat{\tilde{\mathbf{h}}}_b) \quad (199)$$

where

$$\widehat{H}_{\mathrm{DCB}} = \sum \hat{\mathbf{h}}_{\mathrm{D}}(i) + \mathbf{G} \quad (200)$$

$$\hat{\mathbf{h}}_{\mathrm{D}}(i) = c\,\vec{\boldsymbol{\alpha}}_i \hat{\vec{p}}_i + (\boldsymbol{\beta} - \mathbf{I})c^2 + \mathbf{V}_{\mathrm{nuc}}(\vec{r}_i) + \sum \boldsymbol{\Lambda}_{+} \mathbf{U}(\vec{r}_i) \boldsymbol{\Lambda}_{+} \quad (201)$$

$$\mathbf{G} = \frac{1}{2} \sum \boldsymbol{\Lambda}_{+} \hat{\mathbf{g}}_{ij} \boldsymbol{\Lambda}_{+} - \boldsymbol{\Lambda}_{+} \mathbf{U}(\vec{r}_i) \boldsymbol{\Lambda}_{+} \quad (202)$$

Formula (200) represents schematically the unperturbed Dirac – Coulomb – Breit Hamiltonian, $\mathbf{V}_{\mathrm{nucl}}(\vec{r}_i)$ in expression (201) is the nuclear potential at the point of location of the $i$th electron, $\mathbf{U}(\vec{r}_i)$ is the effective Dirac – Hartree – Fock potential, $\hat{\mathbf{g}}_{ij}$ in formula (202) is the two-electron interaction operator with the relativistic Breit correction term, $\boldsymbol{\Lambda}_{+} = \sum |\mathbf{n}\rangle\langle\mathbf{n}|$ is the projection operator to the electron continuum, where $|\mathbf{n}\rangle$ satisfy the one-particle Dirac equation

$$\hat{\mathbf{h}}_{\mathrm{D}} |\mathbf{n}\rangle = \varepsilon_n |\mathbf{n}\rangle$$

From the definition of SSCC in the four-component form represented by expressions (104) and (106), it can be seen that the relativistic SSCC is the real part of the retarded polarization propagator (191) in the static spectral

representation multiplied by a constant. This means that solving the relativistic equation for the EOM propagator is actually finding the relativistic SSCC.

Solution of this equation in the RPA approximation is restricted by the consideration of the lowest class of the excited states $\hat{\mathbf{h}}_2$ consisting of single excitation and de-excitation operators.

In the RPA approximation, the propagator $\langle\langle\, \hat{P}; \hat{Q}\, \rangle\rangle^{r}_{E+i\varepsilon}$ describing the SSCC can be expressed in the following way:[213,315]

$$\langle\langle\, \hat{\mathbf{Z}}_{N\alpha}; \hat{\mathbf{Z}}_{M\beta}\, \rangle\rangle^{r}_{E} = \tag{203}$$

$$= \left(\tilde{\mathbf{Z}}_{N\alpha}, \tilde{\mathbf{Z}}^{*}_{N\alpha}\right) \begin{pmatrix} E\mathbf{I}-\mathbf{A} & -\mathbf{B}^{*} \\ -\mathbf{B} & -E\mathbf{I}-\mathbf{A}^{*} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Z}_{N\beta} \\ \mathbf{Z}^{*}_{N\beta} \end{pmatrix}$$

In this expression, vectors $\mathbf{Z}_{N\alpha}$ consist of the matrix elements of the relativistic magnetic operator

$$\left(\hat{\tilde{\mathbf{Z}}}\right)_{ma} = \left\langle m \left| \hat{\tilde{\mathbf{Z}}} \right| a \right\rangle$$

The matrix elements of matrices **A** and **B** are calculated by the formulae for the matrix elements of matrix **M** from expression (199) as

$$\mathbf{A}_{manb} = \left(\hat{q}^{+}_{ma} \left| \hat{H}_{\mathrm{DCB}} \right| \hat{q}^{+}_{nb}\right) = \tag{204}$$

$$= \delta_{mn}\,\delta_{ab}(\varepsilon_m - \varepsilon_a) + \langle mb \,\|\, an \rangle$$

$$\mathbf{B}_{manb} = \left(\hat{q}_{ma} \left| \hat{H}_{\mathrm{DCB}} \right| \hat{q}^{+}_{nb}\right) = \langle ba \,\|\, mn \rangle \tag{205}$$

In formulae (204) and (205), a shorthand notation for two-electron integrals is introduced

$$\langle mb \,\|\, an \rangle = \langle mb \,|\, an \rangle - \langle mb \,|\, na \rangle,$$

where

$$\langle mb \,|\, an \rangle = \int \boldsymbol{\psi}^{*}_{m}(1)\, \boldsymbol{\psi}^{*}_{b}(2)\, r^{-1}_{12}\, \boldsymbol{\psi}_{a}(1)\, \boldsymbol{\psi}_{n}(2)\, \mathrm{d}(1)\, \mathrm{d}(2)$$

The retarded polarization propagator can be represented in the diagonal form in terms of the matrix of eigenvalues and eigenvectors of the effective matrix

$$\mathbf{M} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \tag{205a}$$

in the following way:

$$\left\langle\!\left\langle\, \hat{P}; \hat{Q}\, \right\rangle\!\right\rangle_{E} = \left(\left(\hat{P} \left| \hat{\tilde{\mathbf{q}}}^{+} \right.\right), \left(\hat{P} \left| \tilde{\mathbf{q}} \right.\right)\right) \begin{pmatrix} \mathbf{Z} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{Z} \end{pmatrix} \times \tag{206}$$

$$\times \begin{pmatrix} E\mathbf{I}-\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & E\mathbf{I}+\boldsymbol{\Omega} \end{pmatrix}^{-1} \begin{pmatrix} \tilde{\mathbf{Z}} & \tilde{\mathbf{Y}} \\ -\tilde{\mathbf{Y}} & -\tilde{\mathbf{Z}} \end{pmatrix} \begin{pmatrix} \left(\hat{\mathbf{q}}^{+} \left| \hat{Q} \right.\right) \\ \left(\hat{\mathbf{q}} \left| \hat{Q} \right.\right) \end{pmatrix}$$

For this purpose, it is necessary to solve the problem for eigenvalues for matrix **M**

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_{\lambda} = \omega_{\lambda} \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_{\lambda} \tag{207}$$

Thus, the key stages involved in SSCC calculation in the RPA approximation in both relativistic and non-relativistic cases are the following:

— solution of the unperturbed DHF problem by a self-consistency procedure, determination of the molecular coefficients, orbital energies and ground state energies;

— calculation of matrix elements of effective matrix (205a) by formulae (204) and (205);

— solution of the generalized problem to find the eigenvalues for effective matrix **M** [see formula (207)];

— calculation of one-electron integrals for properties, which are represented by FC, SD and PSO one-electron integrals in the non-relativistic case and by the operator $\hat{\mathbf{Z}}_{N\alpha}$ integrals in the relativistic case;

— finding the polarization propagator $\langle\langle\, \hat{\mathbf{Z}}_{N\alpha}; \hat{\mathbf{Z}}_{M\beta}\, \rangle\rangle_{E}$ by formula (206) and, finally, determination of the proper SSCC.

#### V.2.b. Four-component DFT method (4DFT)

Despite the rapid progress in the development of calculations of molecular properties by means of non-relativistic *ab initio* approaches such as MCSCF,[316–318] SOPPA,[319–323] EOM-CC,[324] CCSD[325,326] and some other (less popular) approaches, in recent decades, the DFT method[327,328] has occupied the top position in the studies of structures and properties of complex organic molecules and molecular complexes. Computational scaling of DFT is roughly the same as that of the Hartree–Fock method but, depending on more or less lucky combination of the exchange-correlation functional and basis set selected for a particular problem, DFT provides a certain level of the electron correction description and has sufficiently high accuracy comparable with that of high-level *ab initio* methods, which, in turn, require much higher computational expenses. The scope of applicability of DFT is very broad ranging from atomic physics, electronic structure calculations for clusters and molecular dynamics simulation[329,330] and physics of surface phenomena[331,332] to the design of new materials and theoretical biophysics.[333]

As regards the calculation of molecular magnetic properties, this application area of DFT has rapidly increased in recent years.[334–336] Since NMR spectral parameters bearing information about the stereochemical and electronic structures of molecules are very important for modern chemistry, going beyond the scope of the Hartree–Fock method with the minimization of the computational cost is of considerable interest and inevitably leads to DFT-based approaches. The brief discussion of the theoretical and practical aspects of the SSCC calculations using DFT can be found in the reviews of Helgaker *et al.*[238,337] and Rusakov and Krivdin.[1] A more detailed account of this subject is given in a classical monograph.[338]

The DFT is based on the theorems formulated by Hohenberg and Kohn.[339] The first theorem states that there is a one-to-one mapping between the ground state density of the electron subsystem occurring in an external potential of atomic nuclei and the potential of the nuclei. This is an existence theorem, which does not propose an algorithm for constructing this mapping. The second theorem states that the electronic subsystem energy, which is an electron density functional, has a minimum equal to the ground-state energy. It is the variational principle of quantum mechanics formulated for the electron density functional. The practical implementation of the

Hohenberg – Kohn theorems in the form of the well-known DFT method was facilitated by the Kohn and Sham assumption [327, 340, 341] about the existence of some auxiliary system of non-interacting particles with a ground state density exactly coinciding with the ground state density of the system of interacting particles being considered. This system is briefly referred to as the Kohn – Sham (auxiliary) system. The effective Hamiltonian of the auxiliary system looks like a Hamiltonian for a system of uncoupled electrons but the resulting electron density constructed within this model actually corresponds to the real electron density of interacting particles. An indisputable advantage of DFT is that it points out how to find the exact ground state electron density and, as a consequence, all first-order properties of the system in the ground state.

When the non-relativistic DFT method was recognized all over the world, its relativistic analogue, RDFT, started to be considered,[290] since relativistic effects have to be included in the calculations concerning systems with heavy nuclei.[20, 342] An example of early calculation of this type is the atomic calculation reported by Liberman *et al.*[343] The concepts outlined in this work served as the prerequisite to fundamental studies of Rajagopal and Callaway,[344] who formulated for the first time the relativistic extension of the fundamental Hohenberg – Kohn theorems.[339]

In the relativistic formalism, in the ground state, the four-dimensional current (4-current)

$$j^{\mu}(\vec{r}) = (cn(\vec{r}), \vec{j}(\vec{r}))$$

plays the role of the ground state electron density

$$n = \frac{j^0}{c}$$

involved in the non-relativistic DFT approach. The Kohn – Sham statements are reformulated in view of the above, in particular, it is assumed that there exists an auxiliary system of non-interacting relativistic particles, the ground state 4-current of which coincides with the exact ground state 4-current of the interacting relativistic system being described. Typically, the 4-current $j^{\mu}$ unambiguously defines the many-body ground state $\Psi_0$ (up to a gauge transformation) and, hence, defines the ground state energy $E_{\rm tot}$, which is the functional $j^{\mu}$. The direct minimization of $E_{\rm tot}[j^{\mu}]$ with respect to $j^{\mu}$ gives the exact ground state 4-current and, hence, the exact energy $E_{\rm tot}[j^{\mu}]$. Thus, in practice, the problem is reduced to finding the correct form of $E_{\rm tot}[j^{\mu}]$, which is split into the kinetic energy $T_{\rm S}$ of the free auxiliary system, terms involving the external fields $E_{\rm ext}$, the direct Hartree energy $E_{\rm H}$ and the exchange-correlation energy $E_{\rm xc}[j^{\mu}]$, which collects all specific features of the many-body nature. Minimization of $E_{\rm tot}[j^{\mu}]$ with respect to one-particle states of the auxiliary non-interacting system results in one-particle RDFT equations proposed for the first time by Rajagopal and Ramana [345, 346] and MacDonald and Vosko.[347] These Kohn – Sham relativistic equations have the form of the Dirac equation with a multiplicative 4-current-dependent potential $v_{\rm s}^{\mu}$

$$\left\{-{\rm i}c\,\vec{\boldsymbol{\alpha}}\hat{\vec{\nabla}} + \boldsymbol{\beta}mc^2 + \boldsymbol{\alpha}_{\mu}v_s^{\mu}(\vec{r})\right\}\boldsymbol{\varphi}_k(\vec{r}) = \varepsilon_k\boldsymbol{\varphi}_k(\vec{r}) \quad (208)$$

$$v_{\rm s}^{\mu}(\vec{r}) = V^{\mu}(\vec{r}) + v_{\rm H}^{\mu}(\vec{r}) + v_{\rm xc}^{\mu}(\vec{r}) \quad (209)$$

$$v_{\rm H}^{\mu}(\vec{r}) = \int {\rm d}^3\vec{r}'\frac{j^{\mu}(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (210)$$

$$v_{\rm xc}^{\mu} = \frac{\delta E_{\rm xc}[j]}{\delta j_{\mu}(\vec{r})} \quad (211)$$

Here $v_{\rm s}^{\mu}$ comprises the Coulomb $V^{\mu}(\vec{r})$, Hartree $v_{\rm H}^{\mu}(\vec{r})$ and exchange-correlation $v_{\rm xc}^{\mu}(\vec{r})$ potentials.

The conventional DFT is a static theory using only ground state characteristics, which is inapplicable to time-dependent properties or properties of excited states, *e.g.*, SSCCs. For solving problems of this type, the time-dependent electron density functional theory (TD-DFT) was proposed;[291, 348 – 353] this opened up wide prospects for calculation of the properties of excited states, in particular, SSCCs. Like DFT, the TD-DFT method is some trade-off between the accuracy and computational effort.

The TD-DFT approach is based on the same ideas as the conventional DFT. TD-DFT relies on four Runge – Gross theorems,[354] the first of which is, in essence, a theorem of existence and is considered as an analogue of the first Hohenberg – Kohn theorem; the other three theorems describe the algorithm of the TD-DFT method. A key characteristic feature of TD-DFT distinguishing it from the stationary DFT approach is inclusion of time. This means that proceeding from many-electron time-dependent Schrödinger equation, one can obtain a system of time-dependent effective one-particle equations. Solutions of these equations are effective orbitals of the auxiliary system of electrons; they form the time-dependent electron density $n(\vec{r}, t)$ identical to the electron density of the real system at any time point.

The calculations of SSCCs at the level of non-relativistic TD-DFT are widely represented in the scientific literature. Quite a number of exhaustive reviews on this topic have been published.[1, 238, 355]

Strict extension of TD-DFT to the relativistic case from the quantum electrodynamics standpoint in the Born – Oppenheimer approximation [63] was proposed by Rajagopal.[356] This theory was developed in terms of relativistic quantum electrodynamics considering the 4-current, the Dirac spinor fields and four-dimensional potential (4-potential) of the external electromagnetic field on an equal footing. All these functions are main variables in this theory and, hence, they are arguments of the exchange-correlation functional.

The relativistic TD-DFT theory proposed by Rajagopal is too sophisticated for practical use; therefore, there are a number of simplifying assumptions. First, for most physical processes described by quantum chemistry, the creation and annihilation of virtual electron – positron pairs is not of prime importance; therefore, the NVPA approximation can be used.[357] Second, in most cases, description of electromagnetic field in terms of classical (non-quantum) considerations is sufficient. Within the framework of these approximations, the exchange-correlation functional has only one argument — the time-dependent 4-current.

The theoretical grounds of the TD-RDFT method with the above approximations and calculations of the excitation energies can be found in a number of papers (see, for example, Refs 358 – 361). As noted above, the relativistic calculations of SSCCs for heavy nuclei within the four-

component DFT formalism were reported in few papers.[117, 241, 298–300]

### V.2.c. Calculation of spin–spin coupling constants using the four-component electron density functional theory

As applied to the calculation of SSCCs, the relativistic four-component Dirac–Kohn–Sham theory was proposed for the first time by Repisky *et al.*[117] The approach employed by these authors is based on the four-component matrix Dirac–Kohn–Sham (mDKS) theory and uses restricted magnetic kinetic balance. Thus, the full name of this approach was abbreviated as mDKS–RMB. The mDKS–RMB approach was considered in detail in an earlier paper[118] in relation to calculation of the magnetic shielding tensor.

The final expressions for contributions to the reduced SSCC in the mDKS–RMB formalism are found from the following formulae:[117]

$$K_{uv}^{(M,N)} = K_{uv}^{\mathrm{D}(M,N)} + K_{uv}^{\mathrm{P0}(M,N)} + K_{uv}^{\mathrm{P1}(M,N)} \tag{212}$$

$$K_{uv}^{\mathrm{D}(M,N)} = \frac{1}{2c^2}\left(\mathbf{C}_{(i)}^{L+}\mathbf{C}_{(i)}^{S+}\right)\begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}^{\mathrm{D}+}_{\mu_u^M\mu_v^N} \\ \boldsymbol{\Lambda}^{\mathrm{D}}_{\mu_u^M\mu_v^N} & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(i)}^{L} \\ \mathbf{C}_{(i)}^{S} \end{pmatrix} \tag{213}$$

$$K_{uv}^{\mathrm{P0}(M,N)} = \frac{1}{2c}\left[\left(\boldsymbol{\beta}_{ij}^{\mu_u^M}\right)^{*} + \boldsymbol{\beta}_{ji}^{\mu_u^M}\right] \times \left(\mathbf{C}_{(i)}^{L+}\mathbf{C}_{(i)}^{S+}\right)\begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}^{\mathrm{P}+}_{\mu_v^N} \\ \boldsymbol{\Lambda}^{\mathrm{P}}_{\mu_v^N} & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(j)}^{L} \\ \mathbf{C}_{(j)}^{S} \end{pmatrix} \tag{214}$$

$$K_{uv}^{\mathrm{P1}(M,N)} = \frac{1}{c}\mathrm{Re}\left[\boldsymbol{\beta}_{ai}^{\mu_u^M}\left(\mathbf{C}_{(i)}^{L+}\mathbf{C}_{(i)}^{S+}\right) \times \begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}^{\mathrm{P}+}_{\mu_v^N} \\ \boldsymbol{\Lambda}^{\mathrm{P}}_{\mu_v^N} & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(a)}^{L} \\ \mathbf{C}_{(a)}^{S} \end{pmatrix}\right] \tag{215}$$

$$\left(\boldsymbol{\Lambda}^{\mathrm{D}}_{\mu_u^M\mu_v^N}\right)_{\lambda\tau} = \left\langle \chi_\lambda \left| \delta_{uv}\frac{\vec{r}_M\vec{r}_N}{r_M^3 r_N^3} - \frac{(\vec{r}_M)_v(\vec{r}_N)_u}{r_M^3 r_N^3} + \mathrm{i}\boldsymbol{\sigma}_v\frac{[\vec{r}_M\times\vec{r}_N]_u}{r_M^3 r_N^3} - \mathrm{i}\varepsilon_{vuk}(\vec{r}_M)_k\frac{\vec{\boldsymbol{\sigma}}\vec{r}_N}{r_M^3 r_N^3}\right| \chi_\tau \right\rangle \tag{216}$$

$$\left(\boldsymbol{\Lambda}^{\mathrm{P}}_{\mu_v^N}\right)_{\lambda\tau} = \left\langle \chi_\lambda \left| \vec{\boldsymbol{\sigma}}\hat{\vec{p}}\left(\frac{\vec{r}_N\times\vec{\boldsymbol{\sigma}}}{r_N^3}\right)_v \right| \chi_\tau \right\rangle \tag{217}$$

In expressions (213)–(215) $\mathbf{C}_{(i)}^{L,S} \underset{M}{=} \mathbf{C}_{(i)}^{L,S(0,0)}$ are the unperturbed molecular coefficients, $\boldsymbol{\beta}_{ij}^{\mu_u^M}$ and $\boldsymbol{\beta}_{ia}^{\mu_u^M}$ are the linear response coefficients. In the non-relativistic limit, $K_{uv}^{\mathrm{D}(M,N)}$ comes to the classical DSO contribution, $K_{uv}^{\mathrm{P0}(M,N)}$ disappears, while $K_{uv}^{\mathrm{P1}(M,N)}$ comes to the sum of the classical non-relativistic Ramsey contributions — FC, SD and PSO and the FC–SD cross contribution.

The key sequence of SSCC calculation according to the mDKS–RMB method is as follows:

— solving four-component DKS equations in the absence of a magnetic field using the restricted kinetic balance; this gives the unperturbed molecular coefficients for both occupied and vacant 4-spinors $\mathbf{C}_{(p)}^{L,S} \equiv \mathbf{C}_{(p)}^{L,S(0,0)}$ and the corresponding energies;

— self-consistency procedure to solve the equation for the linear coefficients $\boldsymbol{\beta}_{ia}^{\mu_u^M}$ of expansion of the regular components of occupied molecular 4-spinors $\{\varphi_i^{r(1,0)_u^M}\}$ in terms of the vacant unperturbed 4-spinors $\{\varphi_a^{(0,0)}\}$ for every orientation of nuclear fields included in the SSCCs;

— calculation of the discussed contributions to the reduced SSCC from formulae (213)–(217).

In the study cited,[117] the SSCC calculations were performed using the non-relativistic SVWN functionals[362] and BP86 functionals;[363, 364] for the Ge, Sn and Pb atoms, modified relativistic Dyall basis sets were used.[167, 169, 170] According to the authors,[117] for the $CH_4$ molecule, which is the lightest one out of the considered series, the relativistic correction to the $^1J(^{13}C,^1H)$ constant was negligibly small. The corrections were ~3% of the non-relativistic value for $^1J(^{29}Si,^1H)$; about 13% for $^1J(^{73}Ge,^1H)$; about 40% for $^1J(^{119}Sn,^1H)$; and almost 90% for $^1J(^{207}Pb,^1H)$. The mDKS–RMB approach in combination with the chosen functionals and basis sets demonstrated a rather high accuracy, although the deviation of the relativistic $^1J(X,^1H)$ constants from experimental values markedly increased with increasing nuclear charge and reached ~10% (BP86) for heavier nuclei (Sn, Pb). A calculation of SSCC at a non-relativistic level would have resulted in substantial errors [for example, in the case of $^1J(^{207}Pb,^1H)$, the difference would have been about a half of the experimental value].

It was noted that the four-component DKS theory as applied to the calculation of linear response magnetic properties, such as SSCCs, is rather new and there are still only few papers devoted to calculations of SSCCs for heavy nuclei within this formalism. In particular, Wodyński *et al.*[241] reported the results of SSCC calculations carried out using the four-component mDKS–RMB method with various exchange-correlation functionals — B3LYP,[365–367] PBE0,[206, 368, 369] BP86,[363, 364] KT2,[370] and for comparison, they also used the two-component ZORA–DFT (B3LYP/TZP) approach. For C and N atoms, the Sauer basis set (aug-cc-pVTZ-J) modified for SSCC calculation was employed,[135] and the Dyall basis set (dyall.v3z) was used for Hg.[169]

Selected results of the cited paper[241] on the calculation of SSCCs involving mercury are summarized in Table 4. It was noted that, despite the superiority of the four-component approach over the two-component one in the accuracy, in the case of $^1J(^{199}Hg,^{13}C)$, the result of the ZORA–B3LYP calculation in the jcpl basis set[372] proved to be closest to the experimental value (2731 Hz; not given in Table 4). The authors proposed a qualitative explanation for the possible sources of discrepancy between their results and experimental values considering the neglect of the medium effects and vibrational corrections. However, the seeming advantage of the two-component ZORA(B3LYP/jcpl) method over the four-component mDKS–RMB approach was attributed to the use of various nuclear models (point nucleus model in the case of the two-component approach and the Gaussian nuclear model in the case of the four-component scheme).

In our opinion, the discrepancy between the results obtained using the same formalism (in this particular case, DFT) but different Hamiltonians (in one case, this is the full four-component Dirac–Coulomb Hamiltonian, and in the

**Table 4**. Spin–spin coupling constants (Hz) in the $Hg(CN)_2$ molecule calculated using the four-component mDKS–RMB approach and the two-component ZORA scheme (from the data of Ref. 241).

| Functional | $^1J(^{199}Hg,^{13}C)$ | $^2J(^{199}Hg,^{15}N)$ | $^1J(^{13}C,^{15}N)$ |
|---|---|---|---|
| | *mDKS–RMB method* | | |
| B3LYP | 2481 | −62.2 | −6.9 |
| PBE0 | 2476 | −66.5 | −6.1 |
| BP86 | 1964 | −21.3 | 2.9 |
| KT2 | 1973 | 4.6 | 3.9 |
| | *ZORA method* | | |
| B3LYP | 2362 | −37.3 | −12.8 |
| | 3140 [a] | −101 [a] | – |

[a] Experiment.[371]

other case, the approximate two-component ZORA Hamiltonian) is largely due to the fact that the latter refers to A2C type Hamiltonians, which are more or less accurate approximations of the full four-component Hamiltonian. In particular, the widely used ZORA Hamiltonian is not classified as one of the best approximations for calculation of SSCCs, as the asymptotic behaviour of the kinematic parameter of the ZORA Hamiltonian is inadequate near the nucleus.[47]

In the recent years, Krivdin and co-workers [297–300] published several more papers devoted to calculations of SSCCs for heavy nuclei within the DFT formalism at the four-component level. In the first paper of this series,[297] which is devoted to description of vibrational and relativistic effects in the $^1J(^{29}Si,^1H)$ values of halosilanes $SiX_nH_{4-n}$ (X = F, Cl, Br, I) at the four-component DFT(PBE0) level, it was shown that negative (in the sign) relativistic corrections to the negative $^1J(^{29}Si,^1H)$ constant can reach 4–6 Hz (~1%), and inclusion of these corrections together with vibrational corrections markedly increases the calculation accuracy (Fig. 4).

In the second paper of the series, Rusakova *et al.*[298] investigated the relativistic effects in the $^1J(^{29}Si,^{13}C)$ constants for a series of 60 silicon-containing compounds with different carbon atom hybridizations. Non-relativistic calculations were carried out using second-order polarization propagator approach SOPPA(MP2),[322, 373, 374] SOPPA(CC2) [375] and SOPPA(CCSD) [376] methods and the locally dense basis set (LDBS) scheme.[377–379] According to this scheme, the Sauer basis set, aug-cc-pVTZ-J,[135, 380] was applied to silicon and carbon atoms involved in the spin–spin coupling, while for all other atoms, contracted Dunning's basis set, cc-pVDZ, was used.[125–127] The relativistic calculations were performed by the DIRAC program [110] at the four-component DFT(PBE0) level. For large component basis sets, the LDBS scheme was also used (all basis sets were decontracted), and for generating the small component basis sets, the unrestricted kinetic balance was used (UKB). The relativistic corrections were calculated as the differences between the relativistic and the corresponding non-relativistic values found using the DFT(PBE0) formalism. The medium effect was considered using the Tomasi continuum model IEF–PCM [381, 382] at the DFT(PBE0) level. The average absolute and relative deviations of the calculated $^1J(^{29}Si,^{13}C)$ constants from the experimental ones are shown in Fig. 5, in which one can see systematic convergence of the calculated and experimental results upon the successive inclusion of, first, the medium effects and then relativistic effects.

A good agreement with experiment achieved upon inclusion of the medium effects and relativistic corrections

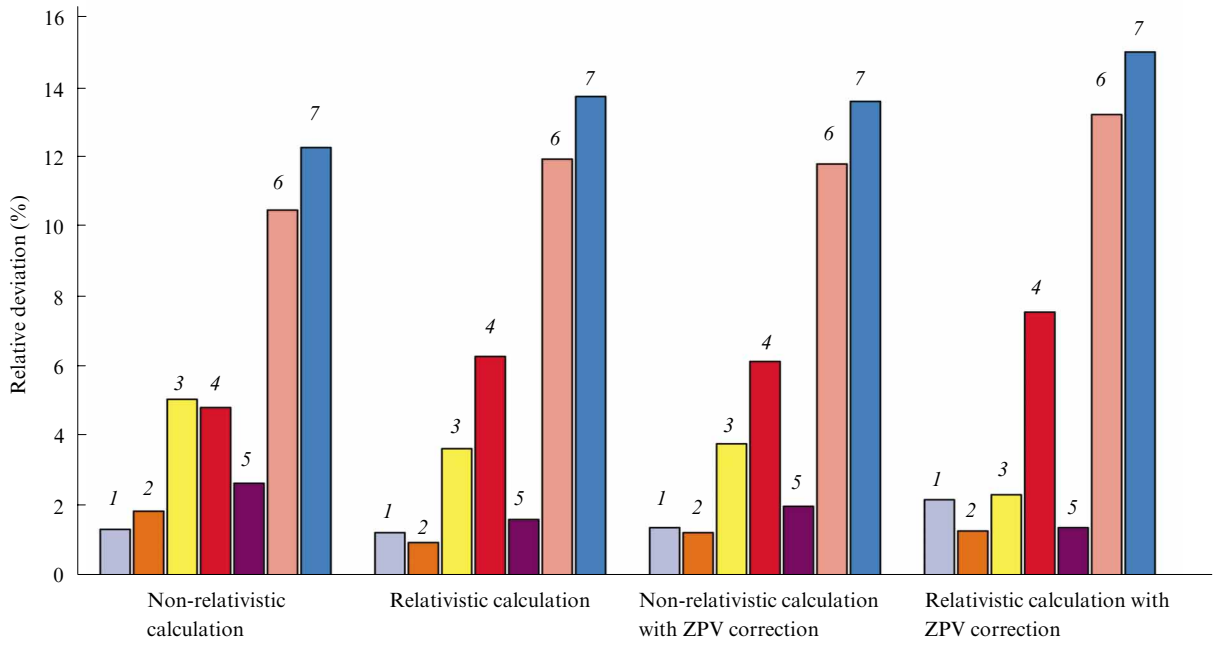



**Figure 4.** Mean relative deviations of the theoretical $^1J(^{29}Si,^1H)$ values calculated by various SOPPA and DFT methods with inclusion of relativistic and vibrational corrections from the experimental values (from the data of Ref. 297).
(*1*) SOPPA, (*2*) SOPPA(CC2), (*3*) SOPPA(CCSD), (*4*) B3LYP, (*5*) PBE0, (*6*) KT2, (*7*) KT3.

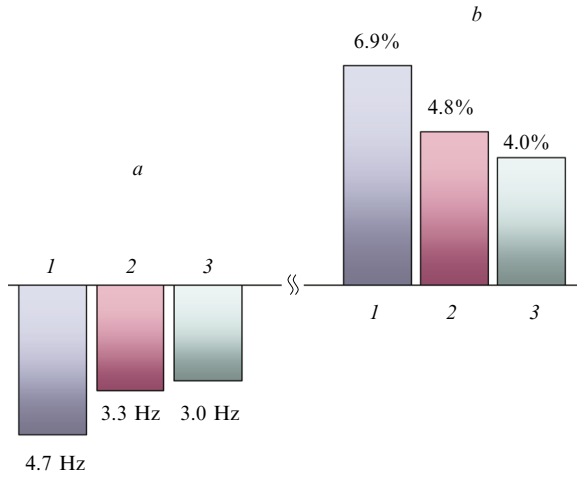



**Figure 5.** Mean absolute (*a*) and relative (*b*) deviations of the theoretical $^1J(^{29}Si,^{13}C)$ values calculated using the SOPPA(CC2) method with successive inclusion of the medium effects and relativistic corrections from the experimental values (from the data of Ref. 298).
(*1*) SOPPA(CC2), (*2*) SOPPA(CC2) + Δsolv, (*3*) SOPPA(CC2) + Δsolv + Δrel.

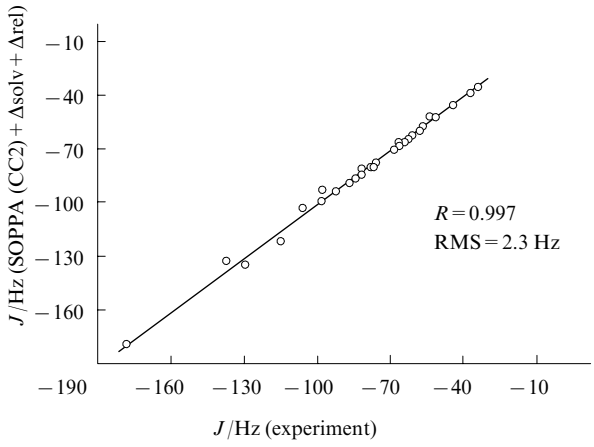



**Figure 6.** Correlation of the $^1J(^{29}Si,^{13}C)$ values calculated using the SOPPA(CC2) method with inclusion of the medium effects and relativistic corrections with the experimental values (from the data of Ref. 298).

is also indicated by the linear correlation between the calculated and experimental values of the $^1J(^{29}Si,^{13}C)$ with a root-mean-square (RMS) deviation of only 2.3 Hz for a ~200 Hz range of variation of the absolute SSCC values (Fig. 6). In the paper cited,[298] it was also shown that the relativistic corrections to the SSCCs involving silicon were fairly low (~1%), although in the representative series of 60 organosilicon compounds, application of these corrections provided a noticeably better agreement between the calculated and experimental results.

The next-mentioned study[299] deals with the SSCCs involving a selenium nucleus, $^1J(^{77}Se,^{13}C)$, in a series of selenium-containing heterocycles and open-chain selenides. It was found that the relativistic corrections to $^1J(^{77}Se,^{13}C)$ are, on average, ~15%–25%, and this is much greater than those for $^1J(^{29}Si,^{13}C)$. The calculations were performed in this study by a scheme analogous to that used in the previous paper.[298] The relativistic corrections were evaluated within the four-component DFT formalism as the differences between the SSCCs obtained using the fully relativistic Dirac–Coulomb and Lèvy-Leblond[59] Hamiltonians. In both cases (relativistic and non-relativistic ones), the same LDBS scheme as in the previous study was used (aug-cc-pVTZ-J basis set for selenium[383] and carbon[378] and cc-pVDZ basis set for all other atoms). In the relativistic DFT calculations, the small component basis set was generated using the unrestricted kinetic balance, while in the non-relativistic four-component DFT calculations, the restricted kinetic balance was used. The relativistic corrections were calculated by the B3LYP,[365,366] PBE0,[206,368] KT2[370] and LDA (SVWN)[384] exchange-correlation functionals.

The best agreement with experimental data was established for the scheme including the relativistic correction at the B3LYP functional level. The plot of correlation of the SSCC values found as the sums of the SOPPA(CC2) calculation result and the DFT(B3LYP) relativistic correction with the experimental values is shown in Fig. 7. It can be seen that this scheme for the $^1J(^{77}Se,^{13}C)$ calculation gives results that are well correlated with experimental data.

In the paper being considered,[299] the total relativistic correction to $^1J(^{77}Se,^{13}C)$ was split into the scalar and spin–orbit contributions. The scalar relativistic contribution was found as the difference between the $^1J(^{77}Se,^{13}C)$ values calculated using the scalar Dirac–Coulomb Hamiltonian and the non-relativistic Lèvy-Leblond Hamiltonian — a four-component analogue of purely non-relativistic one-component Schrödinger Hamiltonian. The spin–orbit contribution was found as the difference between the $^1J(^{77}Se,^{13}C)$ values calculated using the full and scalar Dirac–Coulomb Hamiltonians. The total relativistic correction to $^1J(^{77}Se,^{13}C)$, which was the sum of the scalar and spin–orbital relativistic contributions, was determined as the difference between the full relativistic four-component $^1J(^{77}Se,^{13}C)$ value and the value of this constant calculated using the non-relativistic Lèvy-Leblond Hamiltonian. The results of splitting of the relativistic corrections to $^1J(^{77}Se,^{13}C)$ into the contributions are shown in Fig. 8. It can be seen that the spin–orbit contribution is 4–5 times smaller in magnitude than the relativistic scalar contribution.

Generally, the total relativistic correction to $^1J(^{77}Se,^{13}C)$ is 10–20 Hz, or 15%–25% of the full SSCC value, depending on the functional used;[299] taking this into account is very important when comparing calculated and experimental data.

The fourth-mentioned paper[300] of the series presents the relativistic effects inherent in the SSCCs across one bond involving selenium — $^1J(^{77}Se,X)$, X = $^1H$, $^{13}C$, $^{15}N$, $^{19}F$, $^{29}Si$, $^{31}P$ and $^{77}Se$ — for 14 compounds, namely, $H_2Se$, $CH_3SeH$, $CF_3SeNH_2$, $(CH_3)_2SeF_2$, $SeF_6$, $F_2SeO$, $F_2SeO_2$, $(CH_3)_3SiSeC_2H_5$, $CH_3SeP(CH_3)_2$, $CH_3SePO(CH_3)_2$, $(CH_3)_3PSe$, $F_3PSe$, $Cl_3PSe$ and $Se_2(CH_3)_2$. The chosen scheme for calculation of relativistic corrections was similar to the scheme used in the previous papers[298,299] and differed only in particular calculation methods. The basic SSCC value was calculated at the SOPPA(CCSD) level, and the relativistic corrections were found using the PBE0 functional[206,368] within 4DFT. The calculations confirmed that

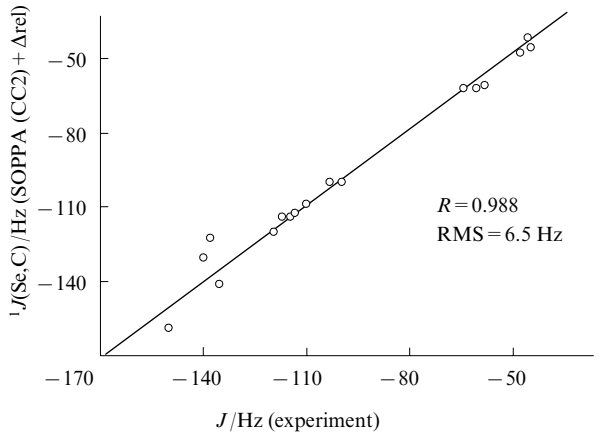



**Figure 7.** Correlation of the $^1J(^{77}Se,^{13}C)$ values calculated using the SOPPA(CC2) method with inclusion of the relativistic correction at the DFT(B3LYP) level with the experimental values (from the data of Ref. 299).

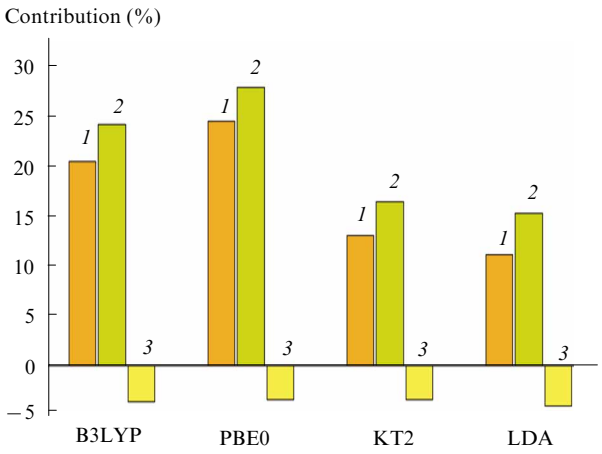



**Figure 8.** Relativistic contributions to the $^1J(^{77}Se,^{13}C)$ values: mean total relativistic (*1*), scalar (*2*) and spin – orbit (*3*) corrections (from the data of Ref. 299).

relativistic effects actually play a crucial role in the SSCCs involving selenium atoms, being as high as 20% – 50% of the total SSCC values of these types. For the $^1J(^{77}Se,^{77}Se)$ constants for the interaction of two atoms of heavy fourth period elements, they reach ~170% of the total value, so that any (even higher-level) calculation of these constants without considering the relativistic effects is inadequate. It was also shown that the scalar relativistic effects in the $^1J(^{77}Se,X)$ constants predominate in all cases over the spin – orbit effects (Fig. 9), and their inclusion brings the theoretical values much closer to experimental values.

To summarize the discussion of the papers dealing with the four-component relativistic calculations of SSCCs, it should be emphasized that considering relativistic effects in these calculations is of prime importance and that in the near future, an avalanche-like increase in the number of publications devoted to calculations of SSCCs for heavy atoms using the full four-component relativistic Dirac theory should be expected.

### V.2.d. Relativistic and non-relativistic exchange-correlation functionals

The exact dependence of the exchange-correlation energy on the electron density is unknown; therefore, numerous non-relativistic exchange-correlation functionals have now been developed and tested, this being done separately for each type of problem. In particular, a specific class of non-relativistic functionals exists for SSCC calculations. They are briefly discussed below.

In the simplest approximation, the exchange-correlation energy is found as the integral of some local electron density functional over the whole three-dimensional space

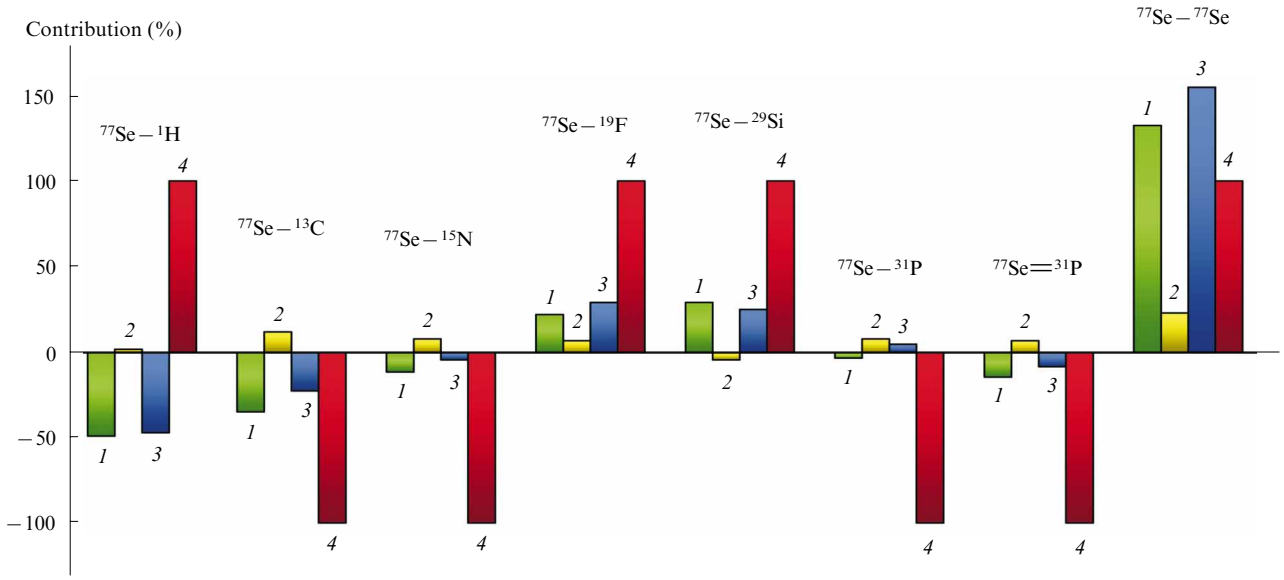



**Figure 9.** Relativistic contributions to the $^1J(^{77}Se,X)$ values, X = H, C, N, F, Si, P and Se: scalar (*1*), spin – orbit (*2*) and mean total relativistic (*3*) corrections; (*4*) complete theoretical SSCC value, which is taken here as either 100% if the SSCC sign is positive or as −100% if the sign is negative (from the data of Ref. 300).

$$\int_V F(n(\vec{r}))\,\mathrm{d}^3\vec{r}$$

This is called the local density approximation (LDA).[362] The LDA exchange-correlation functional is a combination of the Dirac–Slater exchange functional and the Vosko–Wilk–Nusair (VWN) correlation functional,[362] the parameterization of which is based on the common electron gas model.[385] The LDA approximation has been long used in the solid state physics but it has not become popular in quantum chemistry, in particular, for calculation of SSCCs because of insufficient accuracy of the results.

One more approximation of the exchange-correlation functional is the generalized gradient approximation (GGA).[386] The exchange-correlation functional is formed in this approximation upon integration of a functional that depends not only on the electron density in each point of space but also on the electron density gradient

$$\int_V F\left(n(\vec{r}), \hat{\vec{\nabla}} n(\vec{r})\right)\mathrm{d}^3\vec{r}$$

After the advent and development of the GGA exchange-correlation functionals, the Kohn–Sham theory got the deserved recognition, because calculations carried out using these functionals ensured an accuracy comparable with that obtained by the CCSD method, and the DFT technique gained popularity and was included in almost all large program packages.[387, 388] The most widely employed exchange-correlation GGA functionals are BLYP[363, 366] adjusted semiempirically using the inert gas model; PBE,[368] which is an *ab initio* functional based on the properties of slowly changing electron gas; *ab initio* PW91 functional;[206] and NMR-oriented Keal–Tozer functionals, KT2 (see Ref. 370) and KT3 (see Ref. 389). In recent years, there appeared the tendency to combine GGA functionals with some fraction of the Hartree–Fock exact exchange integral operator, which has a beneficial influence on the calculation accuracy. This gave the well-known hybrid functionals such as B3LYP,[365, 366] which is a combination of BLYP[363, 366] and a fraction (20%) of the Hartree–Fock exact exchange potential, and PBE0,[386] a combination of PBE and a fraction (25%) of the Hartree–Fock exact exchange functional. The hybrid modifications of the B97 functional,[390] called B97-1 (see Ref. 391) and B97-2 (see Ref. 392), are rather well-known. The CAMB3LYP hybrid functional is fairly popular.[393, 394]

The first attempts to model a functional of total relativistic energy $E_{\mathrm{tot}}[j^\mu]$ as the sum of kinetic energy $T_{\mathrm{S}}$, interaction energy with the external field $E_{\mathrm{ext}}$, Hartree energy $E_{\mathrm{H}}$ and exchange-correlation energy $E_{\mathrm{xc}}[j^\mu]$ were made by Vallarta and Rosen[395] and Jensen.[396] The authors proposed a new functional based on the relativistic Thomas–Fermi model,[397–399] which is the extension of the homogeneous electron gas model for which the energy functional is a simple function of its density with an additional argument reflecting the inhomogeneity, that is, the density gradient. However, in practice, such models did not demonstrate encouraging results at the non-relativistic level. This is related to the fact that they neither reproduce the atomic shell structure nor do they provide the proper description of the chemical bonding. Meanwhile, these difficulties do not affect the electron–electron interaction; therefore, they actually refer to the orbital-dependent kinetic part of the energy functional $T_{\mathrm{S}}$, which is crucial for correct reproduction of the quantum mechanical properties of the relativistic system. Hence, these drawbacks can be eliminated by starting out from the exact expression for kinetic energy of non-interacting particles.

The renormalization problem also affects the construction of the test relativistic functional $E_{\mathrm{xc}}[j^\mu]$. The simplest way to construct relativistic functionals is based on the relativistic extension of the LDA approximation — RLDA functional,[344, 345, 347] which uses only the dependence on the homogeneous relativistic electron gas density. The full exchange and correlation parts of this functional were presented in a number of publications.[345, 347, 400]

The fact that the RLDA functional depends only on the electron density but not on the total 4-current $j^\mu$ brought about the necessity of looking for alternative RDFT forms that would explicitly take into account the effect of magnetism, namely, spin degrees of freedom. The formalism in which the spatial components $j^\mu$ are replaced by the magnetization density $\vec{m}$ has been proposed.[346, 347, 401] The corresponding $\vec{m}$-dependent version of RLDA has been derived for the exchange part of $E_{\mathrm{xc}}$.[346, 402–404] The one-particle equations have a very complex structure within the framework of this formalism; therefore, the only simplification is the selection of a definite direction collinear to $\vec{m}$ (recently, more general considerations have appeared[405–407]). A drawback of RLDA is the incorrect description of the electronic self-interaction. These difficulties can be overcome by using a special type of orbital-dependent functionals $E_{\mathrm{xc}}$.

However, the subsequent quantum chemical calculations using RLDA demonstrated that this functional does not ensure an adequate description of relativistic exchange-correlation effects in atomic systems and, as a consequence, in the calculation of SSCCs.[408–411]

In practice, the relativistic Kohn–Sham equation is, as a rule, combined with non-relativistic exchange-correlation GGA functionals that are most appropriate for the particular problem. Moreover, since GGA functionals depend also on the electron density gradient, the relativistic extension brings about the necessity of finding relativistic extra terms arising from the gradient part. However, such studies are very few even at the theoretical level.[412–414] These publications propose a semiempirical relativistic form for the RGGA functionals, which were tested in relation to the lightest atoms of the relativistic region (elements in the beginning of the fourth period); this resulted in higher accuracy in the calculations of SSCCs and demonstrated good prospects of these calculations.

For the exchange-correlation potentials $v_\mu^{\mathrm{s}}$, there exists the efficient optimized potential method (OPM).[415–417] This method has attracted attention, as it accurately describes the exchange part,[418–420] thus solving problems of taking into account the electronic self-interaction. The OPM method can be regarded as a method accurately describing the relativistic exchange[421] with the exact Coulombic limit.[422, 423] The early developments of orbital-dependent correlation functionals for the OPM based on the perturbation theory using the auxiliary Kohn–Sham Hamiltonian[420] have been comprehensively described in a review.[424] This formalism can be extended to the relativistic case including vacuum corrections.[421] Practical applicability of these functionals is problematic as yet.[425]

However, it is noteworthy that currently no relativistic functionals have been elaborated for NMR-oriented calculations; therefore, non-relativistic functionals that proved efficient, such as PBE0 and B3LYP, are used in the relativistic four-component or two-component calculations of SSCCs at the DFT levels.

### V.3. Two-component methods for the calculation of spin – spin coupling constants

Since the computational cost of four-component methods is exceptionally high, relativistic calculations based on two-component schemes have been vigorously developing in recent years. The final goal of any two-component formalism is complete separation of the electron and positron continuums, *i.e.*, the separation of the positive and negative parts in the spectrum of the Dirac equation.

The key idea of this separation proceeds from the Foldy – Wouthuysen (FW) transformation,[14] which can be regarded as the procedure of four-component Hamiltonian reduction to the block-diagonal form with the upper block corresponding to the electron continuum and the lower block corresponding to the positron continuum. Thus, if there is no need in a special description for the creation of the electron – positron pair,[426, 427] then after this separation, the positron continuum can be eliminated from consideration, without loss of generality, and this makes the problem much easier. Typically, in four-component methods, there is a special procedure of projection to the electron continuum, which provides a no-pair four-component Hamiltonian; the final goal is the same as in two-component approximations, namely, to get rid of the positron continuum. Thus, the 4-spinor formalism is redefined in terms of bispinors in two-component schemes that actually resemble non-relativistic approaches with explicit consideration of the spin functions $|\alpha\rangle$ and $|\beta\rangle$. The bispinor itself is defined as

$$u_k(\xi) = (f_k^{\alpha}(\vec{r}), f_k^{\beta}(\vec{r}))^{\mathrm{T}} = f_k^{\alpha}(\vec{r})\,|\alpha\rangle + f_k^{\beta}(\vec{r})\,|\beta\rangle$$

The FW transformation suffers also from a number of drawbacks,[35, 428] which make it rather a sort of groundwork for many methods for block-diagonalization of four-component Hamiltonians but not a practically applicable transformation.

In the FW transformation, the fine structure constant $\alpha = c^{-1}$ serves as the expansion parameter in all series. As a rule, two-component Hamiltonians obtained *via* this approach contain a singular operator.[35, 429, 430] A conceptually important two-component Hamiltonian obtained by the FW transformation is the Pauli Hamiltonian.[13] This Hamiltonian is the simplest approximation with the lowest $O(\alpha^2)$ order that includes the main types of relativistic effects in an explicit form,[31, 431] but is unfortunately inapplicable in practice. Any component decoupling scheme should be accompanied, first of all, by renormalization. This means that during diagonalization, the diverging terms should undergo indirect infinite summation, resulting in closed-form terms appearing in the two-component Hamiltonian (in other words, the procedure of cancellation of divergences should be performed). A scheme of this type for construction of a two-component Hamiltonian was first proposed by Douglas and Kroll.[258] After Hess [260, 432] proposed an efficient method for calculating the matrix elements of the Douglas – Kroll Hamiltonian, this scheme was widely spread and used under the name DKH.

Currently, there is a broad range of two-component Hamiltonians capable of reproducing the electron continuum spectrum to a high accuracy. A detailed discussion of the known two-component Hamiltonians can be found in survey papers.[107, 276]

The most popular two-component scheme is the zeroth order regular approximation (ZORA) developed by Autschbach and Ziegler.[202] The ZORA Hamiltonian, which is the well-known Chang – Pellisier – Durand Hamiltonian,[255, 256] was applied in the TD-DFT formalism using Slater orbitals; this formed the foundation for the ZORA – TD-DFT formalism (in short, ZORA – DFT), which was implemented for calculating the SSCCs in the ADF program package.[209 – 211] This approach takes into account both scalar relativistic contributions to the SSCC (Darwin correction and mass – velocity correction) [202] as well as the spin – orbit contribution.[204] The ZORA – TD-DFT approach was tested in some quantum chemical calculations of the SSCCs for platinum and thallium,[433 – 435] mercury,[436, 437] ruthenium,[438] xenon [439, 440] and halogen [441] atoms.

One more two-component approach is the infinite-order regular approximation with modified metric (IORAmm). The IORAmm approximation in combination with the TD-DFT approach in relation to SSCC calculations was software-implemented by Filatov and Cremer.[266] Their program code, unlike the Autschbach and Ziegler's one, implies the use of Gaussian orbitals and takes into account only the scalar relativity. This approach was tested in the SSCC calculations for the $XH_4$ hydrides, where X = C, Si, Ge, Sn, Pb.

The DKH approximation in combination with the TD-DFT and TD-DHF formalisms was implemented for the calculation of SSCCs later than other ones.[187] The results of calculation of $^1J(X,^1H)$ (X = $^{13}$C, $^{29}$Si, $^{73}$Ge, $^{119}$Sn) by the two-component DKH – TDHF method (DKH1 and DKH2 schemes) were compared with the values for the same constants obtained by the four-component 4RPA and IORAmm methods. These calculations demonstrated that the two-component IORAmm and DKH2 schemes give similar results.

The Barysz – Sadlej – Snijders (BSS) approximation differs little from DKH.[285, 442] In both cases, in DKH and BSS, the first step is the free particle FW transformation (fpFW). The subsequent expansion parameter in the component decoupling procedure is an external potential in the case of DKH and the fine structure constant in the case of BSS. A BSS-based scheme of construction of two-component Hamiltonians of an arbitrary order, including the infinite one, was first proposed by Barysz and Sadlej.[286] The DKH procedure, like BSS, can be extended to higher arbitrary orders, including the infinite order.[262, 265, 443, 444] Nakajima and Hirao [445] proposed a new method for elimination of small components (RESC), which, however, did not demonstrate a variational stability for heavy nucleus-containing systems.[446]

#### V.3.a. Foldy – Wouthuysen transformation

The general concept of reduction of the four-component Dirac Hamiltonian to the block diagonal form was proposed by Foldy and Wouthuysen.[14] They obtained the block-diagonalization transformation of the Dirac Hamiltonian for a free particle in an analytical form without using

the operator $\widehat{\mathbf{X}}$; this transformation is called the free particle Foldy–Wouthuysen transformation. In this Section, we present the main concepts of the FW transformation [38, 111] owing to its exceptional significance for two-component SSCC calculation schemes considered in the subsequent Sections.

In the general case (in the presence of the external potential $\widehat{\mathbf{V}}$), the initial system of Dirac equations has the form (19). Elimination of the small component $\boldsymbol{\psi}_S = \widehat{\mathbf{X}}\boldsymbol{\psi}_L$ affords two-component equation (20) but does not give two independent equations for the large and small components.

In order to obtain independent two-component equations, an additional step, called unitary Foldy–Wouthuysen transformation [14] together with the 4-spinor renormalization, is required. This transformation diagonalizes the four-component Dirac Hamiltonian and renormalizes the 4-spinor components, the total 4-spinor having a unit norm

$$\widehat{\mathbf{H}}_\mathrm{D}\,\Psi = E\Psi \rightarrow \widehat{\mathbf{U}}\,\widehat{\mathbf{H}}_\mathrm{D}\,\widehat{\mathbf{U}}^{-1}\,\widehat{\mathbf{U}}\Psi = E\widehat{\mathbf{U}}\Psi \rightarrow \tag{218}$$

$$\rightarrow \tilde{\widehat{\mathbf{H}}}_\mathrm{D}\Phi = E\Phi,\ \widehat{\mathbf{U}}^{+}\,\widehat{\mathbf{U}} = \hat{\mathbf{I}},\ \widehat{\mathbf{U}}^{+} = \widehat{\mathbf{U}}^{-1}$$

where

$$\widehat{\mathbf{U}} = \begin{pmatrix} 1/\sqrt{1+\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}} & \left(1/\sqrt{1+\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}}\right)\widehat{\mathbf{X}}^{+} \\ \left(-1/\sqrt{1+\widehat{\mathbf{X}}\widehat{\mathbf{X}}^{+}}\right)\widehat{\mathbf{X}} & 1/\sqrt{1+\widehat{\mathbf{X}}\widehat{\mathbf{X}}^{+}} \end{pmatrix} \tag{219}$$

$$\widehat{\mathbf{U}}^{-1} = \begin{pmatrix} 1/\sqrt{1+\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}} & -\widehat{\mathbf{X}}^{+}\left(1/\sqrt{1+\widehat{\mathbf{X}}\widehat{\mathbf{X}}}^{+}\right) \\ \widehat{\mathbf{X}}\left(1/\sqrt{1+\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}}\right) & 1/\sqrt{1+\widehat{\mathbf{X}}\widehat{\mathbf{X}}^{+}} \end{pmatrix} \tag{220}$$

The form of transformation (219) can be easily obtained proceeding from the requirements to the transformed Hamiltonian, which should have the diagonal form, while the 4-spinor should be renormalized in such a way as to leave the only preferred component for each class of solutions, *i.e.*, the problem should consist in the derivation of two independent equations. In the general form, $\widehat{\mathbf{U}}$ can be split into two-component blocks in the same way as the proper Dirac operator

$$\widehat{\mathbf{U}} = \begin{pmatrix} \widehat{\mathbf{U}}_{11} & \widehat{\mathbf{U}}_{12} \\ \widehat{\mathbf{U}}_{21} & \widehat{\mathbf{U}}_{22} \end{pmatrix} \tag{221}$$

Then the action of the matrix operator (221) on the 4-spinor $\boldsymbol{\Psi}$ can be expressed as

$$\boldsymbol{\Phi} = \begin{pmatrix} \boldsymbol{\varphi}_L \\ \boldsymbol{\varphi}_S \end{pmatrix} = \widehat{\mathbf{U}}\,\boldsymbol{\Psi} = \tag{222}$$

$$= \begin{pmatrix} \widehat{\mathbf{U}}_{11} & \widehat{\mathbf{U}}_{12} \\ \widehat{\mathbf{U}}_{21} & \widehat{\mathbf{U}}_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L \\ \boldsymbol{\psi}_S \end{pmatrix} = \begin{pmatrix} \widehat{\mathbf{U}}_{11}\boldsymbol{\psi}_L + \widehat{\mathbf{U}}_{12}\boldsymbol{\psi}_S \\ \widehat{\mathbf{U}}_{21}\boldsymbol{\psi}_L + \widehat{\mathbf{U}}_{22}\boldsymbol{\psi}_S \end{pmatrix}$$

Formally, the reduction of the four-component problem to two independent two-component problems implies the appearance of two transformed 4-spinors such that for the first class of solutions,

$$\boldsymbol{\Phi} = (\boldsymbol{\varphi}_L, \mathbf{0})^\mathrm{T}$$

and for the second class of solutions,

$$\boldsymbol{\Phi} = (\mathbf{0}, \boldsymbol{\varphi}_S)^\mathrm{T}$$

Proceeding from this requirement, from expression (222), it is possible to obtain the conditions for the blocks of the matrix operator $\widehat{\mathbf{U}}$:

$$\widehat{\mathbf{U}}_{21}\boldsymbol{\psi}_L + \widehat{\mathbf{U}}_{22}\boldsymbol{\psi}_S = \mathbf{0}$$

for the first class of solutions and

$$\widehat{\mathbf{U}}_{11}\boldsymbol{\psi}_L + \widehat{\mathbf{U}}_{12}\boldsymbol{\psi}_S = \mathbf{0}$$

for the second class of solutions. The small component of the initial 4-spinor is related to the large component *via* the operator $\widehat{\mathbf{X}}$: $\boldsymbol{\psi}_S = \widehat{\mathbf{X}}\boldsymbol{\psi}_L$. The substitution of small components in this form to the conditions for the two classes of solutions gives the following conditions:
for the first class of solutions,

$$\widehat{\mathbf{U}}_{21} = -\widehat{\mathbf{U}}_{22}\widehat{\mathbf{X}} \ \text{ and } \ \widehat{\mathbf{U}}_{21}^{+} = -\widehat{\mathbf{X}}^{+}\widehat{\mathbf{U}}_{22}^{+} \tag{223}$$

and for the second class of solutions,

$$\widehat{\mathbf{U}}_{11} = -\widehat{\mathbf{U}}_{12}\widehat{\mathbf{X}} \ \text{ and } \ \widehat{\mathbf{U}}_{11}^{+} = -\widehat{\mathbf{X}}^{+}\widehat{\mathbf{U}}_{12}^{+} \tag{224}$$

Meanwhile, the transformation $\widehat{\mathbf{U}}$ should be unitary

$$\hat{\mathbf{I}} = \widehat{\mathbf{U}}\widehat{\mathbf{U}}^{+} = \begin{pmatrix} \widehat{\mathbf{U}}_{11} & \widehat{\mathbf{U}}_{12} \\ \widehat{\mathbf{U}}_{21} & \widehat{\mathbf{U}}_{22} \end{pmatrix} \begin{pmatrix} \widehat{\mathbf{U}}_{11}^{+} & \widehat{\mathbf{U}}_{21}^{+} \\ \widehat{\mathbf{U}}_{12}^{+} & \widehat{\mathbf{U}}_{22}^{+} \end{pmatrix} = \tag{225}$$

$$= \begin{pmatrix} \widehat{\mathbf{U}}_{11}\widehat{\mathbf{U}}_{11}^{+} + \widehat{\mathbf{U}}_{12}\widehat{\mathbf{U}}_{12}^{+} & \widehat{\mathbf{U}}_{11}\widehat{\mathbf{U}}_{21}^{+} + \widehat{\mathbf{U}}_{12}\widehat{\mathbf{U}}_{22}^{+} \\ \widehat{\mathbf{U}}_{21}\widehat{\mathbf{U}}_{11}^{+} + \widehat{\mathbf{U}}_{22}\widehat{\mathbf{U}}_{12}^{+} & \widehat{\mathbf{U}}_{21}\widehat{\mathbf{U}}_{21}^{+} + \widehat{\mathbf{U}}_{22}\widehat{\mathbf{U}}_{22}+ \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{I}} & \hat{\mathbf{0}} \\ \hat{\mathbf{0}} & \hat{\mathbf{I}} \end{pmatrix}$$

The substitution of expressions (223) and (224) into Eqn (225) for each class of solutions results in the final equations for the blocks $\widehat{\mathbf{U}}$; as a result, the general form of the transformation is given by formula (219) up to the phase factor. The modified Dirac Hamiltonian obtained by applying transformation (219) to the Hamiltonian of system (19) will be diagonal

$$\tilde{\widehat{\mathbf{H}}}_\mathrm{D} = \begin{pmatrix} \tilde{\hat{\mathbf{h}}}_{11} & \hat{\mathbf{0}} \\ \hat{\mathbf{0}} & \tilde{\hat{\mathbf{h}}}_{22} \end{pmatrix} \tag{226}$$

With the use of this type of transformation, the problem with the modified Hamiltonian (226) is split into two independent two-component problems. The modified 4-spinor $\boldsymbol{\Phi}$ is normalized to unity

$$\langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Phi} \rangle = \langle \boldsymbol{\Psi} \,|\, \widehat{\mathbf{U}}^{+}\widehat{\mathbf{U}} \,|\, \boldsymbol{\Psi} \rangle = \langle \boldsymbol{\Psi} \,|\, \boldsymbol{\Psi} \rangle = 1 \tag{227}$$

In the general case, the operator

$$\widehat{\mathbf{X}}(E) = \left(\hat{\mathbf{I}} + \frac{E - \widehat{\mathbf{V}}}{2c^2}\right)^{-1} \frac{\hat{\vec{\boldsymbol{\sigma}}}\hat{\vec{p}}}{2c}$$

is not expressed in the closed form; therefore, the unitary transformation $\widehat{\mathbf{U}}$ cannot be obtained in the analytical (closed) form, except for several cases, for example, in the problem for a free electron (fpFW) or an electron in a uniform magnetic field.[62]

Thus, the transformation presented here is rather a theoretical prerequisite for various methods of component decoupling. Various two-component approximations differ in the operator expansion methods

$$\widehat{\mathbf{B}}(E) = \left(\hat{\mathbf{I}} + \frac{E - \widehat{\mathbf{V}}}{2c^2}\right)^{-1} \tag{227a}$$

**V.3.b. Pauli approximation**

The two-component Pauli Hamiltonian [38, 447] is the simplest two-component approximation of the Dirac Hamiltonian inapplicable in practical calculations but being very important from the physical standpoint, as it includes all of the most significant relativistic effects.

In order to obtain the Pauli Hamiltonian, it is necessary to expand operator (227a) in a series and restrict the consideration to the terms that do not exceed the second order in fine structure constant,

$$\widehat{\mathbf{B}}(E) = \left(\hat{\mathbf{I}} + \frac{E - \widehat{\mathbf{V}}}{2c^2}\right)^{-1} = \tag{228}$$

$$= \sum_{n=0}^{\infty}\left(-\frac{1}{2c^2}\right)^n \left(E - \widehat{\mathbf{V}}\right)^n = \hat{\mathbf{I}} - \frac{1}{2c^2}\left(E - \widehat{\mathbf{V}}\right) + O(c^{-4})$$

It is necessary to take into account the magnetic field by extending the momentum operator by the magnetic field vector potential $\hat{\vec{p}} \to \hat{\vec{\pi}}$ using formula (91).Then the initial system of stationary equations (19) is transformed into the following one:

$$\begin{cases} \widehat{\mathbf{V}}\boldsymbol{\psi}_L + c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\boldsymbol{\psi}_S = E\,\boldsymbol{\psi}_L \\ c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\boldsymbol{\psi}_L + (\widehat{\mathbf{V}} - 2c^2)\,\boldsymbol{\psi}_S = E\,\boldsymbol{\psi}_S \end{cases} \tag{229}$$

From this system of equations, it follows that the operator $\widehat{\mathbf{X}}$, which connects the large and small components, is also extended by the magnetic field

$$\widehat{\mathbf{X}} = \widehat{\mathbf{B}}(E)\frac{\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c} = \frac{\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c} + O(c^{-3}) \tag{230}$$

The application of the FW transformation to the Hamiltonian in set (229) with truncation of all terms starting from $O(c^{-3})$ results in the two-component Hamiltonian for the independent large component of the transformed 4-spinor

$$\widehat{\mathbf{H}} = \left(\frac{\hat{\vec{\pi}}^2}{2} - \frac{\hat{\vec{p}}^4}{8c^2} - \frac{1}{8c^2}\operatorname{div}\vec{E} + \widehat{V}\right)\mathbf{I}_{2\times 2} - \tag{231}$$

$$-\frac{1}{2c}\vec{\boldsymbol{\sigma}}\operatorname{rot}\vec{A} - \frac{\mathrm{i}}{8c^2}\vec{\boldsymbol{\sigma}}\operatorname{rot}\vec{E} - \frac{1}{4c^2}\vec{\boldsymbol{\sigma}}\left[\vec{E}\times\hat{\vec{p}}\right]$$

If we consider an electron located in a centrally symmetric nuclear field, then $\operatorname{rot}\vec{E} = 0$. Under this condition, the two-component Hamiltonian (231) assumes the form of the Pauli Hamiltonian taking into account the magnetic field [38, 53]

$$\widehat{\mathbf{H}}^{\text{Pauli}} = \left(\frac{\hat{\vec{\pi}}^2}{2} + \widehat{V} - \frac{\hat{\vec{p}}^4}{8c^2} - \frac{1}{8c^2}\operatorname{div}\vec{E}\right)\mathbf{I}_{2\times 2} - \tag{232}$$

$$-\frac{1}{2c}\vec{\boldsymbol{\sigma}}\vec{B} - \frac{1}{4c^2}\vec{\boldsymbol{\sigma}}\left[\vec{E}\times\hat{\vec{p}}\right]$$

where $\hat{\vec{\pi}}^2/2 + \widehat{V}$ is the non-relativistic Hamiltonian; $\hat{\vec{p}}^4/8c^2$ is the mass – velocity operator, which coincides with the third term of expansion of the relativistic electron energy in the powers of $c^{-2}$ and, in essence, it corresponds to the relativistic increase in the electron mass; $\sim \operatorname{div}\vec{E}$ is the Darwin correction related to the so-called Schrödinger zitterbewegung; $(1/2c)\,\vec{\boldsymbol{\sigma}}\vec{B}$ is the interaction operator between the electron spin and the nuclear magnetic field; $\sim \vec{\boldsymbol{\sigma}}\,[\vec{E}\times\hat{\vec{p}}]$ is the spin – orbit coupling, which, in the case of a centrally symmetric field, is proportional to the term

$$-\frac{1}{r}\frac{\partial V}{\partial r}\vec{\boldsymbol{\sigma}}\left[\vec{r}\times\hat{\vec{p}}\right] = -\frac{1}{r}\frac{\partial V}{\partial r}\vec{\boldsymbol{\sigma}}\hat{\vec{L}} \tag{232a}$$

This corresponds to the interaction of the electron spin with the magnetic field generated by its own orbital movement.

In the case of many-electron systems, the Pauli Hamiltonian is supplemented by the terms caused by the relativistic corrections to the electron – electron interaction, which bear the electron spin operator. In this case, we are dealing with the Breit – Pauli Hamiltonian.[13]

The use of the Pauli operator is faced with some serious obstacles that restrict its applicability in the quantum chemical calculations of SSCCs. One obstacle is associated with the mass – velocity operator, which is not bounded from below, and this induces the variational collapse and makes the Pauli Hamiltonian inappropriate for the variational methods of quantum chemistry. One more obstacle is associated with the singularity of the Pauli operator itself. In particular, spin – orbit coupling operator (232a) in the case of the Coulomb potential $V(r) = -Z/r$ behaves as the function $1/r^3$, which tends to infinity at $r \to 0$, while the asymptotic behaviour of the Darwin correction operator has the form of the Dirac δ-function $(\pi/2c^2)\,\delta(\vec{r})$; this also leads to the singularity at $r \to 0$.

**V.3.c. Regular approximation**

The regular approximation (RA) [255, 448] is one of the most popular among the quasirelativistic two-component approximations. The RA formalism proceeds from the exact Foldy – Wouthuysen transformation (EFW) [62] in which the energy-dependent large and small component connection operator

$$\widehat{\mathbf{X}} = \frac{c\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{2c^2 - \widehat{\mathbf{V}} + E}$$

is approximated by an energy-independent operator

$$\widehat{\mathbf{X}}_0 = \frac{c\,\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{2c^2 - \widehat{\mathbf{V}}}$$

The transformed four-component Hamiltonian in this approximation is called regular Hamiltonian (RFW).[267] This approximation generates a number of other known approximations such as ZORA,[52, 202, 255, 256, 267, 360, 449 – 452] FORA [267, 452] and IORA.[267] All these approximations cor-

respond to the maximum order of the expansion parameter $(\widehat{\mathbf{X}}_0^+\widehat{\mathbf{X}}_0)$ of the normalization parameters $(\hat{\mathbf{I}}+\widehat{\mathbf{X}}_0^+\widehat{\mathbf{X}}_0)^{-1/2}$ present in the RFW Hamiltonian, so that ZORA implies to the zeroth order, FORA means the first order and IORA corresponds to the infinite order (in other words, the IORA Hamiltonian is equivalent to the RFW Hamiltonian).[267]

Without resorting to the FW transformation, the regular approximation can be expressed proceeding from the exact equation for the large component

$$\left(\widehat{\mathbf{V}}+\frac{1}{2}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\,\widehat{\mathbf{B}}(E)\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\right)\boldsymbol{\psi}_L = E\,\boldsymbol{\psi}_L$$

by expansion of the operator $\widehat{\mathbf{B}}(E)$ in the parameter $E/(2c^2-\widehat{\mathbf{V}})$

$$\widehat{\mathbf{B}}(E) = \left(\hat{\mathbf{I}}+\frac{E-\widehat{\mathbf{V}}}{2c^2}\right)^{-1} = \tag{233}$$

$$= \frac{2c^2}{2c^2-\widehat{\mathbf{V}}}\left(\hat{\mathbf{I}}+\frac{E}{2c^2-\widehat{\mathbf{V}}}\right)^{-1} = 2c^2\sum_{k=0}^{\infty}\frac{(-E)^k}{(2c^2-\widehat{\mathbf{V}})^{k+1}}$$

The expansion of $\widehat{\mathbf{B}}(E)$ in the form of expression (233), proposed for the first time by Dyall and van Lenthe,[267] is the key issue in the RA approximation. Nevertheless, it is justified only provided that $|E| \ll 2c^2$, which is the case for all bound states of the electron continuum and for a large number of states of the positron continuum. This expansion takes into account various versions of the potential $\widehat{\mathbf{V}}$. Indeed, in the case of large $\widehat{\mathbf{V}}$ values corresponding to the near-nuclear region, the small value of the expansion parameter is largely dictated by the inverse power of $\widehat{\mathbf{V}}$, while in the case of small values of $\widehat{\mathbf{V}}$ for peripheral regions (far from the nuclei), the smallness is provided, first of all, by the condition $|E| \ll 2c^2$. If only the first term is left in expansion (233), we will get an equation for the large component in the ZORA approximation, while if the first two terms are left, an equation in the IORA approximation with a non-unit metric is obtained.[267]

The software implementation of RA schemes such as ZORA or IORA is not so trivial as it may seem at the first glance. First of all, the complexity is in the fact that the Hamiltonians of these schemes include the potential $\widehat{\mathbf{V}}$ in the denominator, and this virtually precludes the calculation of matrix elements of such operators. Filatov's paper [453] opened up the possibility of avoiding this complication by switching to the matrix form using the RI formalism. The calculation of Hamiltonian matrix elements in the IORA [267] and IORAmm [453, 454] approximations was software-implemented. The proposed procedures for the calculation of matrix elements are completely analytical and can be combined with any types of methods, both based on the wave function concept and based on the electron density concept. These two-component approaches are readily embedded in non-relativistic program codes, as they do not operate with any non-standard molecular integrals that cannot be found in a standard non-relativistic calculation.[453, 454] Recently, these schemes were specially adapted for calculations of the analytical gradient,[454] static electrical molecular properties [455] and also SSCCs.[266]

All methods based on the RA formalism, like any other two-component schemes, are not free from drawbacks. One is related to the fact that the RA scheme does not ensure the gauge invariance. If a method is gauge-invariant, the addition of an arbitrary constant $\Delta$ to the potential should shift the Hamiltonian eigenvalues found according to this method by the same constant. Unfortunately, this is not the case for the RA scheme. Using the perturbation theory, it is possible to estimate the error in the energy shift. If an arbitrary constant $\Delta$ is added to the Coulomb potential $V$, *i.e.*,

$$V_\Delta = -\frac{Z}{r}+\Delta$$

then the eigenvalues in the ZORA, FORA [267] and IORA [453] approximations will shift in the following way:

$$E_\Delta^{\mathrm{ZORA}} = E^{\mathrm{ZORA}} + \Delta - \frac{E^{\mathrm{ZORA}}\Delta}{2c^2} \tag{234}$$

$$E_\Delta^{\mathrm{FORA}} = E^{\mathrm{FORA}} + \Delta - \frac{\left(E^{\mathrm{FORA}}\right)^2\Delta}{4c^4} \tag{235}$$

$$E_\Delta^{\mathrm{IORA}} = E^{\mathrm{IORA}} + \Delta - \frac{\left(E^{\mathrm{IORA}}\right)^2\Delta}{4c^4} \tag{236}$$

In order to reduce the gauge dependence, the modified IORAmm approximation was specially developed;[453, 454] according to this approximation, the gauge dependence of the Hamiltonian decreases to such an extent that the changes related to the arbitrary choice of $\Delta$ are vanishingly small even at the stage of optimization of the molecule containing heavy nuclei.[453]

#### V.3.d. Zeroth order regular approximation (ZORA)

The two-component ZORA method for the calculation of SSCCs is based on the stationary one-particle Dirac equation [60] taking into account the external magnetic field, which has the following form:

$$\left(\hat{\mathbf{h}}^{\mathrm{D}}-E\right)\boldsymbol{\psi}^{\mathrm{D}} = \tag{237}$$

$$= \left[(\boldsymbol{\beta}-\mathbf{I})c^2 + \vec{\boldsymbol{\alpha}}\hat{\vec{\pi}}\,c + \mathbf{V}(\vec{r}) - E\mathbf{I}\right]\boldsymbol{\psi}^{\mathrm{D}} = 0$$

In order to obtain the two-component Hamiltonian $\hat{\mathbf{h}}^{\mathrm{D}}$, it is necessary to use the exact unitary EFW transformation,[38, 62, 111] which reduces the initial Hamiltonian $\hat{\mathbf{h}}^{\mathrm{D}}$ to the block-diagonal form. The transformed Hamiltonian takes the form [448]

$$\tilde{\hat{\mathbf{h}}} = \mathbf{U}\hat{\mathbf{h}}^{\mathrm{D}}\mathbf{U}^{-1} \tag{238}$$

where the matrix operators $\widehat{\mathbf{U}}$ and $\widehat{\mathbf{U}}^{-1}$ [see formulas (219) and (220), respectively, contain the operator $\widehat{\mathbf{X}}$ — the 4-spinor large and small component coupling operator $\boldsymbol{\psi}^{\mathrm{D}} = (\boldsymbol{\psi}_S\boldsymbol{\psi}_L)^{\mathrm{T}}$: $\boldsymbol{\psi}_S = \widehat{\mathbf{X}}\,\boldsymbol{\psi}_L$. The elimination of the small component by the EFW procedure results in the two-component stationary equation with Hamiltonian (238) for the transformed large component $\tilde{\boldsymbol{\varphi}}_L$ and the equation for the operator $\widehat{\mathbf{X}}$, which has the form

$$2c^2\widehat{\mathbf{X}} = c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}} - \widehat{\mathbf{X}}\,c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\widehat{\mathbf{X}} - \left[\widehat{\mathbf{X}},\widehat{\mathbf{V}}\right] \tag{239}$$

Numerous methods for solving this equation have been proposed.[456–459] The simplest approach is based on the

ZORA approximation.[52, 202, 204, 255, 256, 372] In the ZORA approximation, the operator $\widehat{\mathbf{X}}$ is merely a zeroth-order term in the Taylor series expansion of the operator $\widehat{\mathbf{B}}$ in the parameter $E/(2c^2 - \widehat{\mathbf{V}})$.

$$\widehat{\mathbf{X}} = \widehat{\mathbf{B}}\frac{\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c}$$

where

$$\widehat{\mathbf{B}} = \left(\hat{\mathbf{I}} + \frac{E - \widehat{\mathbf{V}}}{2c^2}\right)^{-1} = \frac{2c^2}{2c^2 - \widehat{V}}\left(\hat{\mathbf{I}} + \frac{E}{2c^2 - \widehat{\mathbf{V}}}\right)^{-1}$$

In the zeroth order, the operator $\widehat{\mathbf{B}}$ assumes the form

$$\widehat{\mathbf{B}} \approx \frac{2c^2}{2c^2 - \widehat{\mathbf{V}}}$$

while the operator $\widehat{\mathbf{X}}$ is expressed as

$$\widehat{\mathbf{X}} \approx \frac{c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c^2 - \widehat{\mathbf{V}}} \tag{240}$$

Note that in the non-relativistic limit, *i.e.*, when $c \to \infty$, the operator $\widehat{\mathbf{B}}$ becomes an identity operator, while the operator $\widehat{\mathbf{X}}$ has the form

$$\widehat{\mathbf{X}}^{\text{nrel}} = \frac{\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c}$$

In view of the above, the two-component stationary Hamiltonian from formula (238) will have the following form in the ZORA approximation

$$\tilde{\hat{\mathbf{h}}} = \hat{\mathbf{h}}^{\text{ZORA}} = \widehat{\mathbf{V}} + \frac{1}{2}\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\,\widehat{\mathbf{B}}\,\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}} \tag{241}$$

Upon substitution of the 'extended' momentum in an explicit form

$$\hat{\vec{\pi}} = \hat{\vec{p}} + \frac{1}{c}\vec{A} = -\mathrm{i}\hat{\vec{\nabla}} + \frac{1}{c}\vec{A}$$

(with allowance for the negative sign of the electron charge) into formula (241) and use of the properties of the Pauli matrices

$$\boldsymbol{\sigma}_\mu\boldsymbol{\sigma}_\nu = \delta_{\mu\nu} + \mathrm{i}\sum_\lambda \varepsilon_{\mu\nu\lambda}\boldsymbol{\sigma}_\lambda$$

the Hamiltonian $\hat{\mathbf{h}}^{\text{ZORA}}$ takes the following form:[52]

$$\hat{\mathbf{h}}^{\text{ZORA}} = \widehat{\mathbf{V}} + \frac{1}{2}(\hat{\vec{p}}\widehat{\mathbf{B}}\hat{\vec{p}} + \mathrm{i}\vec{\boldsymbol{\sigma}}(\hat{\vec{p}}\widehat{\mathbf{B}}) \times \hat{\vec{p}}) + \tag{242}$$

$$+ \hat{\vec{p}}\widehat{\mathbf{B}}\vec{A} + \vec{A}\,\widehat{\mathbf{B}}\hat{\vec{p}} + \mathrm{i}\vec{\boldsymbol{\sigma}}[\hat{\vec{p}} \times (\widehat{\mathbf{B}}\vec{A}) + \vec{A} \times (\widehat{\mathbf{B}}\hat{\vec{p}})] + \widehat{\mathbf{B}}\vec{A}^2$$

The second and third summands in this expression are the scalar and spin – orbit parts of the Hamiltonian $\hat{\mathbf{h}}^{\text{ZORA}}$ in the absence of an external electromagnetic fields. All other summands involve the vector potential of an external magnetic field and correspond to fine magnetic effects. If the external field is only the overall magnetic field of the nuclei possessing the magnetic moments $\vec{\mu}_N$, then, according to the expression (118) for the nuclear magnetic field vector potential, the last summand $\widehat{\mathbf{B}}\vec{A}^2$ in expression (242) gives the relativistic two-component analogue of the DSO Hamiltonian in the Ramsey theory.

$$\hat{\mathbf{h}}_{\text{ZDSO}} = \frac{1}{2}\sum_{N\neq M}\widehat{\mathbf{B}}\vec{A}_N\vec{A}_M = \tag{243}$$

$$= \frac{\widehat{\mathbf{B}}}{2c^4}\sum_{N\neq M}\frac{(\vec{\mu}_N\vec{\mu}_M)(\vec{r}_N\vec{r}_M) - (\vec{\mu}_N\vec{r}_M)(\vec{\mu}_M\vec{r}_N)}{r_N^3\,r_M^3}$$

The terms $\hat{p}\widehat{\mathbf{B}}\vec{A}$ and $\vec{A}\,\widehat{\mathbf{B}}\hat{p}$ represent an analogue of the PSO Hamiltonian

$$\hat{\mathbf{h}}_{\text{ZPSO}} = \tag{244}$$

$$= \frac{1}{2c^2\mathrm{i}}\sum_N\left[\vec{\mu}_N\frac{\widehat{\mathbf{B}}}{r_N^3}\left(\vec{r}_N \times \hat{\vec{\nabla}}\right) + \vec{\mu}_M\left(\vec{r}_N \times \hat{\vec{\nabla}}\right)\frac{\widehat{\mathbf{B}}}{r_N^3}\right]$$

The other terms containing the magnetic field vector potential define the spin – orbit (SO) contribution to SSCCs

$$\hat{\mathbf{h}}_{\text{ZSO}} = \frac{1}{2c^2}\sum_N\vec{\boldsymbol{\sigma}}\left(\left\{\left(\hat{\vec{\nabla}}\widehat{\mathbf{B}}\right)\frac{\vec{r}_N}{r_N^3}\right\}\vec{\mu}_N - \right. \tag{245}$$

$$\left. -\left\{\left(\hat{\vec{\nabla}}\widehat{\mathbf{B}}\right)\vec{\mu}_N\right\}\frac{\vec{r}_N}{r_N^3} + \widehat{\mathbf{B}}\left\{\vec{\mu}_N\left(\hat{\vec{\nabla}}\frac{\vec{r}_N}{r_N^3}\right) - \left(\vec{\mu}_N\hat{\vec{\nabla}}\right)\frac{\vec{r}_N}{r_N^3}\right\}\right)$$

This contribution in the non-relativistic limit, in view of the fact that $\widehat{\mathbf{B}}^{\text{nrel}} = \hat{\mathbf{1}}$ and $\hat{\vec{\nabla}}\widehat{\mathbf{B}}^{\text{nrel}} = \vec{0}$, correspponds to the sum of FC and SD Hamiltonians in the Ramsey theory.

The reduced SSCC $K_{N\alpha M\beta}$ is expressed as the second derivative of energy with respect to Cartesian components of the nuclear magnetic moments (100). The coefficients of energy expansion in a series in the powers of nuclear magnetic moments are calculated using the double perturbation theory.[460] According to this theory, upon the use of the Hellmann – Feynman theorem,[461, 462] $K_{N\alpha M\beta}$ takes the following form:

$$K_{N\alpha;M\beta} = \left\langle \boldsymbol{\Psi}^{(0,0)}\middle|\widehat{\mathbf{H}}^{(1,1)}_{N\alpha M\beta}\middle|\boldsymbol{\Psi}^{(0,0)}\right\rangle + \tag{246}$$

$$+2\,\mathrm{Re}\left\langle \boldsymbol{\Psi}^{(0,0)}\middle|\widehat{\mathbf{H}}^{(1,0)}_{N\alpha}\middle|\boldsymbol{\Psi}^{(0,1)}_{M\beta}\right\rangle$$

where the superscripts denote the order of perturbation in $\mu_{N\alpha}$ and $\mu_{M\beta}$. The tensors $\boldsymbol{\Psi}^{(0,1)}_{M\beta}$, $\widehat{\mathbf{H}}^{(1,1)}_{N\alpha\,M\beta}$ and $\widehat{\mathbf{H}}^{(1,0)}_{N\alpha}$ are derivatives of the wave function and the Hamiltonian with respect to the corresponding Cartesian components of the nuclear magnetic moments, *i.e.*,

$$\boldsymbol{\Psi}^{(1,0)}_{N\alpha} = \frac{\partial\boldsymbol{\Psi}}{\partial\mu_{N\alpha}}\bigg|_{\vec{\mu}_N=\vec{0}} \tag{247}$$

$$\widehat{\mathbf{H}}^{(1,0)}_{N\alpha} = \frac{\partial\widehat{\mathbf{H}}}{\partial\mu_{N\alpha}}\bigg|_{\vec{\mu}_N=\vec{0}} \tag{248}$$

$$\widehat{\mathbf{H}}^{(1,1)}_{N\alpha M\beta} = \frac{\partial^2\widehat{\mathbf{H}}}{\partial\mu_{N\alpha}\partial\mu_{M\beta}}\bigg|_{\vec{\mu}_N=\vec{\mu}_M=\vec{0}} \tag{249}$$

The components of the tensor operators $\widehat{\mathbf{H}}^{(1,0)}$ and $\widehat{\mathbf{H}}^{(1,1)}$ are derived from the magnetic terms (243)–(245) of the ZORA Hamiltonian

$$\widehat{\mathbf{H}}^{(1,1)}_{N\alpha\,M\beta} = \hat{\mathbf{h}}^{(1,1)}_{\mathrm{ZDSO}\,N\alpha M\beta} = \frac{\widehat{\mathbf{B}}}{c^4}\frac{\delta_{\alpha\beta}(\vec{r}_N\vec{r}_M) - x_{N\alpha}x_{M\beta}}{r_N^3\, r_M^3} \tag{250}$$

$$\widehat{\mathbf{H}}^{(1,0)}_{N\alpha} = \hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZPSO}\,N\alpha} + \hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZSO}\,N\alpha} \tag{251}$$

$$\hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZPSO}\,N\alpha} = -\frac{\mathrm{i}}{2c^2}\left(\frac{\widehat{\mathbf{B}}}{r_N^3}\left[\vec{r}_N\times\hat{\vec{\nabla}}\right]_\alpha + \left[\vec{r}_N\times\hat{\vec{\nabla}}\right]_\alpha\frac{\widehat{\mathbf{B}}}{r_N^3}\right) \tag{252}$$

$$\hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZSO}\,N\alpha} = \frac{1}{2c^2}\left[\vec{\boldsymbol{\sigma}}_\alpha\hat{\vec{\nabla}}\left(\widehat{\mathbf{B}}\frac{\vec{r}_N}{r_N^3}\right) - \vec{\boldsymbol{\sigma}}\hat{\vec{\nabla}}_\alpha\left(\widehat{\mathbf{B}}\frac{\vec{r}_N}{r_N^3}\right)\right] \tag{253}$$

The contribution $\hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZSO}\,N\alpha}$ can be transformed using the following identity:

$$\hat{\nabla}_\alpha\left(\frac{x_\beta}{r^3}\right) = \frac{4\pi}{3}\delta_{\alpha\beta}\delta(\vec{r}) + \frac{\delta_{\alpha\beta}}{r^3} - \frac{3x_\alpha x_\beta}{r^5} \tag{254}$$

Then $\hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZSO}\,N\alpha}$ is split into three independent contributions

$$\hat{\mathbf{h}}^{(1,0)}_{\mathrm{ZSO}\,N\alpha} = \frac{4\pi}{3c^2}\,\widehat{\mathbf{B}}\boldsymbol{\sigma}_\alpha\delta(\vec{r}_N) + \frac{\widehat{\mathbf{B}}}{2c^2}\left(\frac{3(\vec{\boldsymbol{\sigma}}\vec{r}_N)x_{N\alpha}}{r_N^5} - \frac{\boldsymbol{\sigma}_\alpha}{r_N^3}\right) + \tag{255}$$

$$+\frac{1}{2c^2}\frac{1}{r_N^3}\left[\left\{\left(\hat{\nabla}\widehat{\mathbf{B}}\right)\vec{r}_N\right\}\boldsymbol{\sigma}_\alpha - \left(\hat{\nabla}_\alpha\widehat{\mathbf{B}}\right)(\vec{\boldsymbol{\sigma}}\vec{r}_N)\right]$$

The first two summands in expression (255) are the relativistic analogues of the FC and SD contributions (they are ZFC and ZSD in the ZORA formalism), while the last summand is the contribution that has no non-relativistic analogue. Indeed, in the non-relativistic limit

$$\hat{\vec{\nabla}}\widehat{\mathbf{B}}^{\mathrm{nrel}} = \vec{0}$$

so that the last term just disappears.

Details of the asymptotic behaviour of the operator $\widehat{\mathbf{B}}$ were considered by Wolff *et al.*,[205] who derived an expression similar to (255) for the shielding constants within the ZORA formalism. In particular, it was shown in this publication that $\widehat{\mathbf{B}} = 0$ at the location point of the nucleus and $\widehat{\mathbf{B}} \approx 1$ at the periphery. This provides several conclusions regarding the asymptotic behaviour of components of the ZSO contribution. For example, as indicated by Autschbach and Ziegler,[203] at the location points of the nuclei where $\widehat{\mathbf{B}} = 0$, the matrix elements of the first two ZFC and ZSD summands in expression (255) disappear, so that the matrix elements of the ZSO contribution are completely determined by the last summand. In the near-nuclear region, the situation becomes substantially more complicated, the major problem being presented by the ZFC contribution. In Autschbach's study[47] devoted to the relativistic effects in the NMR parameters, it was noted that the presence of the operator $\widehat{\mathbf{B}}$ suppresses the $\delta$-function singularity.

The ZORA approximation has proved efficient in the calculation of properties in which the key role was played by the valence molecular orbitals, the bond orbitals or lone pair orbitals. This is due to the fact that in the ZORA approximation, the operator $\widehat{\mathbf{B}}$ is expanded in the parameter $E/(2c - \widehat{\mathbf{V}})$ and then all terms except for the first one are discarded as vanishingly small. This is justified only in the cases where this parameter is itself small, in particular, when the energy $E$ is small. This is really so for valence orbitals, whereas for the inner orbitals, for example, for the 1s shell, which plays the crucial role in the Fermi-contact interaction, this parameter is not small and the ZORA approximation is not correct in this case.

#### V.3.e. ZORA approximation in the RDFT formalism

A fundamental time-dependent RDFT theory (TD-RDFT) at the two-component level based on the ZORA approximation applicable to the calculation of SSCCs was first proposed and tested in the calculation of excitation energies of molecules in the studies of Peng *et al.*[360] and Wang *et al.*[463–465] The general two-component TD-RDFT theory for the linear response, in particular, within the ZORA approximation, was also described in detail by Romaniello and de Boeij,[466] and particularly for SSCC calculation, the ZORA–DFT approach was first proposed by Autschbach and Ziegler.[202, 204, 372] Currently, this method is available in the commercial ADF program package.[209–211]

The two-component TD-RDFT formalism[466] is based on the time-dependent Dirac–Kohn–Sham equation.[356]

$$\left\{c\vec{\boldsymbol{\alpha}}\hat{\vec{\pi}} + \boldsymbol{\beta}c^2 + v_{\mathrm{s}}(\vec{r},t)\right\}\boldsymbol{\psi}_i(\vec{r},t) = \mathrm{i}\partial_t\boldsymbol{\psi}_i(\vec{r},t) \tag{256}$$

where $\hat{\vec{\pi}}$ is the extended momentum operator: $\hat{\vec{\pi}} = \hat{\vec{p}} + \vec{A}_{\mathrm{s}}(\vec{r},t)/c$; $\partial_t$ is the designation of the derivative with respect to time $\partial_t = \partial/\partial t$. In this consideration, the 4-current $j^\mu(\vec{r},t)$ is time-dependent and is generally expressed as

$$j^\mu(\vec{r},t) = c\sum_i \boldsymbol{\psi}_i^+(\vec{r},t)\boldsymbol{\alpha}^\mu\boldsymbol{\psi}_i(\vec{r},t) \tag{257}$$

The zero component represents (up to an arbitrary factor) the electron density $\rho(\vec{r},t)$, while the spatial part $\vec{j}(\vec{r},t)$ is the current density vector

$$\rho(\vec{r},t) = \frac{j^0(\vec{r},t)}{c} = \sum_i \boldsymbol{\psi}_i^+(\vec{r},t)\,\boldsymbol{\psi}_i(\vec{r},t) \tag{258}$$

$$\vec{j}(\vec{r},t) = c\sum_i \boldsymbol{\psi}_i^+(\vec{r},t)\,\vec{\boldsymbol{\alpha}}\boldsymbol{\psi}_i(\vec{r},t) \tag{259}$$

The system physical characteristics, $\rho(\vec{r},t)$ and $\vec{j}(\vec{r},t)$, satisfy the equation of continuity and unambiguously define the external scalar potential $v_{\mathrm{s}}(\vec{r},t)$ and the vector potential $\vec{A}_{\mathrm{s}}(\vec{r},t)$.

The two-component time-dependent effective DKS Hamiltonian can be obtained by applying the FW transformation[38, 62, 111] to the four-component time-dependent DKS Hamiltonian. Note that for the stationary case, this type of Hamiltonian was reported by van Lenthe *et al.*[256, 449] While considering the time-dependent problem, one should start from the four-component one-particle time-dependent Dirac–Kohn–Sham equations (256). It is more convenient to parameterize the time dependence of the 4-spinor $\boldsymbol{\psi}_i(\vec{r},t)$ right away in order to shift the energy scale below by the rest energy of an electron

$$\boldsymbol{\psi}^{\mathrm{D}}(\vec{r},t)=\begin{pmatrix}\boldsymbol{\psi}_L(\vec{r},t)\\ \\ \boldsymbol{\psi}_S(\vec{r},t)\end{pmatrix}=\exp(-\mathrm{i}c^2t)\,\tilde{\boldsymbol{\psi}}^{\mathrm{D}}(\vec{r},t)= \tag{260}$$

$$=\exp(-\mathrm{i}c^2t)\begin{pmatrix}\tilde{\boldsymbol{\psi}}_L(\vec{r},t)\\ \\ \tilde{\boldsymbol{\psi}}_S(\vec{r},t)\end{pmatrix}$$

Then the four-component equation (256) will assume the form of a system of two-component equations

$$\begin{cases} v_{\mathrm{s}}\tilde{\boldsymbol{\psi}}_L+c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\tilde{\boldsymbol{\psi}}_S=\mathrm{i}\partial_t\tilde{\boldsymbol{\psi}}_L \\ c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\tilde{\boldsymbol{\psi}}_L+(v_{\mathrm{s}}-2c^2)\tilde{\boldsymbol{\psi}}_S=\mathrm{i}\partial_t\tilde{\boldsymbol{\psi}}_S\end{cases} \tag{261}$$

This system of equations allows one to write the initial time-dependent four-component DKS Hamiltonian in the following form:

$$\hat{\mathbf{H}}_{\mathrm{DKS}}=\begin{pmatrix}v_{\mathrm{s}}\mathbf{I}_{2\times2} & c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\\ \\ c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}} & (v_{\mathrm{s}}-2c^2)\mathbf{I}_{2\times2}\end{pmatrix} \tag{262}$$

By analogy with the stationary case, this Hamiltonian should be subjected to the unitary FW transformation $\hat{\tilde{\mathbf{U}}}$, so that

$$\hat{\tilde{\mathbf{U}}}^{-1}=\hat{\tilde{\mathbf{U}}}^{+}, \tag{262a}$$

which allows the initial Hamiltonian (262) to be represented in the block-diagonal form. The transformed four-component equation

$$\hat{\mathbf{H}}_{\mathrm{DKS}}\tilde{\boldsymbol{\psi}}^{\mathrm{D}}(\vec{r},t)=\mathrm{i}\partial_t\tilde{\boldsymbol{\psi}}^{\mathrm{D}}(\vec{r},t)$$

equivalent to set (261) can be transformed to the form [466]

$$\left(\hat{\tilde{\mathbf{U}}}\hat{\mathbf{H}}_{\mathrm{DKS}}\hat{\tilde{\mathbf{U}}}^{-1}-\hat{\tilde{\mathbf{U}}}\left[\mathrm{i}\partial_t,\hat{\tilde{\mathbf{U}}}^{-1}\right]\right)\left(\hat{\tilde{\mathbf{U}}}\,\tilde{\boldsymbol{\psi}}^{\mathrm{D}}\right)=\mathrm{i}\partial_t\left(\hat{\tilde{\mathbf{U}}}\,\tilde{\boldsymbol{\psi}}^{\mathrm{D}}\right) \tag{263}$$

In order to obtain a correct two-component Hamiltonian, some conditions should be imposed on the desired transformation. First, the transformed 4-spinor $\tilde{\boldsymbol{\varphi}}^{\mathrm{S}}$ should have only the large non-zero component

$$\tilde{\boldsymbol{\varphi}}^{\mathrm{S}}=\hat{\tilde{\mathbf{U}}}\begin{pmatrix}\tilde{\boldsymbol{\psi}}_L\\ \tilde{\boldsymbol{\psi}}_S\end{pmatrix}= \tag{264}$$

$$=\hat{\tilde{\mathbf{U}}}\exp\left(\mathrm{i}c^2t\right)\exp\left(-\mathrm{i}c^2t\right)\begin{pmatrix}\tilde{\boldsymbol{\psi}}_L\\ \tilde{\boldsymbol{\psi}}_S\end{pmatrix}=\hat{\mathbf{U}}\begin{pmatrix}\boldsymbol{\psi}_L\\ \boldsymbol{\psi}_S\end{pmatrix}\overset{!}{=}\begin{pmatrix}\tilde{\boldsymbol{\varphi}}\\ 0\end{pmatrix}$$

Second, the unitarity condition (262a) should hold for the matrix operator $\hat{\tilde{\mathbf{U}}}$. From these conditions, the general form of the transformation is as follows:

$$\hat{\mathbf{U}}=\hat{\tilde{\mathbf{U}}}\exp(\mathrm{i}c^2t)$$

(see Ref. 466), where $\hat{\tilde{\mathbf{U}}}$ is identical to the operator $\hat{\mathbf{U}}$ [see formula (219)]. The set of the formulated conditions gives the following expressions for the large and small components:

$$\tilde{\boldsymbol{\varphi}}=(1+\hat{\mathbf{X}}^{+}\hat{\mathbf{X}})^{-1/2}(\tilde{\boldsymbol{\psi}}_L+\hat{\mathbf{X}}^{+}\tilde{\boldsymbol{\psi}}_S) \tag{265}$$

$$0=(1+\hat{\mathbf{X}}\hat{\mathbf{X}}^{+})^{-1/2}(\hat{\mathbf{X}}\tilde{\boldsymbol{\psi}}_L-\tilde{\boldsymbol{\psi}}_S) \tag{266}$$

For condition (266) to be fulfilled, it is necessary that the operator $\hat{\mathbf{X}}$ relates the large and small components in the following way:

$$\tilde{\boldsymbol{\psi}}_S=\hat{\mathbf{X}}\tilde{\boldsymbol{\psi}}_L \tag{266a}$$

*i.e.*, in essence, this should be the kinetic balance operator. Substitution of (266a) into formula (265) gives an expression for the large component

$$\tilde{\boldsymbol{\varphi}}=\sqrt{1+\hat{\mathbf{X}}^{+}\hat{\mathbf{X}}}\,\tilde{\boldsymbol{\psi}}_L \tag{267}$$

Thus, the problem is reduced to the solution of the system of equations for the large component $\tilde{\boldsymbol{\psi}}_L$ and the operator $\hat{\mathbf{X}}$ that is derived from Eqn (263) in combination with formulae (264) and (267).

$$\begin{cases}(v_{\mathrm{s}}+c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\hat{\mathbf{X}})\tilde{\boldsymbol{\psi}}_L=\mathrm{i}\partial_t\tilde{\boldsymbol{\psi}}_L \\ (c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}+(v_{\mathrm{s}}-2c^2)\hat{\mathbf{X}})\tilde{\boldsymbol{\psi}}_L=[\mathrm{i}\partial_t,\hat{\mathbf{X}}]\tilde{\boldsymbol{\psi}}_L+\mathrm{i}\hat{\mathbf{X}}\partial_t\tilde{\boldsymbol{\psi}}_L\end{cases} \tag{268}$$

From the first equation of set (268) and expression (267), one can easily derive the equation of motion of the upper transformed bispinor $\tilde{\boldsymbol{\varphi}}$

$$\hat{\mathbf{h}}^{\mathrm{S}}\tilde{\boldsymbol{\varphi}}=\mathrm{i}\partial_t\tilde{\boldsymbol{\varphi}} \tag{269}$$

In Eqn (269), $\hat{\mathbf{h}}^{\mathrm{S}}$ is the upper right block of the transformed Hamiltonian

$$\hat{\mathbf{h}}^{\mathrm{S}}=v_{\mathrm{s}}+c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\hat{\mathbf{X}}+ \tag{270}$$

$$+\left[\mathrm{i}\partial_t-v_{\mathrm{s}}-c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\hat{\mathbf{X}},\ \sqrt{1+\hat{\mathbf{X}}^{+}\hat{\mathbf{X}}}\right]\left(\sqrt{1+\hat{\mathbf{X}}^{+}\hat{\mathbf{X}}}\right)^{-1}$$

Equation for the operator $\hat{\mathbf{X}}$ can be derived from Eqns (268) by substitution of one equation into another one

$$\left(c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}+\left[v_{\mathrm{s}}-\mathrm{i}\partial_t,\hat{\mathbf{X}}\right]-2c^2\hat{\mathbf{X}}-\hat{\mathbf{X}}c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\hat{\mathbf{X}}\right)\tilde{\boldsymbol{\psi}}_L=0 \tag{271}$$

Actually, Eqn (271) is a time-dependent analogue of Eqn (239). Thus, formula (271) for the operator $\hat{\mathbf{X}}$ and formula (269) for $\tilde{\boldsymbol{\varphi}}$ form the basis of the two-component time-dependent ZORA – DFT approach. For the stationary case, an algorithm for the solution of type (271) operator equation was proposed by Kutzelnigg and Liu,[467] while that for the time-dependent case was proposed by Romaniello and de Boeij.[466] In order to solve the operator equation (271) in the time-dependent case we are interested in, it is convenient to introduce arbitrary functions $v_0(\vec{r},t)$ and $\varepsilon(t)$; hence, it can be presented as

$$\hat{\mathbf{X}}=\left(2c^2-v_0+\varepsilon\right)^{-1}\left(c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}+\Xi(\hat{\mathbf{X}})\right) \tag{272}$$

$$\Xi(\hat{\mathbf{X}})=\left[v_{\mathrm{s}}-v_0+\varepsilon-\mathrm{i}\partial_t,\hat{\mathbf{X}}\right]-\hat{\mathbf{X}}\left(v_0-\varepsilon+c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\hat{\mathbf{X}}\right) \tag{273}$$

The action of the operator $\Xi(\hat{\mathbf{X}})$ on $\tilde{\boldsymbol{\psi}}_L$ is defined as follows:

$$\Xi(\hat{\mathbf{X}})\tilde{\boldsymbol{\psi}}_L=(v_{\mathrm{s}}-v_0+\varepsilon-\mathrm{i}\partial_t)\tilde{\boldsymbol{\psi}}_S \tag{274}$$

Expression (274) can be derived proceeding from the upper equation of set (268) and the relation defining the operator $\widehat{\mathbf{X}}$ as a connection between the small and large components [see formula (266a)]. Initially, $v_0(\vec{r}, t)$ and $\varepsilon(t)$ are arbitrary functions and, if we impose on them certain conditions by assuming that the difference $v_s - v_0$ is small and $\varepsilon(t)$ are close to the orbital energies, then $\Xi(\widehat{\mathbf{X}})\tilde{\boldsymbol{\psi}}_L$ will be a small quantity and it will be possible to solve Eqn (272) iteratively:

$$\widehat{\mathbf{X}}_n = \left(2c^2 - v_0 + \varepsilon\right)^{-1}\left(c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}} + \Xi\left(\widehat{\mathbf{X}}_{n-1}\right)\right) \tag{275}$$

$$\widehat{\mathbf{X}} = \lim_{n\to\infty} \widehat{\mathbf{X}}_n \tag{276}$$

However, while using this approach, one should bear in mind one circumstance: in the case of heavy nuclear, the value $\Xi(\widehat{\mathbf{X}})\tilde{\boldsymbol{\psi}}_L$ is no longer a small perturbation near the nucleus, and this puts in question the efficiency of the iterative procedure. It is important to appropriately select the zeroth approximation for the operator $\widehat{\mathbf{X}}$, which affects the rate of convergence of the iterative procedure. As a rule, the starting operator is

$$\widehat{\mathbf{X}}_0 = \frac{c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c^2 - v_0 + \varepsilon}$$

which has the same form as $\widehat{\mathbf{X}}$ in the stationary problem, although the time dependence remains in the arguments of arbitrary functions. However, these issues are not so significant if a sufficiently large number of iterations is performed and in the limit, the dependence on the artificially introduced parameters $v_0$ and $\varepsilon$ disappears.

The two-component Hamiltonian in the Schrödinger representation can be found after determination of the operator $\widehat{\mathbf{X}}$

$$\hat{\mathbf{h}}^{\mathrm{S}} = v_s + \frac{1}{2}\left(c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\widehat{\mathbf{X}} + \widehat{\mathbf{X}}^{+}c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\right) + \widehat{\mathbf{Y}}[\widehat{\mathbf{X}}] \tag{277}$$

The operator $\widehat{\mathbf{Y}}$, appearing in expression (277), has the following form:

$$\widehat{\mathbf{Y}}[\widehat{\mathbf{X}}] = \sum_{p,q} c_{pq}\left(\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}\right)^{p}\left(\widehat{\mathbf{X}}^{+}c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}} - c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}\widehat{\mathbf{X}}\right)\left(\widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}\right)^{q} \tag{278}$$

where $\widehat{\mathbf{X}}$ and $\widehat{\mathbf{Y}}$ are two related series. The accuracy of two-component Hamiltonian (277) is determined by the number of terms in the series $\widehat{\mathbf{X}}$ and $\widehat{\mathbf{Y}}$ obtained upon the iterative procedure.

The simplest approximation of this theory is based on equating the operator $\Xi(\widehat{\mathbf{X}})$ in expression (272) to zero, then

$$\widehat{\mathbf{X}} = \frac{c\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}}{2c^2 - v_0 + \varepsilon} = \widehat{\mathbf{X}}_0$$

With this selection of the operator $\widehat{\mathbf{X}}$, the operator $\widehat{\mathbf{Y}}[\widehat{\mathbf{X}}]$ [see formula (278)] also turns to zero. With this condition, the direct substitution of $\widehat{\mathbf{X}}$ into expression (277) results in the two-component Hamiltonian in the ZORA–DFT approximation for the time-dependent case [466]

$$\hat{\mathbf{h}}^{\mathrm{ZORA}}(\vec{r}, t) = \tag{279}$$

$$= v_s(\vec{r}, t) + \frac{1}{2}\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}(\vec{r}, t)\frac{2c^2}{2c^2 - V_{\mathrm{KS}}(\vec{r})}\vec{\boldsymbol{\sigma}}\hat{\vec{\pi}}(\vec{r}, t)$$

While expression (279) was derived, arbitrary parameters of this theory were additionally specified: the stationary function $V_{\mathrm{KS}}(\vec{r})$, representing a stationary Kohn–Sham potential in the ground state, was chosen as $v_0(\vec{r}, t)$, while the parameter $\varepsilon(t)$ was taken to be zero.

The first application of this theory was to calculate the linear response functions in solids.[468–470] However, the initial concept is also applicable for calculating SSCCs. A number of papers were devoted to the theory of SSCC calculation in terms of the two-component formalism using the ZORA Hamiltonian (279) at the DFT level. A detailed description of this formalism as applied to NMR parameters, in particular to SSCCs, can be found in a number of papers.[202–205, 471, 472] In Autschbach's paper,[372] the two-component ZORA–DFT formalism for a reduced SSCC is based on the expression formulated, as in the non-relativistic theory, for double perturbation theory

$$K_{\alpha\beta}(A, B) = \tag{280}$$

$$= 2\mathrm{Re}\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}}\frac{\langle\boldsymbol{\chi}_i|\,\widehat{\mathbf{F}}^{(\alpha,0)}\,|\boldsymbol{\chi}_a\rangle\langle\boldsymbol{\chi}_a|\,\hat{\mathbf{h}}^{(0,\beta)}\,|\boldsymbol{\chi}_i\rangle}{\varepsilon_i - \varepsilon_a} +$$

$$+\sum_{i}^{\mathrm{occ}}\langle\boldsymbol{\chi}_i|\,\hat{\mathbf{h}}^{(\alpha,\beta)}\,|\boldsymbol{\chi}_i\rangle$$

where $\boldsymbol{\chi}_{i/a}$ are the unperturbed occupied ($i$) and vacant ($a$) Kohn–Sham molecular 2-spinors, $\varepsilon_{i/a}$ are the corresponding orbital energies. The letters $\alpha$ and $\beta$ designate the order of perturbation with respect to the Cartesian components of nuclear magnetic moments $A$ and $B$, respectively, $\hat{\mathbf{h}}^{(\mu,\nu)}$ are the spin–spin perturbation operators, $\widehat{\mathbf{F}}^{(\mu,\nu)}$ is the perturbed Kohn–Sham–Fock operator, and the operators $\hat{\mathbf{h}}(\mu, \nu)$ actually reproduce their non-relativistic analogues [372]

$$\hat{\mathbf{h}}^{(\alpha,\beta)}_{\mathrm{DSO}} = \frac{\widehat{\mathbf{B}}}{c^4}\frac{\delta_{\alpha\beta}(\vec{r}_A\vec{r}_B) - x_{A;\alpha}x_{B;\beta}}{r_A^3 r_B^3} \tag{281}$$

$$\hat{\mathbf{h}}^{(\alpha,0)}_{\mathrm{PSO}} = \frac{1}{2c^2\mathrm{i}}\left[\frac{\widehat{\mathbf{B}}}{r_A^3}(\vec{r}_A \times \hat{\vec{\nabla}})_\alpha + (\vec{r}_A \times \hat{\vec{\nabla}})_\alpha\frac{\widehat{\mathbf{B}}}{r_A^3}\right] \tag{282}$$

$$\hat{\mathbf{h}}^{(\alpha,0)}_{\mathrm{FC+SD}} = \frac{1}{2c^2}\left[\boldsymbol{\sigma}_\alpha\hat{\vec{\nabla}}\widehat{\mathbf{U}}_A - \vec{\boldsymbol{\sigma}}\hat{\nabla}_\alpha\widehat{\mathbf{U}}_A\right] \tag{283}$$

$$\widehat{\mathbf{U}}_A = \widehat{\mathbf{B}}\frac{\vec{r}_A}{r_A^3} \tag{284}$$

Here

$$\widehat{\mathbf{B}} = \widehat{\mathbf{B}}(\vec{r}) = \frac{2c^2}{2c^2 - V_{\mathrm{KS}}(\vec{r})}\hat{\mathbf{I}}$$

is the Blinder operator specific to ZORA, which appears in the time-dependent ZORA Hamiltonian (279).

It is of interest that in the two-component approach, the FC and SD spin–spin coupling can be transmitted not only through molecular spin density perturbation, as is the case for non-relativistic consideration, but also through electron current density perturbation, while the PSO mechanism can, in turn, induce spin density perturbation.[372] This is possible

because the mixed (FC + SD) × PSO type contribution to the SSCC is non-zero in the two-component formalism only if its scalar approximation is not considered.

The Kohn – Sham – Fock operator $\widehat{\mathbf{F}}^{(\alpha,0)}$ in expression (280) can be represented as the sum of spin – spin magnetic perturbations like $\hat{\mathbf{h}}^{(\alpha,0)}$ and Kohn – Sham potential linear response

$$\widehat{\mathbf{F}}^{(\alpha,0)} = \hat{\mathbf{h}}^{(\alpha,0)} + \widehat{V}_{\mathrm{KS}}^{(\alpha,0)}\mathbf{I} \tag{285}$$

Autschbach [372] reported a definite algorithm for calculating expression (280), which has been implemented in the ADF program package.[209 – 211]

The application of the ZORA – DFT formalism to the calculation of SSCCs has received wide acceptance.[3, 241, 372, 440, 473 – 476] For example, Autschbach [372] presented the calculation of reduced SSCCs across one bond involving lead, platinum, tellurium, phosphorus, halogens and hydrogen nuclei. All of the relativistic calculations were performed using two-component ZORA – DFT with the hybrid functionals PBE [368] and PBE0 [206] in comparison with the functional VWN(LDA).[362] The author [372] emphasized that GGA functionals provide better agreement with the experimental values than VWN(LDA), and this is especially clearly seen for SSCCs involving tellurium and lead. The results of calculation of SSCCs for platinum showed that in some cases, it is very important to take into account the Hartree – Fock exchange.

Generally, it can be stated that the ZORA – DFT method in combination with an appropriately selected functional of the GGA family can ensure fairly high accuracy of the SSCC calculation; however, it should be borne in mind that ZORA is better suited for the description of valence shells. Hence, it follows that the heavier the nuclei involved in the given spin – spin coupling, the lower the accuracy of calculation of SSCCs using the two-component ZORA approach.[372]

#### V.3.f. Infinite-order regular approximation (IORA)

The initial stage in the derivation of an efficient two-component Hamiltonian in the two-component IORA scheme is application of the exact Foldy – Wouthuysen transformation [38, 62, 111] to the Dirac Hamiltonian

$$\widehat{\mathbf{H}}^{\mathrm{EFW}} = \widehat{\mathbf{U}}\widehat{\mathbf{H}}_{\mathrm{D}}\widehat{\mathbf{U}}^{-1}$$

where $\widehat{\mathbf{U}}$ is the exact FW transformation having form (219), while $\widehat{\mathbf{H}}_{\mathrm{D}}$ is the one-particle shifted Dirac Hamiltonian

$$\widehat{\mathbf{H}}_{\mathrm{D}} = \begin{pmatrix} \widehat{\mathbf{V}} & c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} \\ c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} & \widehat{\mathbf{V}} - 2c^2 \end{pmatrix}$$

The exact transformed two-component Hamiltonian has the form

$$\widehat{\mathbf{H}}^{\mathrm{EFW}} = \frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}}} \times \tag{286}$$

$$\times \left[\widehat{\mathbf{V}} + c\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\widehat{\mathbf{X}} + \widehat{\mathbf{X}}^{+}c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} + \widehat{\mathbf{X}}^{+}(\widehat{\mathbf{V}} - 2c^2)\widehat{\mathbf{X}}\right]\frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}^{+}\widehat{\mathbf{X}}}}$$

where $\widehat{\mathbf{X}}$ is the exact large and small component connection operator [kinetic balance operator, see formula (266a)]

$$\widehat{\mathbf{X}}(E) = \frac{1}{2c^2 - \widehat{\mathbf{V}} + E}c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} \tag{287}$$

In most cases, the parameter $E(2c^2 - \widehat{\mathbf{V}})^{-1}$ is small; therefore, the operator $(2c^2 - \widehat{\mathbf{V}} + E)^{-1}$ in expression (287) can be expanded in a series in this parameter

$$\widehat{\mathbf{X}}(E) = \frac{1}{2c^2 - \widehat{\mathbf{V}}}\left(\hat{\mathbf{I}} + \frac{E}{2c^2 - \widehat{\mathbf{V}}}\right)^{-1} c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} = \tag{288}$$

$$= \left(\sum_{k=0}^{\infty}\frac{(-E)^k}{(2c^2 - \widehat{\mathbf{V}})^{k+1}}\right)c\vec{\boldsymbol{\sigma}}\hat{\vec{p}}$$

The regular approximation implies that expansion (288) is restricted to only the first term under the assumption that $E$ is small. Thus, the regular approximation eliminates the dependence of the operator $\widehat{\mathbf{X}}$ on the energy parameter $E$

$$\widehat{\mathbf{X}}_0 = \frac{1}{2c^2 - \widehat{\mathbf{V}}}c\vec{\boldsymbol{\sigma}}\hat{\vec{p}} \tag{289}$$

The substitution of the operator $\widehat{\mathbf{X}}$ into the transformation $\widehat{\mathbf{U}}$ affords the regular Foldy – Wouthuysen Hamiltonian (RFW) [267]

$$\widehat{\mathbf{H}}^{\mathrm{RFW}} = \frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0}}\left(\widehat{\mathbf{V}} + \vec{\boldsymbol{\sigma}}\hat{\vec{p}}\frac{c^2}{2c^2 - \widehat{\mathbf{V}}}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\right)\frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0}} \tag{290}$$

The operator in parentheses is the stationary ZORA Hamiltonian [see formula (241)], so that expression (290) is reduced to the form

$$\widehat{\mathbf{H}}^{\mathrm{RFW}} = \frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0}}\widehat{\mathbf{H}}^{\mathrm{ZORA}}\frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0}} \tag{291}$$

The Hamiltonian $\widehat{\mathbf{H}}^{\mathrm{RFW}}$ is equivalent to the IORA Hamiltonian, which is called so because it contains infinite summation over the powers of the operator product $\widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0$, which appears when the reciprocal roots are expanded in terms of this parameter

$$\widehat{\mathbf{H}}^{\mathrm{IORA}} \equiv \widehat{\mathbf{H}}^{\mathrm{RFW}} = \tag{292}$$

$$= \widehat{\mathbf{H}}^{\mathrm{ZORA}} - \frac{1}{2}\left[\widehat{\mathbf{X}}_0^{+}\widehat{\mathbf{X}}_0, \widehat{\mathbf{H}}^{\mathrm{ZORA}}\right]_{+} + \ldots$$

From this formula, one can see the clear hierarchy of two-component Hamiltonians in the RA approximation: the first term is the Hamiltonian $\widehat{\mathbf{H}}^{\mathrm{ZORA}}$, the first two terms are the Hamiltonian $\widehat{\mathbf{H}}^{\mathrm{FORA}}$ and so on up to infinity, *i.e.*, up to the Hamiltonian $\widehat{\mathbf{H}}^{\mathrm{IORA}}$.

The one-electron equation for the large component in the IORA approximation is obtained from the exact Dirac equation for the large component by discarding all terms of expansion of the Blinder operator

$$\widehat{\mathbf{B}}(E) = \left(\hat{\mathbf{I}} + \frac{E - \widehat{\mathbf{V}}}{2c^2}\right)^{-1} = 2c^2\sum_{k=0}^{\infty}\frac{(-E)^k}{(2c^2 - \widehat{\mathbf{V}})^{k+1}}$$

in the parameter $E(2c^2 - \widehat{\mathbf{V}})^{-1}$, starting from the third term

$$\widehat{\mathbf{B}}(E) \approx 2c^2 \left[ \frac{1}{(2c^2 - \widehat{\mathbf{V}})} - \frac{E}{(2c^2 - \widehat{\mathbf{V}})^2} \right] \tag{293}$$

Then the one-electron equation in the IORA approximation has the form

$$\left( \widehat{\mathbf{V}} + \frac{1}{2} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \frac{1}{1 - \widehat{\mathbf{V}}/2c^2} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\psi}_L = \tag{294}$$

$$= E \left( \hat{\mathbf{I}} + \frac{1}{4c^2} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \frac{1}{\left(1 - \widehat{\mathbf{V}}/2c^2\right)^2} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\psi}_L$$

Note that the Hamiltonian in the left-hand side of expression (294) is equivalent to the ZORA Hamiltonian (241), and if there was no second summand in the right-hand side of Eqn (294), this equation would completely coincide with the one-electron ZORA equation. Thus, the difference between the ZORA and IORA approximations is in the second term of the right-hand side of Eqn (294).

Equation (294) can be software-implemented only after being expressed in the matrix form, because it contains the operator $\widehat{\mathbf{V}}$ in the denominator. This approach was first proposed in the paper of Filatov and Cremer,[453] who expressed the one-particle Dirac equation (294) in the matrix form

$$(\mathbf{V} + \mathbf{K}_1)\,\mathbf{C} = (\mathbf{S} + \mathbf{K}_2)\,\mathbf{C}\,\boldsymbol{\Omega} \tag{295}$$

$$\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{C} \tag{296}$$

where $\boldsymbol{\psi}$ is the matrix of column vectors $\boldsymbol{\psi}_L$, $\boldsymbol{\chi}$ is the row vector of basis bispinors, in which the bispinors $\boldsymbol{\psi}_L$ are expanded; $\mathbf{C}$ is the matrix of the expansion coefficients formed from the column vectors of the coefficients for each $\boldsymbol{\psi}_L$. In expression (295), $\mathbf{V}$ is the matrix of the Coulomb potential, $\mathbf{S}$ is the overlap matrix $||S||_{\mu\nu} = \langle \boldsymbol{\chi}_\mu \,|\, \boldsymbol{\chi}_\nu \rangle$, $\boldsymbol{\Omega} = \mathrm{diag}\{E_1, E_2, \ldots\}$ is the diagonal matrix of the eigenenergies, $\mathbf{K}_1$ and $\mathbf{K}_2$ are the matrices of spin operators from the left- and right-hand sides of expression (294)

$$\| \mathbf{K}_1 \|_{\mu\nu} = \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \hat{\mathbf{k}}_1 \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle = \tag{297}$$

$$= \frac{1}{2} \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \frac{1}{\hat{\mathbf{I}} - \widehat{\mathbf{V}}/2c^2} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle$$

$$\| \mathbf{K}_2 \|_{\mu\nu} = \frac{1}{2c^2} \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \hat{\mathbf{k}}_2 \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle = \tag{298}$$

$$= \frac{1}{4c^2} \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \frac{1}{\left(\hat{\mathbf{I}} - \widehat{\mathbf{V}}/2c^2\right)} \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle$$

In order to get rid of the operator $\widehat{\mathbf{V}}$ in the denominators of the operators $\hat{\mathbf{k}}_1$ and $\hat{\mathbf{k}}_2$, Filatov and Cremer[453] used the identities

$$\hat{\mathbf{k}}_1 = \frac{1}{2} \frac{1}{\hat{\mathbf{I}} - \widehat{\mathbf{V}}/2c^2} = \frac{1}{2} \hat{\mathbf{I}} + \frac{1}{2c^2} \widehat{\mathbf{V}} \hat{\mathbf{k}}_1 \tag{299}$$

$$\hat{\mathbf{k}}_2 = \frac{1}{2} \frac{1}{\left(\hat{\mathbf{I}} - \widehat{\mathbf{V}}/2c^2\right)^2} = \tag{300}$$

$$= 2\hat{\mathbf{k}}_1^2 = \frac{1}{2} \hat{\mathbf{I}} + \frac{1}{c^2} \widehat{\mathbf{V}} \hat{\mathbf{k}}_1 + 2\hat{\mathbf{k}}_1 \frac{\widehat{\mathbf{V}}}{2c^2} \frac{\widehat{\mathbf{V}}}{2c^2} \hat{\mathbf{k}}_1$$

Considering these identities, the matrix elements $\mathbf{K}_1$ and $\mathbf{K}_2$ in expressions (297) and (298) are split into summands where the matrix of the kinetic energy operator is separated

$$\| \mathbf{K}_1 \|_{\mu\nu} = \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \hat{\mathbf{k}}_1 \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle = \tag{301}$$

$$= \| \mathbf{T} \|_{\mu\nu} + \frac{1}{2c^2} \left\langle \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\mu \left| \widehat{\mathbf{V}} \hat{\mathbf{k}}_1 \right| \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\nu \right\rangle$$

$$\| \mathbf{K}_2 \|_{\mu\nu} = \frac{1}{2c^2} \left\langle \boldsymbol{\chi}_\mu \left| \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \hat{\mathbf{k}}_2 \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right| \boldsymbol{\chi}_\nu \right\rangle = \tag{302}$$

$$= \frac{1}{2c^2} \left( \| \mathbf{T} \|_{\mu\nu} + 2 \left\langle \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\mu \left| \frac{\widehat{\mathbf{V}}}{2c^2} \hat{\mathbf{k}}_1 \right| \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\nu \right\rangle + \right.$$

$$\left. + 2 \left\langle \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\mu \left| \hat{\mathbf{k}}_1 \frac{\widehat{\mathbf{V}}}{2c^2} \frac{\widehat{\mathbf{V}}}{2c^2} \hat{\mathbf{k}}_1 \right| \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\nu \right\rangle \right)$$

After the one-electron equation has been written in the matrix form (295), where elements of the matrices $\mathbf{K}_1$ and $\mathbf{K}_2$ are given by (301) and (302), the RI operator is introduced[453] as an identity operator $\hat{\mathbf{I}} = \boldsymbol{\varphi}\,\boldsymbol{\varphi}^+$ composed of the row vector $\boldsymbol{\varphi}$ and auxiliary orthonormal basis bispinors $\{\varphi\}$; the method of construction of $\boldsymbol{\varphi}$ was chosen in the following way:[453,477]

$$\boldsymbol{\varphi} = (\vec{\boldsymbol{\sigma}} \hat{\vec{p}}) \boldsymbol{\chi} \frac{\mathbf{T}^{-1/2}}{\sqrt{2}} \tag{303}$$

Here $\mathbf{T}$ is the matrix of the kinetic energy operator

$$\widehat{\mathbf{T}} = \frac{\vec{\boldsymbol{\sigma}} \hat{\vec{p}} \vec{\boldsymbol{\sigma}} \hat{\vec{p}}}{2} = \frac{\hat{\vec{p}}^2}{2}$$

When RI is substituted between every pair of operators $\widehat{\mathbf{V}}$ and $\hat{\mathbf{k}}_1$ in (301) and (302), the matrices $\mathbf{K}_1$ and $\mathbf{K}_2$ assume the following compact forms:

$$\mathbf{K}_1 = \mathbf{T} + \mathbf{W} \tag{304}$$

$$\mathbf{K}_2 = \frac{1}{2c^2} (\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W}) \tag{305}$$

In expressions (304) and (305), the following auxiliary designations were introduced

$$\| \mathbf{W} \|_{\mu\nu} = \| \mathbf{W}_0 \mathbf{T}^{-1} \mathbf{K}_1 \|_{\mu\nu} \tag{306}$$

$$\| \mathbf{W}_0 \|_{\mu\nu} = \left\langle \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\mu \left| \frac{\widehat{\mathbf{V}}}{4c^2} \right| \left( \vec{\boldsymbol{\sigma}} \hat{\vec{p}} \right) \boldsymbol{\chi}_\nu \right\rangle \tag{307}$$

A combination of expressions (306) and (304) affords an equation that connects the matrices $\mathbf{W}$ and $\mathbf{W}_0$,

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0 \mathbf{T}^{-1} \mathbf{W} \tag{308}$$

By multiplying expression (308) by the matrix $\mathbf{W}_0^{-1}$ on the left and by $\mathbf{W}^{-1}$ on the right, one gets an expression for $\mathbf{W}$

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1} \tag{309}$$

As a result of these transformations, the finite matrix form of the one-particle Dirac equation in the IORA approximation has the form

$$(\mathbf{V} + \mathbf{T} + \mathbf{W})\,\mathbf{C} = \tag{310}$$
$$= \left(\mathbf{S} + \frac{1}{2c^2}(\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W})\right)\mathbf{C}\,\Omega$$

Equation (308) can serve to find the matrix $\mathbf{W}$ from the matrices $\mathbf{W}_0$ and $\mathbf{T}$. Considering expressions (306) and (307), all matrices in Eqn (310) correspond to operators that no longer contain $\widehat{\mathbf{V}}$ in the denominators.

Thus, the problem posed above was solved by transforming Eqn (294) into the matrix form and introducing the RI operator.[453] It is also noteworthy that in this formalism, the equivalent of Eqn (310) for the ZORA approximation can be easily obtained by setting the matrix $\mathbf{K}_2$ equal to a zero matrix, which in essence means discarding of the second summand in the right-hand side of Eqn (310).

For passing to the discussion of SSCCs within the IORA approximation, it is necessary to consider the many-particle case of Eqn (310). The complexity of this consideration is caused by the fact that, apart from the usual one-particle Coulomb potential for electron interaction with an external field, there appears a two-electron component corresponding to electron interaction with all other electrons; the situation is further complicated because in the relativistic case, this is not the simple Coulomb interaction but the Breit interaction, which, in the simplest approximation, takes into account retardation of the potential. Therefore, further modification of the obtained equation is possible only for the methods in which the closed equations have the one-particle form with some efficient one-particle potential. For example, within the Hartree – Fock method, Eqn (310) is transformed to the form

$$\left(\tilde{\mathbf{H}} + \mathbf{J}_i - \mathbf{K}_i\right)\mathbf{C}_i = \mathbf{S}\mathbf{C}_i E_i \tag{311}$$

in which the modified IORA Hamiltonian is given by

$$\tilde{\mathbf{H}} = \left(\mathbf{S}^{1/2}\right)^{+}\left(\mathbf{U}^{-1/2}\right)^{+}(\mathbf{W} + \mathbf{T} + \mathbf{V})\left(\mathbf{U}^{-1/2}\right)\left(\mathbf{S}^{1/2}\right) \tag{312}$$

$$\mathbf{U} = \mathbf{S} + \mathbf{K}_2 \tag{313}$$

Here $\mathbf{J}_i$ and $\mathbf{K}_i$ are the Coulomb and exchange matrices, respectively; $\mathbf{V}$ is the matrix of the one-particle external potential.

According to the DFT method, the Kohn – Sham equations in the IORA matrix form are similar to expression (311), differing only in the description of the exchange part

$$\left(\tilde{\mathbf{H}} + \mathbf{J}_i + \mathbf{V}_{\mathrm{xc}}\right)\mathbf{C}_i = \mathbf{S}\mathbf{C}_i E_i \tag{314}$$

The full theory of SSCCs in the IORA/IORAmm/DFT formalism is given in a paper by Filatov and Cramer.[266] It is noteworthy that the working formulae used by the authors are based on expression (314). The only difference from the formalism outlined above is that the momentum operator is extended by the nuclear magnetic field

$$\hat{\vec{p}} \to \hat{\vec{\pi}} = \hat{\vec{p}} + \frac{1}{c}\vec{A}_N$$

In this case, the matrices $\mathbf{T}$ and $\mathbf{W}_0$ become dependent on the magnetic field in an explicit form, while the matrix $\mathbf{W}$ expressed in terms of $\mathbf{T}$ and $\mathbf{W}_0$ acquires an implicit dependence on the magnetic field.

In the IORA/IORAmm approximation, the formulae for reduced SSCCs in the DFT formalism proceed from the energy expressed as the trace of the product of the electron density and Hamiltonian matrices $\tilde{\mathbf{H}} + \mathbf{J}_i + \mathbf{V}_{\mathrm{xc}}$

$$E_{\mathrm{DFT}}^{\mathrm{IORA/IORAmm}} = \tag{315}$$
$$= \mathrm{tr}\left\{\mathbf{P}\mathbf{S}^{1/2^{+}}\mathbf{U}^{-1/2^{+}}(\mathbf{V}_N + \mathbf{T} + \mathbf{W})\mathbf{U}^{-1/2}\mathbf{S}^{1/2}\right\} +$$
$$+ \frac{1}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}')\mathrm{d}^3\vec{r}\mathrm{d}^3\vec{r}'}{|\vec{r} - \vec{r}'|} + E_{\mathrm{xc}}$$

In this expression, $\mathbf{P} = \mathbf{C}\mathbf{n}\,\mathbf{C}^{+}$ is the density matrix, $\mathbf{C}$ is the matrix of molecular coefficients which is composed of the column vectors of the expansion coefficients $\mathbf{C}_i$ for each spin orbital $i$ in the basis set $\{\chi\}$, $\mathbf{n}$ is the diagonal matrix of the occupation numbers, $\mathbf{V}_N$ is the matrix of the one-electron nuclear potential. Actually, expression (315) differs from its non-relativistic analogue only in the one-electron part, *i.e.*, the first term. According to the fundamental definition, the reduced SSCC is the second derivative of the energy with respect to the nuclear magnetic moments. In the IORA/IORAmm(DFT) approximation, it has the form

$$K_{NM\alpha\beta} = \frac{\partial^2 E_{\mathrm{DFT}}^{\mathrm{IORA/IORAmm}}}{\partial\mu_{N\alpha}\partial\mu_{M\beta}}\Big|_{\vec{\mu}_N = \vec{\mu}_M = \vec{0}} \tag{316}$$

The substitution of $E_{\mathrm{DFT}}^{\mathrm{IORA-IORAmm}}$ (315) into formula (316) leads to a more complex expression,[266] which includes the first and second derivatives of the matrices $\mathbf{G} = \mathbf{U}^{-1/2}\,\mathbf{S}^{1/2}$ (renormalization matrix) and $\mathbf{H} = \mathbf{V}_N + \mathbf{T} + \mathbf{W}$ with respect to the Cartesian components of nuclear magnetic moments and the first derivatives of the density matrix $\mathbf{P}$.

The second derivatives of the two last terms in expression (315) turn to zero provided that the exchange-correlation functional used does not depend on the nuclear magnetic fields in an explicit form. The density matrix $\mathbf{P}$ and its derivatives with respect to the magnetic moments $\partial P/\partial\mu_{N_\alpha}$ are found by means of the perturbed Kohn – Sham spin orbitals. On the one hand, the first corrections to the Kohn – Sham spin orbitals can be represented as the expression [292]

$$\left|\Psi_{k\sigma}^{(\mu_N),\mathrm{X}}(\vec{r})\right\rangle = \sum_{a\sigma'}^{\mathrm{virt}}\frac{\left\langle\Psi_{a\sigma'}^{(0)}\middle|\widehat{\mathbf{F}}^{\mathrm{X}}\middle|\Psi_{k\sigma}^{(0)}\right\rangle}{\varepsilon_k - \varepsilon_a}\left|\Psi_{a\sigma'}^{(0)}\right\rangle \tag{317}$$

and, on the other hand, the Kohn – Sham operator $\widehat{\mathbf{F}}$ can be expressed in terms of spin orbitals *via* electron density. Therefore, the standard magnetic perturbation $\widehat{\mathbf{F}}^{\mathrm{X}}$ (X = FC, SD, PSO) is supplemented by 'response' of the operator $\widehat{\mathbf{F}}$ to the change in the orbitals

$$\widehat{\mathbf{F}}^{\mathrm{X}}_{\mathrm{full}} = \widehat{\mathbf{F}}^{\mathrm{X}} + \sum_{k\sigma}^{\mathrm{occ}} \int \mathrm{d}^3\vec{r} \frac{\delta \widehat{\mathbf{F}}}{\delta \boldsymbol{\psi}_{k\sigma}(\vec{r})} \boldsymbol{\psi}^{(\mu_N),\mathrm{X}}_{k\sigma}(\vec{r}) \qquad (318)$$

Then Eqns (317) and (318) are solved as a system of equations by a self-consistency procedure. This procedure is described in more detail by Sychrovský *et al.*,[292] who considered the theory of the CPDFT method for the calculation of SSCCs.

After the order analysis of the terms in $c^{-1}$ composing $K_{NM\alpha\beta}$ and some asymptotic approximations and simplifications,[266] the final IORA/IORAmm expression (316) for a reduced SSCC in the DFT formalism can be represented as

$$K_{NM\alpha\beta} = \mathrm{tr}\left\{ \left( \frac{\partial \mathbf{P}}{\partial \mu_{N\alpha}} \right) \left( \mathbf{G}^{+} \left[ \frac{\partial \mathbf{H}}{\partial \mu_{M\beta}} \right] \mathbf{G} \right) \right\} + \qquad (319)$$

$$+\mathrm{tr}\left( \mathbf{P}\mathbf{G}^{+} \left[ \frac{\partial^2 \mathbf{H}}{\partial \mu_{N\alpha} \partial \mu_{M\beta}} \right] \mathbf{G} \right) =$$

$$= \mathrm{tr}\left\{ \left( \frac{\partial \mathbf{P}}{\partial \mu_{N\alpha}} \right) \mathbf{G}^{+} \left[ \mathbf{H}^{\mathrm{FC}}_{M\beta} - \mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{FC}}_{M\beta}\mathbf{T}^{-1}\mathbf{W} + \right. \right.$$

$$+\frac{3}{4}\left( \mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{FC}}_{M\beta}\mathbf{W}_0^{-1}\mathbf{W} + \mathbf{W}\mathbf{W}_0^{-1}\mathbf{H}^{\mathrm{FC}}_{M\beta}\mathbf{T}^{-1}\mathbf{W} \right) +$$

$$+\mathrm{i}\left( \mathbf{H}^{\mathrm{PSO}}_{M\beta} - \mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{PSO}}_{M\beta}\mathbf{T}^{-1}\mathbf{W} \right) + \mathbf{H}^{\mathrm{SD}}_{M\beta} -$$

$$\left. \left. -\mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{SD}}_{M\beta}\mathbf{T}^{-1}\mathbf{W} \right] \mathbf{G} \right\} + \mathrm{tr}\left( \mathbf{P}\mathbf{G}^{+} \left[ \mathbf{H}^{\mathrm{DSO}}_{NM\alpha\beta} - \right. \right.$$

$$\left. \left. -\mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{DSO}}_{NM\alpha\beta}\mathbf{T}^{-1}\mathbf{W} \right] \mathbf{G} \right)$$

Filatov and Cremer[266] reported the results of the first IORAmm/TD-DFT/SSCC calculations of the $^1K$(X,H) constants, X = C, Si, Ge, Sn, Pb, and $^1K$(Pb,H), $^1K$(Pb,C), $^1K$(Cd,C) and $^1K$(Hg,C) constants. The theoretical values obtained within the IORAmm/TD-HF/SSCC and IORAmm/TD-DFT/SSCC formalisms were compared with the corresponding values found by the full TD-DHF (4RPA) method[183] and the non-relativistic TD-DFT method with the same exchange-correlation functionals — BHHLYP (50% HF exchange),[478] B3LYP (20% HF exchange),[365, 367] BLYP[479] and large component basis sets. All of the quasirelativistic calculations were performed using the COLOGNE 2004 software[480] at the scalar level (without considering the spin – orbit coupling). The results obtained using the IORAmm/TD-HF/SSCC method proved to be close to the 4RPA results; however, it was shown[266] that the deviation substantially increases with increasing atomic number. First, this is due to the fact that the scalar level of theory does not reproduce the mixed FC–PSO component; second, Filatov and Cremer[266] used the point nucleus model, whereas the 4RPA calculations[183] were carried out using the finite-size nucleus model. The latter approach is more correct, because the use of the point model results in incorrect description of the electron density on the nucleus: it unnaturally increases and, hence, the calculated SSCC value is overestimated.[202]

Thus, in most cases, the IORAmm formalism applied to SSCC calculation provides rather high accuracy by itself. However, worth noting is some decrease in the SSCC calculation accuracy with increasing nuclear charge starting from the fifth period elements, which is illustrated by the data of Table 5.

**Table 5**. Reduced $^1K$(X,H) constants for hydrides of Group IV elements calculated by various methods (from the data of Ref. 266).

| Molecule | TD-HF(RPA)[183] | IORAmm/ TD-HF[266] | 4RPA[183] |
|---|---|---|---|
| $CH_4$ | 52.40 | 52.95 | 52.60 |
| $SiH_4$ | 102.40 | 103.80 | 104.40 |
| $GeH_4$ | 262.70 | 299.24 | 294.80 |
| $SnH_4$ | 430.50 | 600.37 | 588.30 |
| $PbH_4$ | 711.40 | 2079.79 | 1819.00 |

**Note**. The reduced SSCCs are given in the SI units: $10^{19} \times \mathrm{T}^2\ \mathrm{J}^{-1}$ or $10^{19} \times \mathrm{H}\ \mathrm{A}^{-2}\ \mathrm{m}^{-3}$.

**V.3.g. Elimination of the small component with renormalization**

In recent decades, methods based on the ESC procedure and suitable, among other applications, for SSCC calculation have become widespread.[121, 255, 256, 273, 431, 445, 449, 481–483]

One of the forms of ESC proposed by Dyall[277] and known as NESC is accurate and versatile. In particular, both the Douglas–Kroll–Hess approximation and equations for various RA schemes can be derived as approximations of NESC.[277, 283] Filatov and Cremer[283] discussed in detail the relationship of the RA and NESC in the relativistic quantum theory. The authors developed a special approach suitable for representing the modified Dirac equation in the matrix form in the NESC approximation and comparing it with the matrix representations of some RA schemes that they reported in earlier communications, namely, IORA, ZORA and SORA.[453, 454]

In a later study,[283] the same researchers demonstrated that the exact matrix form of the IORA equations obtained by means of RI corresponds to the zeroth order regular approximation of the NESC scheme, *i.e.*, NESC–ZORA. The NESC–ZORA equations were also used as the starting equations for the development of the NESC–SORA approximation; the choice of starting equations was substantiated by considering the equivalence of the NESC–ZORA and IORA approximations; the latter is known[267] to be regular.

A great advantage of ESC-based approaches is simple separation of the spin–orbit part,[97] which markedly increases the computational cost at every stage of quantum chemical calculations; the scalar part can be reformulated in such a way that the 'relativistic superstructure' is embedded without significant difficulty into a non-relativistic program code.

The ESC scheme gives an equation formally equivalent to the initial Dirac equation and, upon a certain transformation, it can be represented as a non-relativistic Schrödinger equation with some additional relativistic terms.

In the simplest, one-particle case in the absence of external magnetic fields, the general concept of ESC stems from the modified Dirac equation,[97] which has been obtained from the exact system of two equations for the large and small components of 4-spinor, equivalent to the four-component Dirac equation. This procedure is performed by elimination of the small component, which is accompanied by its renormalization by means of the restricted kinetic balance operator $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}/2c$, arising upon

transition to the non-relativistic limit in the relation connecting the large and small components ($\lim_{c\to\infty} 2c\,\psi_S = \vec{\sigma}\hat{\vec{p}}\,\psi_L$). Actually, this is equivalent to representing the initial 4-spinor as the following transformation:

$$\begin{pmatrix}\psi_L\\ \psi_S\end{pmatrix} = \begin{pmatrix}\mathbf{1}_{2\times 2} & \mathbf{0}_{2\times 2}\\ \mathbf{0}_{2\times 2} & \dfrac{\vec{\sigma}\hat{\vec{p}}}{2c}\mathbf{1}_{2\times 2}\end{pmatrix}\begin{pmatrix}\psi_L\\ \varphi_L\end{pmatrix} \tag{320}$$

According to this expression, the initial small component

$$\psi_S = \frac{\vec{\sigma}\hat{\vec{p}}}{2c}\varphi_L$$

is represented as a projection of some pseudolarge component $\varphi_L$ to the set of small components kinetically balanced in the non-relativistic approximation

$$\{\chi_S\} \supseteq \{\vec{\sigma}\hat{\vec{p}}\chi_L\}$$

This is due to the fact that the restricted kinetic balance operator $\vec{\sigma}\hat{\vec{p}}/2c$ is the operator $\widehat{\mathbf{X}}$ at the Blinder identity operator $\hat{\mathbf{B}}(E) = \hat{\mathbf{I}}$. It can be easily seen that this operator transforms elements of the large component set into elements of the small component set; therefore, $\varphi_L$ possess the same symmetry properties as the large component set elements. This, in turn, makes it possible to use the same basis set for the large and small components of the new 4-spinor as $(\psi_L, \varphi_L)^{\mathrm{T}}$. This transformation gives a modified Dirac equation,[97] which underlies the NESC method

$$\begin{pmatrix}\widehat{\mathbf{V}} - E & \widehat{\mathbf{T}}\\ \widehat{\mathbf{T}} & \dfrac{\vec{\sigma}\hat{\vec{p}}(\widehat{\mathbf{V}} - E)\vec{\sigma}\hat{\vec{p}}}{4c^2} - \widehat{\mathbf{T}}\end{pmatrix}\begin{pmatrix}\psi_L\\ \varphi_L\end{pmatrix} = \begin{pmatrix}\mathbf{0}\\ \mathbf{0}\end{pmatrix} \tag{321}$$

where

$$\widehat{\mathbf{T}} = \frac{\vec{\sigma}\,\hat{\vec{p}}\vec{\sigma}\,\hat{\vec{p}}}{2} = \frac{\hat{\vec{p}}^2}{2}$$

is the kinetic operator.

It can be seen from expression (321) that, by utilizing the property of the Pauli matrix, one can separate the spin part of the modified four-component Hamiltonian. It was noted above that expansion of the modified 4-spinor requires only one basis set for large components $\{\chi_k\}$

$$\psi_L = \sum_k a_k\chi_k, \quad \varphi_L = \sum_k b_k\chi_k$$

The substitution of the modified 4-spinor as expansion in the $\{\chi_k\}$ gives the matrix form of the modified system of Dirac equations[277]

$$\begin{cases}\mathbf{Va} + \mathbf{Tb} = \mathbf{Sa}E\\ \mathbf{Ta} + \left(\dfrac{1}{4c^2}\mathbf{W} - \mathbf{T}\right)\mathbf{b} = \dfrac{1}{2c^2}\mathbf{Tb}E\end{cases} \tag{322}$$

Here **V**, **T** and **W** are matrices of the operators $\widehat{\mathbf{V}}$, $\widehat{\mathbf{T}}$ and $\vec{\sigma}\hat{\vec{p}}\widehat{\mathbf{V}}\vec{\sigma}\hat{\vec{p}}$, respectively, in the basis set $\{\chi_k\}$, **S** is the overlap matrix of the basis functions $\{\chi_k\}$, **a** and **b** are the column vectors of the expansion coefficients of the large $\psi_L$ and pseudolarge $\varphi_L$ components, respectively.

If we assume that the column vectors **a** and **b** are related by the non-unitary transformation

$$\mathbf{b} = \mathbf{Ua} \tag{323}$$

then matrix **U** is determined from the second equation of system (322)

$$\mathbf{U} = \left[\mathbf{T}\left(1 + \frac{1}{2c^2}E\right) - \frac{1}{4c^2}\mathbf{W}\right]^{-1}\mathbf{T} \tag{324}$$

And then the first equation of system (322) assumes the following form:

$$\mathbf{Va} + \bar{\mathbf{T}}\mathbf{a} = \mathbf{Sa}E, \quad \bar{\mathbf{T}} = \mathbf{TU} \tag{325}$$

In this expression, $\bar{\mathbf{T}}$ can be identified as the matrix of the modified kinetic energy with relativistic corrections starting from the terms $O(c^{-2})$ (this conclusion is based on Dyall's derivation[277]). Thus, Eqn (325) is nothing but the Schrödinger equation with modified kinetic energy, which is equivalent to the exact Dirac equation. Expressions (324) and (325) presented as a system of equations

$$\begin{cases}(\mathbf{V} + \bar{\mathbf{T}})\mathbf{a} = \mathbf{Sa}E\\ \bar{\mathbf{T}} = \mathbf{T}\left[\mathbf{T}\left(1 + \dfrac{1}{2c^2}E\right) - \dfrac{1}{4c^2}\mathbf{W}\right]^{-1}\mathbf{T}\end{cases} \tag{326}$$

form actually the basis of the ESC approach.

The ESC equations can also be presented in a different form. They can be obtained from the same system (322) by multiplying the last equation by the matrix $\mathbf{U}^+$ on the right-hand side and summing it up with the first equation. This gives a modified Schrödinger equation in which the relativistic terms have been added to all matrices[277]

$$(\tilde{\mathbf{V}} + \tilde{\mathbf{T}})\mathbf{a} = \tilde{\mathbf{S}}\mathbf{a}E \tag{327}$$

where the modified matrices have the form

$$\tilde{\mathbf{T}} = \mathbf{TU} + \mathbf{U}^+\mathbf{T} - \mathbf{U}^+\mathbf{TU} \tag{328}$$

$$\tilde{\mathbf{V}} = \mathbf{V} + \frac{1}{4c^2}\mathbf{U}^+\mathbf{WU} \tag{329}$$

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2c^2}\mathbf{U}^+\mathbf{TU} \tag{329a}$$

Equation (326) and Eqns (327) – (329a) can be solved in a standard way. The first stage is the symmetric orthogonalization procedure[484, 485]

$$\mathbf{G}^{-1/2}\mathbf{F}\mathbf{G}^{-1/2}\mathbf{G}^{1/2}\mathbf{a} = \mathbf{G}^{1/2}\mathbf{a}E \tag{330}$$

where **F** is $\mathbf{V}+\bar{\mathbf{T}}$ (in the former case) or $\tilde{\mathbf{V}} + \tilde{\mathbf{T}}$ in the latter case), **G** is the metric matrix equal to **S** (in the former case) or $\tilde{\mathbf{S}}$ (in the latter case). The second stage is diagonalization of the matrix $\mathbf{F}' = \mathbf{G}^{-1/2}\mathbf{F}\mathbf{G}^{-1/2}$ finally giving the eigenpair (**a**, *E*).

Apart from different methods of inclusion of relativistic corrections to the characteristic energy terms of the Schrödinger equation, the presented two forms of the ESC equations differ in one more important point. The former form (326) gives a solution normalized to unity *via* a usual non-relativistic matrix **S**, *i.e.*, $\mathbf{a}^+\mathbf{Sa} = \mathbf{1}$, while the latter one

ensures normalization *via* the matrix $\tilde{\mathbf{S}}$ modified taking into account the relativistic corrections, *i.e.*, $\mathbf{a}^{+}\tilde{\mathbf{S}}\mathbf{a} = \mathbf{1}$. In order to find the large component $\boldsymbol{\psi}_L$, in the former case, it is first necessary to renormalize the eigenvector, while in the latter case, this is not required. Therefore, the former form of the ESC approach specified by equations (326) is called UESC, while the latter one specified by equation (327) is called NESC.

The ESC concept is also retained for the many-particle case. In particular, the DHF equation for closed-shell systems can be represented in the following way in the NESC formalism:

$$\left[\tilde{\mathbf{T}} + \tilde{\mathbf{V}} + 2\tilde{\mathbf{J}} - \tilde{\mathbf{K}}\right]\mathbf{A} = \tilde{\mathbf{S}}\mathbf{A}\mathbf{E} \tag{331}$$

where $\mathbf{E}$ is the diagonal matrix of eigenvalues; $\mathbf{A}$ is the matrix of eigenvectors; $\tilde{\mathbf{T}}$, $\tilde{\mathbf{V}}$, $\tilde{\mathbf{J}}$, $\tilde{\mathbf{K}}$ are the modified matrices of the kinetic energy, one-particle potential energy, direct Hartree energy and exchange energy operators, respectively; $\tilde{\mathbf{S}}$ is the modified overlap matrix. The modified matrices $\tilde{\mathbf{T}}$, $\tilde{\mathbf{V}}$ and $\tilde{\mathbf{S}}$ differ from their analogues in the one-particle formalism because they contain relativistic corrections expressed in terms of two-electron integrals that are present in the matrix $\mathbf{U}$, which has a much more complex structure in the many-particle case. The matrices $\tilde{\mathbf{J}}$ and $\tilde{\mathbf{K}}$ are composed of modified two-electron integrals such as $(\tilde{\boldsymbol{\mu}}\tilde{\boldsymbol{\lambda}}\,|\,\tilde{\boldsymbol{\kappa}}\tilde{\boldsymbol{\nu}})$, which are sums of the integrals $(\boldsymbol{\mu}\boldsymbol{\lambda}\,|\,\boldsymbol{\kappa}\boldsymbol{\nu})$ with the appropriate relativistic corrections and the matrix elements of the relativistic density matrix $\mathbf{D}$

$$\tilde{J}_{\mu\nu} = (\tilde{\boldsymbol{\mu}}\tilde{\boldsymbol{\nu}}\,|\,\tilde{\boldsymbol{\kappa}}\tilde{\boldsymbol{\lambda}})D^{LL}_{\kappa\lambda} \tag{332}$$

$$\tilde{K}_{\mu\nu} = \left[(\tilde{\boldsymbol{\mu}}\tilde{\boldsymbol{\lambda}}|\,\tilde{\boldsymbol{\kappa}}\tilde{\boldsymbol{\nu}}) + (\tilde{\boldsymbol{\mu}}\tilde{\boldsymbol{\kappa}}\,|\,\tilde{\boldsymbol{\lambda}}\tilde{\boldsymbol{\nu}})\right]D^{LL}_{k\lambda} \tag{333}$$

$$D^{LL}_{k\lambda} = \sum_i a_{\lambda i}a_{ki} \tag{334}$$

Here, a special designation is used for two-electron space integrals

$$(\boldsymbol{\mu}\boldsymbol{\nu}\,|\,\boldsymbol{\kappa}\boldsymbol{\lambda}) = \int \boldsymbol{\chi}^{*}_{\mu}(\vec{r}_1)\boldsymbol{\chi}_{\nu}(\vec{r}_1)\hat{\mathbf{g}}_{12}\boldsymbol{\chi}^{*}_{\kappa}(\vec{r}_2)\boldsymbol{\chi}_{\lambda}(\vec{r}_2)\mathrm{d}^3\vec{r}_1\mathrm{d}^3\vec{r}_2$$

The ESC formalism has a number of benefits. First of all, it refers to the class of DE methods [273] comprising quasirelativistic one- or two-component methods, which can exactly reproduce one-electron energies obtained by the four-component Dirac method.[55,56] The theoretical accuracy of the NESC scheme is somewhat higher than the accuracy of the UESC scheme: the eigenenergies calculated using NESC differ from those obtained at the appropriate four-component level (Dirac energies) by a value of about $O(c^{-4})$, whereas for UESC this value is $O(c^{-2})$.[277]

To date, NESC has been ultimately developed in both the one-component spin-free form and the two-component spin-dependent form. It can be used in combination with known quantum chemical methods such as Hartree–Fock (NESC–HF), DFT (NESC–DFT) and with various correlated purely *ab initio* methods such as the Möller–Plesset method (NESC–MP) or coupled cluster method (NESC–CC). The one-component version of NESC taking into account only scalar relativistic effects is applied to calculate first-order properties — analytical energy gradients,[486] which are used, in particular, in the geometry optimization and calculation of electric dipole moments;[487] electric field gradients;[488] isotropic hyperfine structure constants;[489] and some other parameters.[490] In addition, within the framework of two-component NESC (in spin-free or spin-dependent form), it is possible to compute the second-order response properties such as vibration frequencies in the harmonic approximation,[487,491] static electric dipole polarizabilities and the IR radiation spectra.[487] In the near future, the list of properties that can be calculated using the NESC approach would be evidently rapidly extended; in particular, these are anharmonic corrections for vibration frequencies and, of course, SSCCs.

The extension of the NESC matrix equations to the case of the presence of nuclear magnetic fields, which is needed for calculation of SSCCs, has already been performed.[492] The proposed approach is based on the special Kutzelnigg basis sets taking into account the presence of a magnetic field [493]

$$\boldsymbol{\psi}_p = \sum_{\mu}\begin{pmatrix}\mathbf{Z}_{11} & \mathbf{Z}_{12}\\ \mathbf{Z}_{21} & \mathbf{Z}_{22}\end{pmatrix}\begin{pmatrix}\boldsymbol{\chi}_{\mu}\mathbf{A}_{\mu p}\\ \dfrac{1}{2c}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\boldsymbol{\chi}_{\mu}B_{\mu p}\end{pmatrix} \tag{335}$$

Here transformation $\mathbf{Z}$ extends the usual basis set to the presence of nuclear magnetic fields, $\mathbf{A}$ and $\mathbf{B}$ are matrices composed of column vectors of the expansion coefficients of large and small components of the molecular 4-spinors in the basis set $\{\boldsymbol{\chi}_{\mu}\}$.

#### V.3.h. Douglas–Kroll–Hess approximation

The Douglas–Kroll–Hess approximation [258,260,264,432] is one of the methods for large and small component decoupling in the four-component Dirac Hamiltonian, which has been lately widely used in quantum chemical calculations of molecular properties.[262,264,494] The principal benefits of the DKH method include variational stability and possibility of a systematic increase in accuracy.[443] The initial theoretical grounds of the DKH formalism with inclusion of electrical and magnetic perturbations have been developed by Dyall.[495]

The general concepts of DKH application for calculating SSCCs were initially considered in detail by Melo *et al.*[187] The magnetic Hamiltonian terms that make contributions to SSCCs in the two-component form were obtained in an analytical form. The authors cited [187] employed the two-component DKH approach in combination with the generalized Kohn–Sham theory to calculate the SSCCs in model $XH_4$ hydrides, X = $^{13}$C, $^{29}$Si, $^{73}$Ge, $^{119}$Sn; the results were compared with the values obtained using the four-component TD-DHF formalism (4RPA).

In the general case, the kinetic balance operator $\widehat{\mathbf{X}}$, specified by Eqn (239) in the stationary case and by Eqn (271) in the time-dependent case, cannot be expressed in a closed form. Therefore, the unitary transformation $\mathbf{U}$ depending on $\widehat{\mathbf{X}}$ and reducing the initial four-component Hamiltonian to the block diagonal form can be represented as an infinite sequence of transformations

$$\mathbf{U} = \prod_{i=0}^{\infty}\mathbf{U}_i \tag{336}$$

The meaning of each of transformations $\mathbf{U}_i$ is decreasing the order of the secondary block diagonal of the Hamiltonian in the parameter specified in advance. In each stage, transformations $\mathbf{U}_i$ should be parameterized in such a way

that only terms of the principal block diagonal remain in the limit of an infinite number of these transformations.

The first stage in the DKH sequence of transformations is the free particle Foldy – Wouthuysen transformation (fpFW),[14, 38] which has a closed form. For a free particle, the kinetic balance operator $\widehat{\mathbf{X}}$ in the momentum representation is given by

$$\widehat{\mathbf{X}} \approx \frac{c\vec{\boldsymbol{\sigma}}\vec{p}}{c^2 + E_p} \tag{337}$$

where

$$E_p = \pm\sqrt{c^4 + \vec{p}^{\,2}c^2}$$

The substitution of expression (337) into FW transformation formula (219) gives the following expression for $\mathbf{U}_0$ for the fpFW:

$$\mathbf{U}_0 = \mathbf{A}_p(\mathbf{I} + \boldsymbol{\beta}\mathbf{R}_p\vec{\boldsymbol{\alpha}}\vec{p}) \tag{338}$$

$$\mathbf{A}_p = \sqrt{\frac{E_p + c^2}{2E_p}} \tag{339}$$

$$\mathbf{R}_p = \frac{c}{E_p + c^2} \tag{339a}$$

In formulae (338) – (339a), positive roots can be considered without loss of generality (for the negative continuum, the procedure is similar). The fpFW transformation in the form (338) applied to the free one-particle Dirac Hamiltonian leads to the block diagonal form of the Hamiltonian. A similar procedure is applicable in the case where certain conditions are imposed on the potential $\widehat{\mathbf{V}}$, namely, commutation with the operator $\widehat{\mathbf{X}}$, *i.e.*, $[\widehat{\mathbf{X}}, \widehat{\mathbf{V}}] = \mathbf{0}$, the block diagonal form of $\widehat{\mathbf{V}}$ and the absence of other inhomogeneous fields. Then the application of transformation (338) to the four-component Dirac Hamiltonian with such a potential diagonalizes the Hamiltonian, resulting in the following expression for the upper left block in (286). The substitution of $\widehat{\mathbf{X}}$ [see (337)] into the formula for the upper left block gives the expression

$$\widehat{\mathbf{H}}^{\mathrm{FW}} = \sqrt{c^4 + \hat{\vec{p}}^{\,2}c^2} - c^2 + \widehat{\mathbf{V}} \tag{340}$$

which is the classical form for the relativistic energy of a single particle located in the potential $\widehat{\mathbf{V}}$.

Thus, the only FW transformation that can be written in the closed form is the fpFW transformation applicable as a valid diagonalizing transformation only for a very narrow range of problems, namely, for a free particle or a particle located in an external diagonal spatially homogeneous potential. In other cases, $\widehat{\mathbf{V}}$ and $\widehat{\mathbf{X}}$ do not commutate, and in some cases, the matrix operator $\widehat{\mathbf{V}}$ is not block diagonal; therefore, special methods suitable for taking into account this circumstance to one or another extent were developed, in particular, the DKH transformation.

The first step of the DKH procedure is the application of the fpFW transformation to the Dirac Hamiltonian with allowance for the magnetic field. This does not provide complete component decoupling. In the general case, the transformed constrained Hamiltonian $\mathbf{U}_0\mathbf{h}^{\mathrm{D}}\mathbf{U}_0^+$ can be expressed in the momentum representation by **E**, **O** notation, where **E** are even terms (located on the principal block diagonal) and **O** are odd terms (located on off-diagonal blocks)

$$\mathbf{h}_1^{\mathrm{D}} = \mathbf{U}_0\mathbf{h}^{\mathrm{D}}\mathbf{U}_0^+ = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{O}_1 \tag{341}$$

Formula (341) is the first-order DKH approximation (DKH1). The even and odd terms in it can be classified into two types: terms that contain only the electrical potential $\mathbf{V}_N$ ($V$ types) and the terms that contain only the magnetic field vector potential $\vec{A}$ ($A$ type). For example, $\mathbf{E}_1$ is split into constituents, $\mathbf{E}_1^V$ and $\mathbf{E}_1^A$, the former of which contains the spin – orbit (SO) operator and the second of which is the two-component approximation of magnetic perturbation (perturbative magnetic Hamiltonian), which is the target quantity in the whole DKH procedure, as the SSCC is a function of the linear response from the magnetic perturbing operators. The perturbative magnetic Hamiltonian is linear with respect to the field $\vec{A}$, *i.e.*, it has no diamagnetic term, and, hence, this approximation level (DKH1) is insufficient for the calculation of SSCCs. However, in this stage, it is already possible to identify the spin-dependent (prototypes of the FC and SD contributions) and orbital (analogue of the PSO contribution) parts.

The next step of the DKH procedure is the unitary transformation as an infinite series, which can be represented as

$$\mathbf{U}_1 = \exp(\mathbf{W}) \tag{342}$$

The matrix **W** is skew-Hermitian,[496] *i.e.*, $\mathbf{W}^+ = -\mathbf{W}$. With this condition, the Hamiltonian in the DKH2 approximation has the form

$$\mathbf{h}_2^{\mathrm{D}} = \mathbf{U}_1\mathbf{U}_0\,\mathbf{h}^{\mathrm{D}}\mathbf{U}_0^+\mathbf{U}_1^+ = \boldsymbol{\beta}E_p + \mathbf{E}_1 + \mathbf{O}_1 + \tag{343}$$

$$+ [\mathbf{W}, \boldsymbol{\beta}E_p] + [\mathbf{W}, \mathbf{O}_1] + \frac{1}{2}[\mathbf{W}, [\mathbf{W}, \boldsymbol{\beta}E_p]] + [\mathbf{W}, \mathbf{E}_1] + \ldots$$

The matrix **W** is defined in such a way as to eliminate the odd term $\mathbf{O}_1$, which appeared in the previous step. For this purpose, the term $[\mathbf{W}, \boldsymbol{\beta}E_p]$ is selected to counterbalance $\mathbf{O}_1$

$$[\mathbf{W}, \boldsymbol{\beta}E_p] \stackrel{!}{=} -\mathbf{O}_1 = -(\mathbf{O}_1^A + \mathbf{O}_1^V) \tag{344}$$

This equality imposes the following condition on the matrix **W**: the term **W** should be odd; therefore, after the mutual cancellation of $\mathbf{O}_1$ and $[\mathbf{W}, \boldsymbol{\beta}E_p]$, the next odd expansion term is $[\mathbf{W}, \mathbf{E}_1]$. In view of condition (344), the even part of expression (343) can be represented as

$$\mathbf{h}_2^{\mathrm{D-Even}} = \boldsymbol{\beta}E_p + \mathbf{E}_1^A + \mathbf{E}_1^V + \frac{1}{2}\left[\mathbf{W}, \mathbf{O}_1^A + \mathbf{O}_1^V\right] \tag{345}$$

Since the goal is to trace the magnetic perturbations, it is reasonable to split **W** into parts $V$ and $A$, which, according to Eqn (344), should meet the following conditions:[497]

$$[\mathbf{W}^V, \boldsymbol{\beta}E_p] \stackrel{!}{=} -\mathbf{O}_1^V \tag{346}$$

$$[\mathbf{W}^A, \boldsymbol{\beta}E_p] \stackrel{!}{=} -\mathbf{O}_1^A \tag{347}$$

Taking account of these conditions, the even DKH2 Hamiltonian (345) is split into the non-perturbed part $\mathbf{H}_0^{\mathrm{DKH2}}$ and perturbative part consisting of linear and

**Table 6**. $^1J(X,^1H)$ constants (Hz) for $XH_4$ tetrahydrides calculated using various DKH schemes in combination with the TD-HF formalism and the TD-DHF (4RPA) and IORAmm/TD-HF methods.

| Method | $CH_4$ | $SiH_4$ | $GeH_4$ | $SnH_4$ | Ref. |
|---|---|---|---|---|---|
| TD-HF(RPA) | 158.4 | −243.5 | −108.2 | −1930.6 | 187 |
| DKH1-scalar | 150.6 | −229.1 | −110.3 | −2371.0 | 187 |
| DKH1-SO | 150.6 | −229.1 | −109.9 | −2392.3 | 187 |
| DKH2-scalar | 157.1 | −245.9 | −122.5 | −2616.0 | 187 |
| DKH2-SO | 157.1 | −245.9 | −121.9 | −2629.3 | 187 |
| TD-DHF (4RPA) | 159.1 | −250.1 | −123.9 | −2650.2 | 183 |
| IORAmm–TD-HF | 160.1 | −248.7 | −125.8 | −2704.6 | 266 |

**Table 7**. $^1J(X,^1H)$ constants (Hz) for $XH_4$ tetrahydrides calculated using the DKH2-SO scheme at the DFT level and found experimentally.

| $E_{xc}$ | $CH_4$ | $SiH_4$ | $GeH_4$ | $SnH_4$ | Ref. |
|---|---|---|---|---|---|
| PBE | 117.8 | −186.3 | −86.8 | −1883.3 | 187 |
| PBEh | 121.9 | −194.1 | −92.5 | −1727.0 | 187 |
| B3LYP | 131.2 | −209.6 | −99.6 | −1922.6 | 187 |
| Experiment | 120.1 | −201.1 | −97.6 | −1933.3 | 502–505 |

quadratic terms with respect to the field, $\widehat{\mathbf{H}}_A^{\mathrm{DKH2}}$ and $\widehat{\mathbf{H}}_{A^2}^{\mathrm{DKH2}}$

$$\widehat{\mathbf{H}}_0^{\mathrm{DKH2}} = \boldsymbol{\beta} E_p + \mathrm{E}_1^V + \frac{1}{2}[\mathbf{W}^V, \mathbf{O}_1^V] \tag{348}$$

$$\widehat{\mathbf{H}}_A^{\mathrm{DKH2}} = E_1^A + \frac{1}{2}[\mathbf{W}^V, \mathbf{O}_1^A] + \frac{1}{2}[\mathbf{W}^A, \mathbf{O}_1^V] \tag{349}$$

$$\widehat{\mathbf{H}}_{A^2}^{\mathrm{DKH2}} = \frac{1}{2}[\mathbf{W}^A, \mathbf{O}_1^A] \tag{350}$$

Expressions (349) and (350) contain all necessary magnetic perturbation terms. Thus, the DKH2 approximation is the minimal admissible theoretical level for the calculation of SSCCs. The introduction of the DKH approach into some *ab initio* methods and the software implementation of this approach were reported by Samzow and Hess [498] and by Knappe and Rösch.[499]

Melo *et al.*[187] compared the accuracy of calculations of $^1J(X,^1H)$, X = $^{13}C$, $^{29}Si$, $^{73}Ge$ and $^{119}Sn$, for a model series of $XH_4$ hydrides using different DKH schemes and the 4RPA [183, 218, 239, 240, 295] and IORAmm [266] methods. Four DKH schemes were used: DKH1-scalar (scalar DKH1), DKH1-SO (full DKH1), DKH2-scalar (scalar DKH2) and DKH2-SO (full DKH2) in combination with the HF and DFT methods (PBE,[368] PBEh,[500, 501] B3LYP [365]). The obtained results are summarized in Tables 6 and 7.

It can be seen from the presented data that the DKH1 scheme in combination with both formalisms (TD-HF and DFT) gives relativistic values underestimated in magnitude, whereas the full DKH2-SO/TD-HF scheme gives results close to those of 4RPA. The DKH2-SO/PBE//PBEh approach provides values resembling most closely the experimental results in the case of lighter molecules ($CH_4$ and $SiH_4$), while the DKH2-SO/B3LYP scheme gives such results for heavier molecules ($GeH_4$ and $SnH_4$).

#### V.3.i. Barysz–Sadlej–Snijders approximation

The Barysz–Sadlej–Snijders (BSS) scheme, or IOTC scheme, is an exact scheme for component decoupling, which results in construction of exact two-component relativistic operators.[285–288, 442] In essence, it is very close to DKH; their comparison can be found in a paper [443] devoted to detailed consideration of various exact schemes for separation of positron and electron continuums by unitary transformations.

First of all, the BSS/IOTC scheme differs from DKH by the fact that in the hierarchy of DKH schemes, the closed equations have an explicit operator form, whereas in the case of BSS/IOTC, some basis set is introduced and the Dirac Hamiltonian is considered in the matrix form, so that the block diagonal Hamiltonian obtained in this procedure is also in the matrix form. The BSS/IOTC scheme, like DKH, is closely connected with the operator $\widehat{\mathbf{X}}$ formalism, and the first step of this transformation coincides with the DKH first step,[258, 260, 264, 432] which is the fpFW transformation.[14, 38] Thus, the whole block-diagonalization procedure of the Dirac Hamiltonian in the BSS/IOTC formalism is split into two stages, the first one being $\widehat{\mathbf{U}}_0 \equiv$ fpFW and the second one being the transformation $\mathbf{U}_1$, which is equivalent to the infinite set of all subsequent transformations in the DKH scheme,

$$\widehat{\tilde{\mathbf{H}}}^{\mathrm{D}} = \widehat{\mathbf{U}}_1 \widehat{\mathbf{U}}_0 \widehat{\mathbf{H}}^{\mathrm{D}} \widehat{\mathbf{U}}_0^+ \widehat{\mathbf{U}}_1^+ = \tag{351}$$

$$= \widehat{\mathbf{U}}_1 \begin{pmatrix} \widehat{\tilde{\mathbf{H}}}_{LL}^{\mathrm{D(fpFW)}} & \widehat{\tilde{\mathbf{H}}}_{LS}^{\mathrm{D(fpFW)}} \\ \widehat{\tilde{\mathbf{H}}}_{SL}^{\mathrm{D(fpFW)}} & \widehat{\tilde{\mathbf{H}}}_{SS}^{\mathrm{D(fpFW)}} \end{pmatrix} \widehat{\mathbf{U}}_1^+ = \begin{pmatrix} \widehat{\tilde{\mathbf{H}}}_{(+)}^{\mathrm{D}} & \mathbf{0} \\ \mathbf{0} & \widehat{\tilde{\mathbf{H}}}_{(-)}^{\mathrm{D}} \end{pmatrix}$$

According to the requirements to the transformation $\widehat{\mathbf{U}}_1$ formulated within the framework of the exact EFW transformation,[62] the matrix operator $\widehat{\mathbf{U}}_1$ should have the form

$$\widehat{\mathbf{U}}_1(\widehat{\mathbf{R}}) = \tag{352}$$

$$= \begin{pmatrix} (\hat{\mathbf{I}} + \widehat{\mathbf{R}}^+\widehat{\mathbf{R}})^{-1/2} & (\hat{\mathbf{I}} + \widehat{\mathbf{R}}^+\widehat{\mathbf{R}})^{-1/2}\widehat{\mathbf{R}}^+ \\ -(\hat{\mathbf{I}} + \widehat{\mathbf{R}}\,\widehat{\mathbf{R}}^+)^{-1/2}\widehat{\mathbf{R}} & (\hat{\mathbf{I}} + \widehat{\mathbf{R}}\,\widehat{\mathbf{R}}^+)^{-1/2} \end{pmatrix}$$

Here a special designation is used — the operator $\widehat{\mathbf{R}}$, which, in essence, acts as the operator $\widehat{\mathbf{X}}$; however, the action of $\widehat{\mathbf{R}}$, unlike $\widehat{\mathbf{X}}$, is defined for the set of fpFW

transformed bispinors rather than for the set of usual components. For off-diagonal Hamiltonian blocks to turn to **0** in the second stage, the operator $\widehat{\mathbf{R}}$ should meet the following condition:

$$\widehat{\mathbf{R}} = \frac{1}{\widehat{\widetilde{\mathbf{H}}}_{LL}^{\mathrm{D(fpFW)}}} \left( -\widehat{\widetilde{\mathbf{H}}}_{LS}^{\mathrm{D(fpFW)}} + \widehat{\mathbf{R}}\widehat{\widetilde{\mathbf{H}}}_{LL}^{\mathrm{D(fpFW)}} + \widehat{\mathbf{R}}\widehat{\widetilde{\mathbf{H}}}_{LS}^{\mathrm{D(fpFW)}}\widehat{\mathbf{R}} \right) \quad (353)$$

From this equation, one can easily obtain the corresponding matrix equation for the operator $\widehat{\mathbf{R}}$ matrix in a particular one-particle basis set by applying the fpFW transformation to the initial Dirac Hamiltonian and expanding the spinors in this basis set. The matrix equation thus obtained is solved iteratively, which furnishes the matrix **R** with a specified accuracy. Then the matrix of the Dirac Hamiltonian upper left block $\widehat{\widetilde{\mathbf{H}}}_{(+)}^{\mathrm{D}}$ is found from the matrix equation derived from the expression for the Hamiltonian upper left block modified during the EFW transformation

$$\widehat{\widetilde{\mathbf{H}}}_{(+)}^{\mathrm{D}} = \frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{R}}^{+}\widehat{\mathbf{R}}}} \left( \widehat{\widetilde{\mathbf{H}}}_{LL}^{\mathrm{D(fpFW)}} + \widehat{\widetilde{\mathbf{H}}}_{LS}^{\mathrm{D(fpFW)}}\widehat{\mathbf{R}} + \right. \quad (354)$$

$$\left. + \widehat{\mathbf{R}}^{+}\widehat{\widetilde{\mathbf{H}}}_{SL}^{\mathrm{D(fpFW)}} + \widehat{\mathbf{R}}^{+}\widehat{\widetilde{\mathbf{H}}}_{SS}^{\mathrm{D(fpFW)}}\widehat{\mathbf{R}} \right) \frac{1}{\sqrt{\hat{\mathbf{I}} + \widehat{\mathbf{R}}^{+}\widehat{\mathbf{R}}}}$$

Ilias and Saue [276] also proposed a similar infinite-order approach. However, in this approach, the first fpFW step is omitted, and all transformations are performed in a single step, *i.e.*, formally it can be assigned to the X2C family. This approach was embedded in the DIRAC program package.[110] According to this approach, the Dirac equation is first constructed in the atomic orbital basis set, only the Gauss basis functions being used in the program code, and the basis set for small components is constructed in conformity with the unrestricted kinetic balance conditions.[506] Then the equation is converted to the orthonormalized molecular orbital basis set by the particular non-unitary transformation described by Visscher and Saue.[507] After that, the eigenvalue problem is solved for the modified Dirac Hamiltonian matrix *via* its diagonalization, and the matrix elements of the matrix **R** are found in parallel; this provides the matrix elements of the matrix $\mathbf{U}_1$ and, hence, of the upper diagonal block of the modified Hamiltonian in the basis set of the molecular spin – orbit large components. Subsequently, the obtained Hamiltonian is projected to the large component space of the atomic spin orbitals. In the DIRAC program package,[110] the BSS/IOTC Hamiltonian is adjusted for the use in a number of methods — HF,[506, 508] DFT,[290] MP2,[509] MCSCF,[510] CI [511, 512] and CC.[513, 514]

An advantage of this approach is application of the universally used matrix algebra, which makes it possible, in particular, to represent the component decoupling transformation in the explicit matrix form and to use it at once for the transformation of property operator matrices, and this automatically rules out the PCE error.[30, 495, 515] The DIRAC package can be used to calculate the linear [516] and quadratic [517] response functions at the BSS/IOTC level within the HF and DFT formalisms, *i.e.*, this covers a broad range of the second- and third-order electrical and magnetic properties, including SSCCs.

The DIRAC program package [110] implements several modifications of the BSS/IOTC scheme for the calculation of SSCCs. The BSS/IOTC + AMFI MFSSO scheme is most accurate among them.

The spin – orbit part of the two-component Breit – Pauli Hamiltonian [13, 15 – 17] is known to be split into one-electron and two-electron terms, the latter arising due to inclusion of the Breit interaction. In turn, the two-electron spin – orbit part is also split into two classes of contributions, SSO and SOO.[13, 38] The SSO contribution describes the interaction of the spin of electron *i* with its own orbital magnetic moment relative to electron *j*, whereas the SOO contribution describes the interaction of the spin of electron *i* with the orbital magnetic moment of electron *j* relative to electron *i*. Inclusion of all these terms provides an exact description of the spin – orbit corrections to energies and other properties. However, the Breit – Pauli Hamiltonian or some other two-component form that fully takes into account all spin – orbit components implies the necessity of computing a very large number of multicentre two-electron spin – orbit integrals of various types, which appears to be associated with a very high computational cost.[518] Elimination of all two-electron spin – orbit contributions from consideration brings about a serious faulty overestimation of the spin – orbit interaction in the calculated properties. Hess *et al.*[519] proposed a way out of this situation consisting in the introduction of the mean field approximation (MFA). This approach is based on the introduction of effective one-electron spin – orbit Hamiltonian, the operators of which are similar to the Coulomb and exchange operators in the standard Hartree – Fock theory. Correspondingly, in the MFSSO approximation [520] implemented in the DIRAC program package,[110] the SSO part is represented by the effective one-electron operator. This approximation was implemented in the AMFI method,[521 – 524] which does not take into account the multicentre spin – orbit integrals.

### V.4. Direct perturbation theory methods

The relativistic corrections to the SSCCs can be calculated using the four-component direct perturbation theory (4DPT) [428, 459, 525 – 533] with the quadratic response theory in the simplest approximation.[250]

The application of 4DPT theory to SSCCs has not yet been developed in full measure; however, some steps towards the development of this approach were made by Kutzelnigg in a large theoretical study [251] devoted to calculation of the relativistic corrections to the magnetic properties of arbitrary order of $c^{-1}$ within the 4DPT formalism in one-electron approximation. The unperturbed Hamiltonian in this theory is the non-relativistic limit of the four-component Dirac Hamiltonian, namely, the Lèvy-Leblond Hamiltonian,[59] and the perturbations are divided into two types, relativistic and magnetic ones. The description of SSCCs requires the use of at least triple perturbation theory (two magnetic type perturbations and relativistic perturbation). The theory proposed by Kutzelnigg [251] has not been brought to completion, which would include the calculation of matrix elements of magnetic perturbations present in the SSCC theory. However, this theory has good prospects and its development is in progress. The issue concerning the calculation of the matrix elements of magnetic operators is the subject of a paper of Helgaker and co-workers.[252]

In practice, only the spin – orbit coupling has been chosen so far as the relativistic perturbation. The first one-

component theory and the computer implementation of this approach were developed by Oddershede's group.[269] As a basis, the authors took the quadratic response function in the static limit [534]

$$\lim_{\varepsilon_1,\varepsilon_2\to 0^+}\left\langle\!\!\left\langle \hat{A};\, \hat{V}^{\omega_1=0},\, \hat{V}^{\omega_2=0}\right\rangle\!\!\right\rangle_{0,+i\varepsilon_1\,0+i\varepsilon_2}= \tag{355}$$

$$=\sum_{kn>0}\Big(\Big\langle 0\Big|\,\hat{A}\,\Big|k\Big\rangle\Big\langle k\Big|\hat{\bar{V}}^{\omega_1=0}\Big|n\Big\rangle\Big\langle n\Big|\hat{V}^{\omega_2=0}\Big|0\Big\rangle+$$

$$+\Big\langle 0\Big|\hat{V}^{\omega_2=0}\Big|n\Big\rangle\Big\langle n\Big|\hat{\bar{V}}^{\omega_1=0}\Big|k\Big\rangle\Big\langle k\Big|\hat{A}\Big|0\Big\rangle+$$

$$+\Big\langle 0\Big|\hat{V}^{\omega_1=0}\Big|k\Big\rangle\Big\langle k\Big|\hat{\bar{A}}\Big|n\Big\rangle\Big\langle n\Big|\hat{V}^{\omega_2=0}\Big|0\Big\rangle+$$

$$+\Big\langle 0\Big|\hat{A}\Big|k\Big\rangle\Big\langle k\Big|\hat{\bar{V}}^{\omega_2=0}\Big|n\Big\rangle\Big\langle n\Big|\hat{V}^{\omega_1=0}\Big|0\Big\rangle+$$

$$+\Big\langle 0\Big|\hat{V}^{\omega_1=0}\Big|n\Big\rangle\Big\langle n\Big|\hat{\bar{V}}^{\omega_2=0}\Big|k\Big\rangle\Big\langle k\Big|\hat{A}\Big|0\Big\rangle+$$

$$+\Big\langle 0\Big|\hat{V}^{\omega_2=0}\Big|k\Big\rangle\Big\langle k\Big|\hat{\bar{A}}\Big|n\Big\rangle\Big\langle n\Big|\hat{V}^{\omega_1=0}\Big|0\Big\rangle\Big)/\omega_k\omega_n$$

where $\omega_n$ are the excitation energies $\omega_n = E_n - E_0$, the operators with a bar reflect the shifts by the mean value in the ground state of these operators

$$\hat{\bar{A}} = \hat{A} - \Big\langle 0\Big|\hat{A}\Big|0\Big\rangle$$

The lower-order spin – orbit corrections to the SSCCs can be obtained from expression (355) by choosing the pair of operators $\hat{A}$ and $\hat{V}^{\omega_1=0}$ out of the set of standard non-relativistic Ramsey magnetic perturbation operators [212] — $\hat{H}_{\rm PSO}$, $\hat{H}_{\rm FC}$, $\hat{H}_{\rm SD}$ and $\hat{H}_{\rm DSO}$, while the spin – orbit coupling operator $\hat{H}_{\rm SO}$, which is triplet, is chosen as $\hat{V}^{\omega_2=0}$. The spin – orbit coupling operator $\hat{H}_{\rm SO}$ consists of one-electron and two-electron parts

$$\hat{\mathbf{H}}_{\rm SO} = \frac{g_{\rm e}h{\rm e}^2}{32\pi^2\varepsilon_0 m_{\rm e}^2 c^2}\left(\sum_N\sum_j \frac{Z_N}{r_{jN}^3}s_j\,l_{jN} - \sum_{i<j}\frac{(2s_i+s_j)l_{ij}}{r_{ij}^3}\right) \tag{356}$$

The first term (one-electron part) corresponds to the sum of interaction operators between electron spins and their orbital moments relative to nuclei, while the second term (two-electron part) can be regarded as a sum of two contributions — SOO and SSO.[35] However, in order to reduce the computational cost (two-electron SO integrals substantially increase the computation time), Kirpekar *et al.*[269] replaced the operator $\hat{H}_{\rm SO}$ (356) by the effective one-electron spin – orbit coupling operator $\hat{H}_{\rm SO}^{\rm ef}$, which models the interaction of the chosen electron $j$ with all other electrons as some additional shielding of the nuclei, which can be expressed by introducing the effective nuclear charges $Z_N^{\rm ef}$.

In view of the choice of the operators $\hat{A}$, $\hat{V}^{\omega_1=0}$ and $\hat{V}^{\omega_2=0}$ and considering formula (356), several groups of spin – orbit corrections to SSCCs can be distinguished:

— *a*: FC – FC – SO,
— *b*: PSO – FC – SO,
— *c*: FC – SD – SO,
— *d*: PSO – SD – SO,
— *e*: SD – SD – SO.

The HERMIT program package developed by Helgaker's group † and other researchers [535–537] actually implies the calculation of only type *b* and *d* functions. The type *a* quadratic function, which is expected to make the largest contribution if the Fermi-contact interaction predominates, in reality turns to zero, which was proved [269] on the basis of the Wigner – Eckart theorem.[538] The contributions of types *c* and *e* contain each three triplet operators; however, the possibility of calculation of these quadratic response functions has not yet been implemented.

Kirpekar *et al.*[269] noted that the value of function *c* is much lower than the value of function *b*, while function *d* is vanishingly small compared with any other contribution. This is due to the fact that functions *c* and *d* contain the SD operator, which most often makes a negligibly small contribution to the SSCC. In our opinion, this explanation does not justify the neglect of quadratic response functions with three triplet operators, because in some cases, the spin dipole mechanism can make a considerable contribution to the full SSCC value.[539]

The spin – orbit corrections to all four contributions to SSCCs calculated using one-component DPT at the HF level with the above-described constraints were reported [269] for a model series of $XH_4$ hydrides, X = C, Si, Ge and Sn. The spin – orbit corrections to the $^1J(X,^1H)$ constants for this series were found to be not more than 1% of the total value of the constant. Kirpekar and Sauer [540] used the same DPT approach to find the PSO – FC – SO relativistic correction in terms of a one-electron model for the $^1J(^{207}Pb,^1H)$ and $^2J(^1H,^1H)$ constants of $PbH_4$. The calculations were carried out by means of various non-relativistic *ab initio* methods such as RPA, SOPPA and SOPPA(CCSD). However, the obtained results do not attest to a considerable increase in the calculation accuracy in comparison with the experimental results and, as indicated by the authors themselves, scalar relativistic effects are more significant than the spin – orbit effects.

Further software implementation of DPT for the inclusion of spin – orbit corrections to SSCCs was done by Vaara *et al.*,[270] who developed and computerized the calculation of the SO corrections at the MCSCF level and tested the developed software application in the calculation of SSCCs for series of hydrides, HX (X = F, Cl, Br, I) and $H_2X$ (X = O, S, Se, Te). The SO corrections to SSCCs were also calculated using the DPT formalism at the DFT level for $H_2X$ (X = O, S, Se, Te) and $XH_4$ (X = C, Si, Ge, Sn, Pb).[271]

Unlike the spin – orbit corrections to the shielding constants, unfortunately, corrections to SSCCs tend to diverge with increasing basis set.[250] As follows from analysis of scattered and scanty data obtained mainly at the ZORA level, scalar corrections predominate in many cases, whereas the spin – orbit corrections may be significant only in special cases, for example, if the SSCC in question involves two heavy or, conversely, two light nuclei separated by heavy nuclei and the Fermi contact contribution does not predominate.[355] Thus, the absence of scalar relativity operators as perturbations in the DPT is a problem to be solved in due time, while now the corresponding scalar corrections can also be calculated by other methods, for

† T Helgaker, P R Taylor, K Ruud, O Vahtras, H Koch. HERMIT, a molecular integral program.

example by IORAmm,[266] which is able to take into account only these corrections at the given stage of theoretic development.

**V.4.a. Picture change error**

A unitary transformation of the four-component Dirac Hamiltonian into the two-component form is accompanied by the 4-spinor transformation to the upper bispinor form. As a result, the small component in the transformed 4-spinor turns to zero, which can be regarded as a sort of 'reduction' of the 4-spinor to 2-spinor (bispinor).

However, the calculation of matrix elements of Hermitian operators that initially have a matrix representation of $4 \times 4$ dimension brings about a serious error in the basis set of ('reduced') 4-spinors, the so-called picture change error (PCE).[30, 515] In order to avoid this error, calculation of the matrix elements of operators should be started from their transformation from a four-component (Dirac) representation to a two-component (DKH) representation.

The generation of PCE was considered in more detail in a monograph [38] in relation to calculation of an arbitrary observable physical quantity described by the operator $\widehat{\mathbf{X}}$ defined in the single-particle wave function space.

The mean value of the operator $\widehat{\mathbf{X}}$ over the state $\boldsymbol{\psi}$ is found as

$$\langle \widehat{\mathbf{X}} \rangle_{\psi} = \left\langle \boldsymbol{\psi} \middle| \widehat{\mathbf{X}} \middle| \boldsymbol{\psi} \right\rangle = \mathrm{tr}(\mathbf{DX}) = \left\langle \boldsymbol{\psi}_L \middle| \widehat{\mathbf{X}}^{LL} \middle| \boldsymbol{\psi}_L \right\rangle + \tag{357}$$

$$+ \left\langle \boldsymbol{\psi}_L \middle| \widehat{\mathbf{X}}^{LS} \middle| \boldsymbol{\psi}_S \right\rangle + \left\langle \boldsymbol{\psi}_S \middle| \widehat{\mathbf{X}}^{SL} \middle| \boldsymbol{\psi}_L \right\rangle + \left\langle \boldsymbol{\psi}_S \middle| \widehat{\mathbf{X}}^{SS} \middle| \boldsymbol{\psi}_S \right\rangle$$

The density matrix $\mathbf{D}$ has the dimension $4 \times 4$

$$\mathbf{D} = |\boldsymbol{\psi}\rangle\langle\boldsymbol{\psi}| = \begin{pmatrix} |\boldsymbol{\psi}^L\rangle \\ |\boldsymbol{\psi}^S\rangle \end{pmatrix} \left(\langle\boldsymbol{\psi}^L|, \langle\boldsymbol{\psi}^S|\right) = \tag{358}$$

$$= \begin{pmatrix} |\boldsymbol{\psi}^L\rangle\langle\boldsymbol{\psi}^L| & |\boldsymbol{\psi}^L\rangle\langle w^S| \\ |\boldsymbol{\psi}^S\rangle\langle\boldsymbol{\psi}^L| & |\boldsymbol{\psi}^S\rangle\langle\boldsymbol{\psi}^S| \end{pmatrix} = \begin{pmatrix} \mathbf{D}_{LL} & \mathbf{D}_{LS} \\ \mathbf{D}_{SL} & \mathbf{D}_{SS} \end{pmatrix}$$

Each block of this matrix is expressed *via* components of bispinors

$$|\boldsymbol{\psi}^{L/S}\rangle\langle\boldsymbol{\psi}^{L/S}| = \begin{pmatrix} \psi_1^{L/S} \\ \psi_2^{L/S} \end{pmatrix} (\psi_1^{L/S*}, \psi_2^{L/S*}) = \tag{359}$$

$$= \begin{pmatrix} \psi_1^{L/S}\psi_1^{L/S*} & \psi_1^{L/S}\psi_2^{L/S*} \\ \psi_2^{L/S}\psi_1^{L/S*} & \psi_2^{L/S}\psi_2^{L/S*} \end{pmatrix}$$

Formulae (357) – (359) form the so-called Dirac representation.

The mean value of the physical operator $\widehat{\mathbf{X}}$ can be found in the two-component form. For the unitary transformation $\widehat{\mathbf{U}}$ ($\widehat{\mathbf{U}}^+\widehat{\mathbf{U}} = \mathbf{I}$), which reduces the 4-spinor

$$|\boldsymbol{\psi}\rangle = \begin{pmatrix} |\boldsymbol{\psi}^L\rangle \\ |\boldsymbol{\psi}^S\rangle \end{pmatrix}$$

to the upper 2-spinor form

$$\widehat{\mathbf{U}}\,|\boldsymbol{\psi}\rangle = |\tilde{\boldsymbol{\psi}}\rangle = \begin{pmatrix} |\tilde{\boldsymbol{\psi}}^L\rangle \\ 0 \end{pmatrix}$$

the mean value of the operator $\widehat{\mathbf{X}}$ can be written as follows:

$$\langle \widehat{\mathbf{X}} \rangle_{\psi} = \langle\boldsymbol{\psi}|\,\widehat{\mathbf{X}}\,|\boldsymbol{\psi}\rangle = \langle\boldsymbol{\psi}|\,\widehat{\mathbf{U}}^+\widehat{\mathbf{U}}\widehat{\mathbf{X}}\widehat{\mathbf{U}}^+\widehat{\mathbf{U}}\,|\boldsymbol{\psi}\rangle = \tag{360}$$

$$= \left\langle \tilde{\boldsymbol{\psi}} \middle| \widehat{\mathbf{U}}\widehat{\mathbf{X}}\widehat{\mathbf{U}}^+ \middle| \tilde{\boldsymbol{\psi}} \right\rangle = \left\langle \tilde{\boldsymbol{\psi}}^L \middle| \widehat{\tilde{\mathbf{X}}}^{LL} \middle| \tilde{\boldsymbol{\psi}}^L \right\rangle = \mathrm{tr}(\tilde{\mathbf{D}}^{LL}\tilde{\mathbf{X}}^{LL})$$

Formula (360) gives $\langle \widehat{\mathbf{X}} \rangle_{\psi}$ in the DKH representation. As follows from this formula, to obtain the exact mean value of the operator $\widehat{\mathbf{X}}$, one needs only the upper left block of the transformed operator $\widehat{\mathbf{X}}$

$$\widehat{\tilde{\mathbf{X}}}^{LL} = \left(\mathbf{U}\widehat{\mathbf{X}}\mathbf{U}^+\right)^{LL} = \mathbf{U}^{LL}\widehat{\mathbf{X}}^{LL}\mathbf{U}^{LL+} + \tag{361}$$

$$+\mathbf{U}^{LL}\widehat{\mathbf{X}}^{LS}\mathbf{U}^{LS+} + \mathbf{U}^{LS}\widehat{\mathbf{X}}^{SL}\mathbf{U}^{LL+} + \mathbf{U}^{LS}\widehat{\mathbf{X}}^{SS}\mathbf{U}^{LS+}$$

In some two-component schemes, the calculation of mean $\langle \widehat{\mathbf{X}} \rangle_{\psi}$ involves a simplification, particularly, the upper left block of the transformed operator (361) is replaced by the upper left block of the initial (non-transformed) operator $\widehat{\mathbf{X}}^{LL}$

$$\langle \widehat{\mathbf{X}} \rangle_{\psi} = \left\langle \tilde{\boldsymbol{\psi}}^L \middle| \widehat{\mathbf{X}}^{LL} \middle| \tilde{\boldsymbol{\psi}}^L \right\rangle \tag{362}$$

In other words, the change on going from the Dirac representation to the DKH representation is just neglected for physical operators and an additional error, called the picture change error, is intentionally introduced

$$\mathrm{PCE}(\widehat{\mathbf{X}}) = \langle \widehat{\mathbf{X}} \rangle - \bar{\widehat{\mathbf{X}}} \tag{363}$$

Here $\langle \widehat{\mathbf{X}} \rangle$ is the mean value of the operator $\widehat{\mathbf{X}}$ calculated in the incomplete DKH representation by formula (362), while $\bar{\widehat{\mathbf{X}}}$ is the mean value of the operator $\widehat{\mathbf{X}}$ in the Dirac representation. It should be emphasized once again that this error is specially embedded in some two-component schemes at a deep theoretical level.

In a review of Autschbach,[52] PCE is considered as some additional relativistic effect having the second order in the reciprocal of the speed of light $O(c^{-2})$, which makes it equivalent to major relativistic effects — scalar and spin – orbit effects. Indeed, we can agree with this, as the relativistic effect in the parameters being calculated is due to the difference between the complete and incomplete relativistic or non-relativistic representations. Any lack of consideration of the relativity, which shifts the values found using some scheme away from the values found in the Dirac representation (which is fully relativistic) leads to 'relativistic effects', some of which can be physically interpreted, while the other of which cannot. The picture change error refers exactly to the latter type.

One should expect that this error would substantially decrease the accuracy of calculation of SSCCs for heavy nuclei by two-component schemes in which it is embedded. In the variational approaches used for the calculation of SSCCs that operate with the electron density function, the difference between the accurate and inaccurate DKH representations of this characteristics affects strongly the

description of inner shells and affects much weaker the description of outer shells.[459, 541] This is of prime importance for the SSCC calculations as they are determined in most cases by particularly inner electrons.

The problem of the picture change error has started to be actively addressed in scientific literature when the Foldy–Wouthuysen component decoupling concept appeared,[14, 542] in particular, the numerical estimation of this error in various quantum chemical methods is considered in a number of papers.[52, 459, 515, 543–545]

## V.5. Computational models for partial or complete exclusion of relativity

### V.5.a. Exclusion of the spin–orbit coupling. Dyall–Kutzelnigg transformation

The relativistic effects appearing both in the electronic structure calculation and in the SSCC calculation can be separated into two classes — electron spin-dependent and spin-free ones. At the two-component level, both types of relativistic effects can be easily identified. Vivid examples are the Pauli Hamiltonian (in one-particle case) and the Breit–Pauli Hamiltonian (in the many-particle case). In the Pauli Hamiltonian, the terms describing effects of the former type correspond to the spin–orbit coupling, while the terms for the latter type effects correspond to scalar relativity, *i.e.*, the Darwin and mass–velocity corrections.

The problem of separation of the spin-dependent (spin–orbit) part is topical at any level of theory, as scalar effects are the predominant relativistic effects manifested in SSCCs, except for special cases.[355] Furthermore, spin–orbit integrals have the highest computational cost.

In four-component schemes, the separation of the spin–orbit part is a non-trivial task, whereas in most two-component schemes, this is done explicitly. A method for separation of the spin–orbit coupling was proposed by Dyall[97] for the Breit–Pauli Hamiltonian (Dyall–Kutzelnigg transformation). This method can be extended to the four-component case.

The general concept behind this method for separation of the spin–orbit term is based on the transformation of the 4-spinor [see (320)].[97] The application of transformation (320) to the four-component Dirac equation (16) results in its modified form

$$\begin{pmatrix} \widehat{\mathbf{V}}(\vec{r}) & \widehat{\mathbf{T}} \\ \widehat{\mathbf{T}} & \dfrac{\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\widehat{\mathbf{V}}(\vec{r})\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{4c^2} - \widehat{\mathbf{T}} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_L(\vec{r}) \end{pmatrix} = \tag{364}$$

$$= E \begin{pmatrix} \mathbf{1}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \dfrac{\widehat{\mathbf{T}}}{2c^2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_L(\vec{r}) \end{pmatrix}$$

where $\widehat{\mathbf{T}}$ is the kinetic energy operator.

The operator $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\widehat{\mathbf{V}}(\vec{r})\vec{\boldsymbol{\sigma}}\hat{\vec{p}}$ can be separated into two parts, those containing and those free from the spin operator

$$\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\widehat{\mathbf{V}}(\vec{r})\vec{\boldsymbol{\sigma}}\hat{\vec{p}} = \boldsymbol{\sigma}_i\boldsymbol{\sigma}_j\hat{p}_i\widehat{\mathbf{V}}(\vec{r})\hat{p}_j = \tag{365}$$

$$= (\delta_{ij} + \mathrm{i}\varepsilon_{ijl}\boldsymbol{\sigma}_l)\hat{p}_i\widehat{\mathbf{V}}(\vec{r})\hat{p}_j = \hat{\vec{p}}\,\widehat{\mathbf{V}}(\vec{r})\hat{\vec{p}} + \mathrm{i}\vec{\boldsymbol{\sigma}}[\hat{\vec{p}} \times \widehat{\mathbf{V}}(\vec{r})\hat{\vec{p}}]$$

The substitution of relation (365) into Eqn (364) gives the transformed Hamiltonian as the sum of spin-dependent and spin-free parts, the latter being imaginary

$$\tilde{\widehat{\mathbf{H}}} = \begin{pmatrix} \widehat{\mathbf{V}}(\vec{r}) & \widehat{\mathbf{T}} \\ \widehat{\mathbf{T}} & \dfrac{\hat{\vec{p}}\widehat{\mathbf{V}}(\vec{r})\hat{\vec{p}}}{4c^2} - \widehat{\mathbf{T}} \end{pmatrix} + \tag{366}$$

$$+ \begin{pmatrix} \mathbf{0}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \dfrac{\mathrm{i}}{4c^2}\vec{\boldsymbol{\sigma}}[\hat{\vec{p}} \times \widehat{\mathbf{V}}(\vec{r})\hat{\vec{p}}] \end{pmatrix}$$

Thus, elimination of the spin-dependent part from the four-component Hamiltonian can be conceived as removal of the imaginary part from the transformed four-component Hamiltonian (366).

### V.5.b. Four-component Lèvy-Leblond approximation

The separation of four-component Dirac Hamiltonian into the scalar and spin–orbit parts [see formula (365)] is a method for partial exclusion of relativity. However, in four-component calculations of relativistic corrections to SSCCs, the selection of a method for complete exclusion of relativity, *i.e.*, the selection of the non-relativistic limit, seems very important. Theoretically, non-relativistic limit can be reached in only two ways. One is based on the well-known tending to infinity of the speed of light in the key equations of the scheme, which gives the so-called Schrödinger limit. In this case, the relativistic four-component scheme degenerates to a classical one-component non-relativistic scheme. The second way is a special procedure for complete relativity exclusion from the four-component Hamiltonian *via* some transformations in combination with the speed of light tending to infinity.[59] In this case, the scheme dimension remains invariable. The spin operator is retained in the final Hamiltonian, which leads to a valid non-relativistic four-component analogue fully equivalent to the Schrödinger equation.[546] This method was called the Lèvy-Leblond procedure [59] (the corresponding Hamiltonian bears the like name). Note that retention of spin on going to this non-relativistic limit indicates that spin is not inherent only in relativistic consideration.

In our opinion, none of the two methods for selection of the non-relativistic limit should be preferred, as they both do not contradict the definition of relativistic effects, which has no constraints for the non-relativistic representation.

Theoretically, the SSCC values calculated using a one-component non-relativistic method should coincide with the values found by the two above-discussed methods, *i.e.*, by the relativistic four-component method in the $c \to \infty$ limit and by the four-component Lèvy-Leblond scheme. However, in practical application, these two methods are not equivalent for several reasons. First, replacement of the theoretical limit $c \to \infty$ with some finite value equal to $nc$ ($n \geqslant 5$) introduces some error, on the one hand, and can cause numerical instability of some four-component schemes, on the other hand. Second, four-component non-relativistic schemes, *e.g.*, the Lèvy-Leblond scheme, or another four-component scheme with an artificial increase in the speed of light are considered using a finite four-component basis set, whereas in the standard non-relativistic calculation, usual one-component basis functions are employed. In the complete basis set limit, a difference in the dimensions is insignificant; however, in practice, the use of finite-size basis sets brings abut some differences.

The Lèvy-Leblond scheme stems from a non-unitary transformation of 4-spinors

$$\begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\psi}_S(\vec{r}) \end{pmatrix} = \begin{pmatrix} \mathbf{I}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \frac{1}{c}\mathbf{I}_{2\times 2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_S(\vec{r}) \end{pmatrix} \tag{367}$$

The substitution of 4-spinors as expression (367) into the Dirac equation (16) results in the four-component equation

$$\begin{pmatrix} \hat{\mathbf{V}}(\vec{r}) & \vec{\boldsymbol{\sigma}}\hat{\vec{p}} \\ \vec{\boldsymbol{\sigma}}\hat{\vec{p}} & -2\left(\mathbf{I} - \frac{\hat{\mathbf{V}}(\vec{r})}{2c^2}\right) \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_S(\vec{r}) \end{pmatrix} = \tag{368}$$

$$= E \begin{pmatrix} 1 & \mathbf{0} \\ \mathbf{0} & c^{-2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_S(\vec{r}) \end{pmatrix}$$

Transition to the non-relativistic limit is performed by making the speed of light in expression (368) tend to infinity ($c \to \infty$)

$$\begin{pmatrix} \hat{\mathbf{V}}(\vec{r}) & \vec{\boldsymbol{\sigma}}\hat{\vec{p}} \\ \vec{\boldsymbol{\sigma}}\hat{\vec{p}} & -2\mathbf{I}_{2\times 2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_S(\vec{r}) \end{pmatrix} = \tag{369}$$

$$= E \begin{pmatrix} \mathbf{1}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \mathbf{0}_{2\times 2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_L(\vec{r}) \\ \boldsymbol{\varphi}_S(\vec{r}) \end{pmatrix}$$

The four-component Hamiltonian in this equation is the Lèvy-Leblond Hamiltonian.[59] When a many-particle problem is considered in the one-particle approximation, the key equations for molecular spinors look approximately in the same way as in Eqn (369). For example, the Kohn – Sham equation can be written as follows according to the Lèvy-Leblond approach:

$$\begin{pmatrix} \hat{\mathbf{V}}^{\mathrm{ef}}[\rho,\vec{j}] & \vec{\boldsymbol{\sigma}}\hat{\vec{p}} \\ \vec{\boldsymbol{\sigma}}\hat{\vec{p}} & -2\mathbf{I}_{2\times 2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_{iL}(\vec{r}) \\ \boldsymbol{\varphi}_{iS}(\vec{r}) \end{pmatrix} = \tag{370}$$

$$= \varepsilon_i \begin{pmatrix} \mathbf{1}_{2\times 2} & \mathbf{0}_{2\times 2} \\ \mathbf{0}_{2\times 2} & \mathbf{0}_{2\times 2} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_{iL}(\vec{r}) \\ \boldsymbol{\varphi}_{iS}(\vec{r}) \end{pmatrix}$$

The Lèvy-Leblond approach is equivalent to the Schrödinger equation. This can be demonstrated by applying the ESC procedure to the system of equations (369), from which it is possible to obtain expressions for transformed small and large components

$$\boldsymbol{\varphi}_{\mathrm{s}}(\vec{r}) = \frac{\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{2}\boldsymbol{\psi}_L(\vec{r}) = c\boldsymbol{\psi}_S(\vec{r}) \tag{371}$$

$$\left(\hat{\mathbf{V}}(\vec{r}) + \frac{\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}}{2} - E\right)\boldsymbol{\psi}_L(\vec{r}) = 0 \tag{372}$$

where $\vec{\boldsymbol{\sigma}}\hat{\vec{p}}\vec{\boldsymbol{\sigma}}\hat{\vec{p}}/2$ is the non-relativistic kinetic energy operator.

Thus, Eqn (372) is a one-particle non-relativistic Schrödinger equation. According to Eqn (371), the small component turns to zero in the non-relativistic limit ($c \to \infty$), so that small components are missing in this formalism.

### V.6. Correlated relativistic methods

The electron correlation energy is known to be defined as the difference between the Hamiltonian exact eigenvalue and the mean value in the Hartree – Fock approximation.[547] This definition also holds for relativistic consideration. The relativistic *ab initio* methods describing the wave function at a level higher than the Dirac – Hartree – Fock approximation are correlated. The development of non-relativistic quantum chemical methods taking account of both dynamic and static electron correlations has been in progress for many decades, while the development of the same methods at the relativistic level started quite recently (in 2000). Currently, there are only few correlated relativistic *ab initio* methods. The up-to-date advances in this field are surveyed in a recent review of Fleig.[228]

The development and software implementation of relativistic correlated methods is faced with much more difficulties than those for non-relativistic analogues. Most of these difficulties are caused by the in-depth theoretical aspects of quantum electrodynamics (QED).[548] The relativistic four-component quantum theory, which underlies practicable relativistic quantum chemical methods, is rather some semiempirical approximation of the complete QED description, but it still retains some features of QED, which markedly complicate the description of such issue as electron correlation.

The Dirac – Coulomb – Breit Hamiltonian in the Born – Oppenheimer approximation is a fairly accurate four-component Hamiltonian, which underlies the relativistic four-component quantum theory. The operators, from which the DCB Hamiltonian is constructed, and the operators that appear on switching to the two-component level (Breit – Pauli Hamiltonian) are very complicated for being embedded in the program code, and the calculations of one- and two-electron atomic and molecular integrals are much more costly than non-relativistic computations. Among the most computationally demanding are two-electron spin – orbit integrals of the two-particle spin – orbit coupling operators, SOO and SSO, appearing in the Breit – Pauli Hamiltonian, which are derived from the Gaunt term [78] in the four-component DCB Hamiltonian.[60, 549]

Yet another restricting aspect in the construction of a correlated relativistic approach is the fact that the single-determinant method for the construction of a model wave function does not provide a sufficient level for description of the static correlation in heavy element-containing systems. In the non-relativistic case, when a closed-shell system with a nearly equilibrium geometry is considered, this type of electron correlation does not appear highly significant. It should be taken into account in specific cases, for example, for open-shell systems or systems occurring in the state of chemical bond cleavage, *i.e.*, where there is a number of degenerate states. However, in the relativistic case, everything looks in a different way. Some heavy elements, in particular, d- and f-elements have degenerate (or nearly degenerate) shells, on the one hand, and can occur in open-shell states, on the other hand. Examples are provided by transition metals, lanthanides or actinides. Yet another illustrative example of inadequacy of using single-determinant approach to the calculation of ground-state (and especially excited-state) properties is unsatisfactory accuracy of calculation of the thallium dimer $Tl_2$.[550]

Thus, the theory of a valid relativistic correlated method for the calculation of any properties, particularly SSCCs, should be constructed on the basis of a multideterminantal model of the ground state wave function. Multideterminan-

tal approaches have not found wide use in quantum chemistry even at the non-relativistic level; the progress in this field is reported now and then in the world scientific literature (see, for example, reviews [551, 552]). Some of the multideterminantal methods for the calculation of SSCCs were extended to the relativistic area.

One more problem in the relativistic description of the electron correlation is the presence of the positron continuum spinors (so-called negative energy states). The most popular approach for solving this problem is considering the negative energy spinors as a subset of virtual spinors that always remain vacant, which is called the 'empty Dirac sea'.[37] The application of the 'empty Dirac sea' concept in many-particle relativistic variational calculations with a finite basis set is possible by using the variational Talman principle.[181] The key issue in handling the Fock (or Kohn–Sham) space is the correct elimination of the positron spinor subspace from consideration. This issue is addressed using the *a posteriori* no-pair approximation with respect to the Fock (or Kohn–Sham) operator after every SCF iteration. The theoretical aspects of this problem have been considered by Mittleman.[51] The Brown–Ravenhall [81] problem (or dissolution into the continuum [50]) does not arise with this type of construction of the Fock space, which is an early step in various correlated approaches to SSCC calculation, as this method is equivalent to the application of modified Brown–Ravenhall Hamiltonian.[81]

The influence of other QED effects (*e.g.*, vacuum polarization) on the electron correlation, which has to be taken into account for calculation of molecular properties at the relativistic level, is most often small and overridden by the incomplete basis set error. However, single publications devoted to QED effects manifested in correlated relativistic calculations have already appeared.[553, 554]

Other requirements to an effective relativistic correlated approach are, in principle, the same as the requirements to the correlated non-relativistic approaches to the calculation of SSCCs. Any correlated method for the calculation of SSCCs should possess at least the following properties:

— size extensivity;[555–559] this property comes from thermodynamics and literally means the following: the correlation energy of a system consisting of $N$ interacting subsystems ($A$) in the great $N$ limit is linear in $N$, *i.e.*,

$$\lim_{N\to\infty} \frac{E_{\mathrm{cor}}(N \times A)}{N} = \mathrm{const} > 0$$

This property can also be interpreted in a more simple way, namely, it ensures that the accuracy of the correlation energy calculated using a particular method does not depend on the system dimension;

— core and valence extensivity;[559] this is the property of size extensivity formulated for the core (inactive) and valence (active) electrons.[560] For the calculation of SSCCs, the core extensivity is more significant than the valence extensivity;

— size consistency;[559, 561, 562] the energy of an electron system consisting of non-interacting subsystems should be equal to the sum of the energies of these subsystems. Practically, this means that the configuration space of a complex system is equal to the direct (Cartesian) product of the configuration spaces of its subsystems.

The size extensivity and size consistency properties are not apparently interrelated and, furthermore, the former corresponds to a system consisting of interacting subsystems, while the latter concerns a set of non-interacting subsystems. However, it was claimed [559] that size extensivity is sufficient for size consistency as long as we do not require a description of a certain state.

The first software implementation of the four-component configuration interaction (4CI) method [512] was accomplished in the MOLFDIR program package.[563] This method is restricted to the CISD approximation (the configuration space comprises both single and double excitations), as the full configuration interaction (FCI) method has no practical value for the relativistic case because of absolutely inadmissible computational cost. A considerable drawback of the CISD method is the lack of size extensivity (as opposed to FCI), *i.e.*, this method does not provide a correct scaling of the correlation energy with increase in the number of electrons, which, in turn, may bring about considerable errors in the calculation of SSCCs in bulky molecules. Therefore, the most interest is aroused by the development of relativistic correlated methods for SSCC calculation possessing the size extensivity property.

The most popular size-extensive methods for the calculation of SSCCs are CCSD (see Refs 326 and 564) and CCSD(T) (see Ref. 565). Apart from this, methods based on the coupled cluster (CC) theory provide higher accuracy of description of the correlation energy at lower computational cost than the CI-based approaches at the same level.[566]

The relativistic extension of the CC methods has been reported.[567, 568] Recently, the GAS–CC [237, 569–571] and MRCC [572] methods promising for relativistic calculations of SSCCs have been developed and embedded into the DIRAC program package.[110] Both methods are based on the formalism of spin strings [573, 574] — a universal method for the storage and manipulation of coupled cluster operators.[573] An advantage of the GAS–CC and MRCC methods is the possibility of using exact single-step X2C component decoupling procedures.[275] Ilias and Saue [276] proposed a one-step procedure for finding the relativistic two-component IOTC Hamiltonian [285–288] in the matrix form, which can be used in the CC formalism embedded in the DIRAC package.[110] The researchers cited [276] tested the procedure operability by calculating the excitation and ionization energies for a radon atom.

Unfortunately, the calculation of SSCCs in the relativistic CC formalism has not yet been software implemented; however, there are all prerequisites for such implementation in the future, in particular, in the DIRAC program package.[110] For example, the four-component CI and CC theory for shielding constants already exists and has been practically tested.[575] This attests to the presence of the complete four-component theory of linear response to magnetic perturbations within these formalisms, which serves as the basis, in particular, for the calculation of SSCCs.

The implementation of four-component coupled cluster methods, GAS–CC [237, 571] and MRCC,[572] implies the use of both single-determinant and multideterminantal initial states. The former method is based on a formalism with construction of the excitation space by the selective method.[573, 576] The multideterminantal version of the relativistic GAS–CC approach was applied [577] to calculate the vertical excitation energies in molecules containing atoms of heavy elements. The MRCC method can use the selective state (SS) formalism [578] provided that the size extensivity condition is met. In view of the possibility of calculating the excitation energies by these approaches, in the near future one should expect the development of software for SSCC calculation based on them.

Nevertheless, as mentioned above, for valid relativistic four-component calculation of properties of systems containing heavy elements able to exist in degenerate states, methods based on multideterminantal starting wave function formalism are required. Even a highly accurate method such as 4CCSD(T), which takes into account a considerable part of static correlation, cannot ensure an adequate description of relativistic systems containing heavy elements.

The foundations of the 4MCSCF formalism were reported by Jensen *et al.*,[510] while the relevant program code was implemented in the BERTHA package,[579] which is suitable for four-component relativistic quantum chemical calculations.[106] A version of this formalism called KR – MCSCF [580, 581] has also been embedded in the DIRAC package.[110] Unfortunately, four-component MCSCF methods have not been implemented for the calculation of SSCCs.

Propagator methods form one more group of high-accuracy *ab initio* methods taking into account the electron correlation at different levels. To date, only one propagator method, 4RPA, has been software implemented in the DIRAC package [110] for the calculation of SSCCs, while other relativistic propagator methods beyond the framework of the 4RPA have not yet been applied to SSCCs.

The most popular effective non-relativistic propagator method for the SSCC calculation is SOPPA(MP2) [373, 374, 582, 583] and its two modifications — SOPPA(CC2) [375] and SOPPA(CCSD).[322, 376] However, these methods have not yet been extended to the relativistic area even at a theoretical level.

One more, less well-known non-relativistic propagator approach to the calculation of SSCCs is based on the algebraic diagrammatic construction (ADC) theory proposed by Schirmer.[584] The theory of this method as applied to SSCCs was reported by Trofimov and co-workers.[585] The presence of the ready non-relativistic ADC theory for SSCCs opens up the possibility of extending the theory to the relativistic area. In particular, the last version of the DIRAC14 program [110] envisages the possibility of calculating the electron excitation energies by the ADC method. The paper of Pernpointer [586] outlines the principles of extending the polarization propagator ADC method to the relativistic area, and, hence, the development of a program code for calculation of SSCCs at the level of relativistic ADC approaches is only a matter of time.

### V.7. Software tools for the calculation of spin – spin coupling constants

In this Section, we list the program packages that can be used to calculate SSCCs at non-relativistic, quasirelativistic (one- and two-component) and relativistic (four-component) levels. The list includes only widely used program packages, while local or poorly known programs are not mentioned. The references given to program packages correspond to the latest versions at the time this review was written, and the names of program packages strictly correspond to author's requirements.

**ACES II (Florida version)**,[587] **ACES III (Florida version)**.[588] ACES III is the parallelized version of ACES II. ACESII/III is suitable for SSCC calculation at the non-relativistic TD-HF (RPA) [213, 589 – 594] and EOM-CCSD [324, 595] levels. The software employs special Gaussian basis sets [596] supplied together with the program packages.

**CFOUR/ACES II MAB (Mainz-Austin-Budapest version)**.[597] The SSCC calculation is possible at the non-relativistic TD-HF,[590] MP2,[222, 223] CCSD [326, 564] and CCSD(T) [565] levels. The possibility of using Gaussian basis sets from internal and external libraries is envisaged (*e.g.*, the EMSL basis set library [598, 599]).

**ADF**.[209 – 211] The SSCCs are calculated at the non-relativistic TD-DFT level (CP – DFT) [600 – 604] using the LDA and GGA functionals. The relativistic calculations of SSCCs are performed at the two-component level within the ZORA – DFT approximation (either including or not including spin – orbit coupling) [466] using the same functionals. The ADF program uses the integrated Slater basis sets (which are known to describe most accurately the near-nuclear region) of various types (SZ, DZ, DZP, TZP, TZ2P and QZ4P) for all elements ($Z = 1 – 118$). The basis sets include both non-relativistic and relativistic ones and are optimized in the ZORA approximation.[202, 204] In early versions of ADF, only the point nucleus model was available,[194] and starting from the version ADF2009.01, the spherical Gaussian nuclear charge distribution model has become available.[194, 196, 201] The medium effects can be included using the COSMO model [605 – 607] or the QM/MM model.[608]

**DALTON** [186] is a quantum chemical program package, named after John Dalton, the founder of the atomic theory of the structure of matter. The SSCCs are calculated at the non-relativistic TD-HF,[589 – 594] TD-MCSCF,[217, 609] TD-DFT,[600 – 603] SOPPA(MP2),[373, 374, 582, 583] SOPPA(CC2) [375] and SOPPA(CCSD) [322, 376] levels. It is possible to find the vibrational corrections and medium effect-related corrections within the IEF – PCM model [610, 611] and the RFM model,[612 – 615] known also as MPE.[616, 617]

**DIRAC**.[110] The SSCCs can be calculated at the relativistic 4RPA level [183, 217, 240, 295] and TD-4DFT level [117, 241, 358 – 361] using the four-component Dirac – Coulomb or Dirac – Coulomb – Gaunt Hamiltonian. The presence of the Gaunt component in the four-component Hamiltonian sharply increases the time of calculation; however, it is needed for considering the spin – orbit coupling, as it is responsible for the two-electron SOO and SSO contributions in the two-component Breit – Pauli Hamiltonian. Complete elimination of the spin – orbit coupling from consideration (scalar approximation) at the four-component Hamiltonian level is also envisaged. This is done using the four-component spin-free Dyall – Kutzelnigg Hamiltonian.[97] The four-component non-relativistic 4RPA and TD-4DFT calculations of SSCCs can be performed using the four-component Lèvy-Leblond Hamiltonian.[59] The non-relativistic limit can also be found by mere 9 – 10-fold increase in the velocity of light.

There is a broad choice of two-component TD-HF and TD-DFT schemes, including exact component decoupling schemes, such as X2C,[276] X2Cmmf [618] or BSS,[285, 286] and approximate A2C approaches:[507] ZORA,[372, 449, 451] DKH1, DKH2.[264] In fact, the choice of two-component schemes available for a DIRAC user is much wider, as there are a number of secondary parameters. These parameters control some aspects such as switching on/off of two-electron integrals of various types (SS |SS), (SL|SS), (SL|SL), (SL|LL) and switching on/off of the AMFI approximation,[521 – 524] which simulates the two-electron spin – orbit SSO and SOO contributions as an effective one-electron spin – orbit Hamiltonian. Switching off of the AMFI approximation reduces the computation time but removes from consideration any two-electron spin – orbit coupling, which finally evolves in a substantial overestimation of the spin – orbit contribution to SSCCs.

The possibility of SSCC calculation at the two-component level in the scalar approximation is envisaged. Note that in this case, the two-component level loses its meaning and the scheme is reduced to an one-component scheme taking into account only scalar relativistic effects. A non-relativistic calculation of SSCCs can also be performed in this package within the one-component Schrödinger formalism.

In four-component calculations using the DIRAC package, it is possible to choose the type of kinetic balance, particularly, in the case of SSCC calculation, this may be either a restricted kinetic balance (RKB)[105,107,108] or an unrestricted kinetic balance (UKB).[105,108] The restricted magnetic balance (RMB)[117,118] has not yet been included in the DIRAC program. One can choose between two nucleus models, Gaussian[194,196] and point[194] ones; the program operates with Gaussian basis sets from internal and external libraries, in particular, large component basis sets from the DALTON library can be used.[186] In the latest DIRAC version, it is possible to include the medium effects in the relativistic calculations of SSCCs using both the non-relativistic PCM model[610,611] and the relativistic four-component PCM model.[619]

**Gaussian09**[620] is a multidimensional quantum chemical program package, which can be used to calculate SSCCs at the non-relativistic TD-HF and TD-DFT levels. Medium effect-related corrections can be calculated by means of the IEF–PCM model.[610,611] The Gaussian09 program code uses the Gaussian basis sets. The latest version has special options for calculation of SSCCs related to improved basis sets for increasing the accuracy of TD-DFT description of inner shells, which largely determine the Fermi-contact contribution. As applied to SSCCs, Gaussian09 performs automatically a two-step calculation procedure, first, using the standard basis sets and then using modified basis sets, particularly for the calculation of the Fermi-contact contribution.

**NWChem 6.5** (see Ref. 621) is a quantum chemical program package with a parallelized code directed at effective solution of quantum chemical problems for large systems. The SSCC calculation by means of this package is possible at the non-relativistic TD-HF and TD-DFT levels.

**ReSpect**[296] is a quantum chemical program package with a completely parallelized code directed at high-accuracy calculation of the spectroscopic properties of systems containing heavy nuclei. Using this package, it is possible to calculate SSCCs[600,602,622] at the four-component DHF and DFT (DKS) levels using the restricted magnetic balance.[117,118] The SSCC calculation can be performed in terms of either the point model[194] or Gaussian model[194,196] of the nucleus.

**COLOGNE 2006**[480] is a quantum chemical program package with an embedded code for the calculation of SSCCs[266] at the quasirelativistic two-component IORA[267] and IORAmm[453] levels using TD-HF and TD-DFT formalisms. The non-relativistic code for calculation of SSCCs using the same formalisms is also envisaged.[292]

* * *

This review of modern relativistic methods for quantum chemical calculation of spin–spin coupling constants in the NMR spectra demonstrated the exceptional importance of inclusion of relativistic effects in NMR-oriented high-level calculations for molecules containing atoms of the fourth and subsequent periods of the Periodic Table using either the full four-component relativistic Dirac equation or various two-component approximations. The review covers examples and discusses the prospects of application of relativistic calculations of SSCCs in the structural studies of organic and heteroorganic compounds and gives practical recommendations for performing such calculations using modern software. Unfortunately, owing to the very high computational cost of relativistic calculations of SSCCs (which are incommensurable with the cost of analogous non-relativistic calculations), they are still few. However, we are confident that the progress has already taken shape and that in view of the vigorous development of computational power, in the upcoming decade, one should expect a breakthrough in this field and large-scale advent of *ab initio* methods for calculation of SSCCs for organometallic and heteroorganic compounds in the quantum chemical practice.

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