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Modern quantum chemical methods for calculating spin – spin coupling constants: theoretical basis and structural applications in chemistry

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Abstract. The modern quantum chemical methods for calculating spin – spin coupling constants in NMR spectra are reviewed. The theoretical basis of these methods and author's vision of the prospects of their development and practical applications in structural and stereochemical studies are presented. The bibliography includes 288 references.

I. Introduction

During the last two decades quantum chemical methods for calculating molecular structures and molecular properties have been widely applied in practical chemical investigations. Rapid progress in computer technologies, primarily based on personal computers and the development of readily available quantum chemical packages and modern tools for visualizing molecules and spatial electron density distribution were a revolution in the quantum chemical applications for most diverse fields of chemistry. Quite a short time ago only small teams of professional theoreticians were involved in quantum chemical calculations of molecular properties, whereas currently these calculations have become a part of routine work of most large chemical laboratories of the world.

Search for stationary points on the potential energy surface, which leads to localization of ground and transition states of molecules, optimization of geometric parameters and estimation of the relative stability of configurational and conformational isomers, as well as calculation of charge density distribution and dipole electric and magnetic moments, can be performed relatively rapidly and at a high theoretical level using modern personal multiprocessor computers. All this holds true for the calculation of other first-order molecular properties, defined as the mean values of the corresponding perturbation operators for molecular system over unperturbed wave function of the ground state and for the study of mechanisms of reactions applying the method of gradient tracking over an internal coordinate of reaction.

The situation with *ab initio* calculation of spectral NMR parameters — chemical shifts (magnetic shielding constants) and spin – spin coupling constants (SSCCs), which are determined by the linear response function with allowance for all excited states (*i.e.*, are second-order molecular properties) — is much more difficult.

Despite the exceptional importance of SSCCs in structural and stereochemical studies of chemical molecules [assignment of configurations, conformational analysis, 'tracing out the carbon skeleton' (*i.e.*, establishing carbon – carbon connectivity patterns based on measuring $^{13}C-^{13}C$ SSCCs between neighbouring carbon nuclei), study of the nature of chemical bonding and stereoelectronic effects and many other problems], *ab initio* calculation remains a fairly complex problem for chemists, because it contains many pitfalls and requires to take into account electronic correlations (especially when inner electrons are involved) not lower than at the level of second-order perturbation theory, use special basis sets and consider effects of environment and vibrational corrections (as well as relativistic effects for heavy nuclei). All these factors make the resource intensity of calculation programmes very high, exceeding of several orders of magnitude the resource intensity for standard calculations of ground-state energies, optimization of geometric parameters and determination of the first-order molecular properties.

This review generalizes the long-term experience of the authors in the theory and chemical applications of high-precision quantum chemical calculations of SSCCs at the high level of modern nonempirical theory; the main attention is paid to the publications of our numerous colleagues and our own results obtained during the two last decades.

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There is a good many of comprehensive reviews (see, *e.g.*, Refs 1 and 2) and chapters in books [3–6] and monographs [7,8] in the world literature that are devoted to the problems of spin–spin coupling theory and SSCC calculations; their authors are well-known experts in this field. However, almost all of them are theoreticians and, as a result, these publications are focused on specifically fundamental theoretical problems of spin–spin coupling, whereas much less attention is paid to purely practical aspects of nonempirical SSCC calculations. The latest versions of the GAUSSIAN programme finally implemented the SSCC calculation procedure in a user-friendly key words fashion at the level of density functional theory (DFT). This approach is very convenient for user. When the aforementioned GAUSSIAN versions were released, researchers all over the world were actively engaged in SSCC calculations; many of them were novices in this field. As a result, many authors are not always aware of possible inadequacy of these calculations in view of some DFT limitations in calculations of second-order molecular properties (to which SSCCs belong), which call for consideration of excited molecular states.

Simultaneously with the DFT methods, much more exact, purely *ab initio* methods for calculating SSCCs, based on the formalism of wave function perturbation theory (primarily, the polarization propagator methods) and, on the one hand, the coupled-cluster theory, are being elaborated. Although these techniques were developed and implemented in corresponding programmes a long time ago, they have been used in practice only recently because of evident computational limitations. Indeed, on the resource intensity scale, these approaches are characterized by the numbers of involved molecular orbitals on the orders of 10^5 and 10^6, respectively; *i.e.*, they are incomparably more resource-intensive in comparison with the DFT methods. Nevertheless, against the background of overall dominance of DFT methods, the polarization propagator approach and coupled-cluster theory are actively developed and implemented in the practice of SSCC calculations for real organic molecules. The latest achievements in this field were recently generalized in the review by Krivdin and Contreras,[9] the emphasis of which was on the structural applications of modern theoretical SSCC calculations. This review is a logical continuation of Ref. 9; it is focused mainly on the theoretical basis and purely practical aspects of *ab initio* SSCC calculations for organic molecules of intermediate size and, to a smaller extent, structural applications of these calculations. The latter are restricted to the most striking and significant results, obtained mainly in the last decade.

After a brief introduction to the spin–spin coupling theory at the nonrelativistic level, we discuss the relative advantages and drawbacks of the main quantum chemical methods applied in SSCC calculations, including semiempirical and early *ab initio* Hartree–Fock methods, along with more novel methods, which take into account the electronic correlation effects at the DFT level, configuration interaction theory, coupled-cluster theory and the polarization propagator theory (Green's function theory). A list of available licensed and commercial programme products implementing the aforementioned SSCC calculation methods is presented. From the purely practical point of view, we analyze the main factors affecting the accuracy of SSCC calculations, including the quality of basis sets (particular attention is paid to special basis sets that are extended by tight functions used in SSCC calculations), consideration of vibrational corrections, influence of environment and relativistic effects.

The second part of the review contains the most illustrative examples of structural applications of modern SSCC calculation methods, including the analysis of the nature of chemical bonding in sterically strained systems, configuration assignment of azomethines, conformational analysis of organic and organometallic compounds, stereochemical studies of carbohydrates (configuration of anomeric centre, conformational analysis of carbohydrate ring, rotational conformers of hydroxyl groups) and study of hydrogen bonds and intermolecular complexes.

This review is addressed not to theoreticians but rather to chemical researchers (especially the young ones), who use the NMR method in combination with high-precision theoretical SSCC calculations at the modern quantum chemical level to solve structural chemical problems.

II. Theory of spin–spin coupling constants in NMR spectra

Spin–spin coupling arises as a result of magnetic interaction between individual nuclei in a molecule and is propagated either directly through space or through electrons involved in chemical bonds. The first-type interaction is experimentally observed in crystals with a lattice characterized by pronounced anisotropy. The second-type interaction, which is also referred to as indirect spin–spin coupling, is mainly observed in liquids and gases, *i.e.*, in isotropic media. SSCCs for specifically the second case are considered in this review. A more detailed analysis of the theoretical aspects of nuclear spin–spin coupling can be found, for example, in the recent comprehensive reviews [1–3,10] and in many earlier reviews cited therein.

The energy (E) of indirect nuclear spin–spin coupling is defined as the part of the total energy of the system that contains the scalar product of nuclear spin vectors (**I**) (h is Planck's constant):

$$E = \sum_{N>N'} h J_{NN'} \mathbf{I}_N \mathbf{I}_{N'} \qquad (1)$$

The quantity $J_{NN'}$ in expression (1) has the dimension of frequency and is the SSCC between nuclei N and N'. Generally, the SSCC value depends both on the electronic structure of the system and spatial arrangement of nuclei and on the characteristics of coupled nuclei. Therefore, SSCC is most often written in the form

$$\mathbf{J}_{KL} = h\frac{\gamma_K}{2\pi}\frac{\gamma_L}{2\pi}\mathbf{K}_{KL} \qquad (2)$$

where γ_K and γ_L are the gyromagnetic ratios of the corresponding nuclei and $\mathbf{K}_{KL}$ is referred to as the reduced SSCC, which is independent of the specific type and isotopic composition of coupled nuclei.

The nuclear spin–spin coupling energy is too small in comparison with the total electron energy of molecule;[2] therefore, the interaction energy of nuclear magnetic moments is considered as a perturbation of the electronic system. In the presence of this perturbation, the energy of the system can be written as an expansion in Taylor series in

perturbation powers, in our case, in powers of nuclear magnetic moments (**M**):

$$E = E_0 + \sum_K \frac{\partial E}{\partial \mathbf{M}_K}\bigg|_{\mathbf{M}_K=0} \mathbf{M}_K + \tag{3}$$

$$+\frac{1}{2}\sum_{K,L} \frac{\partial^2 E}{\partial \mathbf{M}_K \partial \mathbf{M}_L}\bigg|_{\mathbf{M}_K,\mathbf{M}_L=0} \mathbf{M}_K \mathbf{M}_L + \ldots$$

The nuclear magnetic moments are expressed in terms of nuclear spins as follows:

$$\mathbf{M}_N = \gamma_N \hbar \mathbf{I}_N \tag{4}$$

The expressions at first powers of magnetic moments in formula (3) are assigned to the so-called first-order properties, the expressions at second powers of magnetic moments are assigned to second-order properties *etc*.

Having compared the third term in expansion (3) with expression (1) and taking into account formulas (2) and (4), one can conclude that the expression for the reduced SSCC is the second derivative of energy with respect to the magnetic moments of interacting nuclei and, therefore, is a second-order property:

$$\mathbf{K}_{KL} = \frac{\partial^2 E(\mathbf{M})}{\partial \mathbf{M}_K \partial \mathbf{M}_L}\bigg|_{\mathbf{M}=0} \tag{5}$$

According to the nondegenerate stationary Rayleigh–Schrödinger perturbation theory, the second correction to the energy of the system under mixed perturbation can be presented by expression (6).[2]

$$\frac{\mathrm{d}^2 E(\mathbf{x})}{\mathrm{d}x_i\,\mathrm{d}x_j} = \langle \Psi_0 | \frac{\mathrm{d}^2 \widehat{H}}{\mathrm{d}x_i\,\mathrm{d}x_j} | \Psi_0 \rangle - \tag{6}$$

$$-2\sum_{n\neq 0} \frac{\langle \Psi_0 | \mathrm{d}\widehat{H}/\mathrm{d}x_i | \Psi_n \rangle \langle \Psi_n | \mathrm{d}\widehat{H}/\mathrm{d}x_j | \Psi_0 \rangle}{E_n - E_0}$$

The first term in expression (6) is the mean of the second mixed derivative of the Hamiltonian with respect to the ground state of the system, whereas the second term is the so-called sum over states for each excited state of the system, Ψ_n, with an energy E_n.

Based on expression (6) and in correspondence with the nonrelativistic Ramsey theory,[11] the reduced SSCC for nuclei K and L can be written as

$$\mathbf{K}_{KL} = \langle 0 | \mathbf{h}_{KL}^{dso} | 0 \rangle - 2\sum_{n_S\neq 0} \frac{\langle 0 | \mathbf{h}_K^{pso} | n_S \rangle \langle n_S | (\mathbf{h}_L^{pso})^T | 0 \rangle}{E_{n_S} - E_0} - \tag{7}$$

$$-2\sum_{n_T} \frac{\langle 0 | \mathbf{h}_K^{sd} + \mathbf{h}_K^{fc} | n_T \rangle \langle n_T | (\mathbf{h}_L^{sd})^T + (\mathbf{h}_L^{fc})^T | 0 \rangle}{E_{n_T} - E_0}$$

where **h** are single-particle perturbation operators.

Summation in the second term of expression (7) is over singlet excited states, whereas summation in the third term is over triplet excited states.

It is generally accepted to select four contributions to SSCC in expression (7): diamagnetic spin–orbit (DSO) contribution, corresponding to the first term of the expression; paramagnetic spin–orbit (PSO) contribution, corresponding to the second term; as well as the spin-dipolar (SD) contribution and the contribution related to Fermi contact (FC) interaction, which occur in the third term of the expression. The form of these operators is set by formulas (8)–(11).

$$\mathbf{h}_{KL}^{dso} = \frac{\alpha^4}{2} \sum_i \frac{(\mathbf{r}_{iK}\mathbf{r}_{iL})\mathbf{I} - \mathbf{r}_{iK}\mathbf{r}_{iL}^T}{r_{iK}^3, r_{iL}^3} \tag{8}$$

$$\mathbf{h}_K^{pso} = \alpha^2 \sum_i \frac{\mathbf{l}_{iK}}{r_{iK}^3} \tag{9}$$

$$\mathbf{h}_K^{sd} = \alpha^2 \sum_i \frac{3(\mathbf{s}_i \mathbf{r}_{iK})\,\mathbf{r}_{iK} - \mathbf{r}_{iK}^2 \mathbf{s}_i}{r_{iK}^5} \tag{10}$$

$$\mathbf{h}_K^{fc} = \frac{8\pi\alpha^2}{3} \sum_i \delta(\mathbf{r}_{iK})\,\mathbf{s}_i \tag{11}$$

Here, $\mathbf{r}_{iK}$ is the radius vector of the ith electron with respect to the Kth nucleus; α is the fine-structure constant; $\mathbf{s}_i$ and $\mathbf{l}_i$ are, respectively, the spin and orbital angular momentum operators.

Spin–orbit coupling, including both diamagnetic and paramagnetic ones, is implemented through the effect of nuclear magnetic moments of one nucleus K on the orbital angular momenta of the molecular electrons, as a result of which induced electron currents arise. The latter, in turn, generate magnetic field at the point where the second nucleus L is located. Thus, the spin–orbit coupling between nuclear magnetic moments propagates through the orbital angular momenta of electrons.

Spin–dipole coupling occurs between the magnetic moment of nucleus and the magnetic spin moments of electrons; this process causes electron–spin polarization of the molecular electronic shell. In turn, the magnetic spin moment induced by the first nucleus interacts with the magnetic moment of the second nucleus.

Fermi contact interaction occurs directly between the magnetic spin moment of electron and the nuclear magnetic moment if the probability of finding electron on the nucleus surface is nonzero. In particular, this primarily concerns electrons within the hydrogen-like atom model. As in the case of spin–dipole coupling, the induced magnetic spin moment (which arises due to the contact Fermi interaction) is transferred *via* bond electrons to the second nucleus.

It is noteworthy that Fermi contact interaction generally dominates in the total SSCC value, especially for nuclei separated by one chemical bond; however, there are exceptions. For example, it was shown[12] that paramagnetic spin–orbit and spin–dipole contributions dominate in the ClF_3 molecule. In many other molecules the PSO and SD contributions for the fluorine–fluorine SSCC are important just like the FC contribution.[13] In addition, for long-range SSCCs (*i.e.*, SSCCs for interacting nuclei separated by two or more chemical bonds), the FC contribution to the coupling constant is often of the same order of magnitude with other contributions.

Expression (7) implies the following: to calculate the contributions of spin–dipole and Fermi contact interactions to SSCC, one must know the energies of triplet excited states; this knowledge, in turn, calls for qualitative consideration of electronic correlations. This factor is also important for the orbital paramagnetic contribution, which

includes summation over excited singlet states. To calculate directly the sum over states in expression (7), one must know all singlet and triplet excited states; this calculation is fairly difficult to perform in practice. Instead of this, the contributions to the coupling constant that require knowledge of excited states are often calculated using the so-called linear response theory.[14, 15]

III. Methods for calculating spin–spin coupling constants

Almost all calculations of properties of polyatomic molecules are based on approximate solutions of the Schrödinger equation. Out of the two basic approaches in the theory of the chemical bond, the valence-bond method and the molecular orbital method, the latter has significant advantages in programme realization. Therefore, almost all main calculation methods of modern quantum chemistry use the approximation of molecular orbitals within the scheme of linear combination of atomic orbitals.

The existing methods for calculating SSCCs can be divided into two large classes: semiempirical and *ab initio*. Let us note at once that the latest advances in computational tools make (and almost have made) semiempirical methods to be the attributes of the past; nowadays, they are of purely historical interest. Nevertheless, semiempirical methods played an important role in the development of modern *ab initio* methods for calculating SSCCs; therefore, we will briefly dwell on them and their specific features in this review.

1. Semiempirical and early *ab initio* methods

It is noteworthy that almost all semiempirical methods that are used in SSCC calculations are valence-bond methods; *i.e.*, in contrast to nonempirical methods, they take into account only the valence electrons and the atomic orbitals of valence shells. The following three semiempirical versions of perturbation theory are most widespread in SSCC calculations: sum-over-states (SOS) formalism, finite perturbation theory (FPT) and self-consistent perturbation theory (SCPT).

The SOS formalism, which was developed by Pople and Santry,[16] was one of the first methods used in SSCC calculations. Within this method the FC contribution to SSCC is expressed in terms of mutual atom–atom polarizabilities in the mean excitation energy approximation.[17] When SSCC is calculated within the FPT method,[18–20] numerical differentiation is performed in expression (5) with some perturbing parameter introduced. In this approach, the SSCC value is proportional to the difference in molecular energies at different orientations of nuclear magnetic moments, which play the role of perturbation. Blizzard and Santry[21] proposed the SCPT method for SSCC calculations, which differs from the FPT method by a more efficient computational algorithm. Application of the perturbation theory in this method with respect to the Fock–Dirac density matrix allows one to avoid direct use of perturbed states in calculations.

Semiempirical SSCC calculations were generally performed in valence neglect-of-differential-overlap (NDO) approximations, such as complete neglect of differential overlap (CNDO), intermediate neglect of differential overlap (INDO) and modified neglect of differential overlap (MNDO).

The CNDO method[22] considers explicitly only valence electrons. The NDO approximation is applied for all atomic two-electron integrals and the electronic repulsion is considered to depend on only the nature of atoms rather than individual orbitals. The CNDO method introduces an empirical parameter, referred to as the resonance integral, which is chosen individually for each atom.

A significant drawback of the CNDO method is the absence of exchange integrals, as a result of which one cannot calculate singlet and triplet excited states, whereas the latter play a key role in SSCC calculations. This drawback can partly be overcome in the INDO method,[23] where one-centre Coulomb and exchange integrals are retained. In contrast to the CNDO and INDO approximations, within the MNDO method[24–26] only the two-electron integrals containing products of atomic orbitals centred at different atoms are equated to zero.

Ab initio calculations, in contrast to semiempirical ones, are based on solutions to quantum chemical equations, which contain no experimental parameters, except for fundamental physical constants. Undoubtedly, the main calculation method of quantum chemistry is the Hartree–Fock method,[27, 28] although it disregards electronic correlation effects, while the latter, as will be shown below, are a factor of fundamental importance in SSCC calculations.

The Hartree–Fock method is an approximate method for solving the Schrödinger equation by reducing a many-particle problem to a single-particle one on the assumption that each particle moves in some mean self-consistent field induced by all other particles of the system. This method includes several stages. In the first stage, it is necessary to solve the problem of electron motion in a certain model potential, which should reflect as exactly as possible the interaction of moving electron with atomic nuclei and other electrons. The found wave functions are used to determine the interaction potential of the electron under consideration with other electrons. Furthermore, the problem of finding the wave functions of electron for the new potential and determining the next, more exact potential from it is solved repeatedly. This procedure, which is also known as the method of self-consistent field, is continued until it reaches the convergence in energy.

There are two versions of the Hartree–Fock method: one for the systems with closed electron shells and one for the systems with open shells. This method makes it possible to calculate the total energy of molecules with an error of few percent, which is generally too large for calculating relatively fine energy characteristics, such as SSCCs. The main drawback of this method is that it disregards the electron correlation energy and, therefore, incorrectly determines excited states. However, the main advantage of the Hartree–Fock method is that the wave functions obtained in it are a good initial approximation for other, more exact methods.

Due to the rapid progress in the development of modern personal computers and computational clusters, the range of application of more exact and more complex SSCC calculation methods, which take into account electronic correlation and exchange interactions, constantly increases. These are primarily the methods based on electron-density functional theory, configuration interaction theory, coupled-cluster theory and polarization propagator theory. It is noteworthy that the factor of key importance in SSCC calculations, as will be shown below, is the consideration of

internal electronic correlation, *i.e.*, electronic correlation with participation of inner (core) electrons.

2. DFT-based methods

The electron-density functional method has become extremely popular in the last years. This is especially true for calculations of second-order molecular properties, such as chemical shifts and spin – spin coupling constant, because the resource intensity of these calculations for DFT methods is much lower than for the classical *ab initio* methods based on the formalism of wave function perturbation theory.

It should be recalled that this method was preceded by the Thomas – Fermi model, which was proposed as early as in 1927. Within this model the energy of an atom was presented as the sum of its kinetic energy, expressed in the form of electron density functional and the potential energy of interaction of electrons with nucleus and with each other; the interaction energy was also expressed in terms of electron density. Despite the significant role played by the Thomas – Fermi model in the development of quantum mechanics, its accuracy was insufficient, because it disregards the exchange interaction, in contrast to (for example) the aforementioned Hartree – Fock method.

The basic concept of the density functional theory is that the electronic subsystem is described using the electron density matrix rather than the many-electron wave function, in contrast to classical *ab initio* methods. This approach significantly simplifies the problem, because the many-electron wave function depends on $3N$ variables, where N is the number of electrons in the molecular system, whereas the electron density is a function of only three spatial coordinates.

The formalism of electron-density functional theory is based on two Hohenberg – Kohn theorems.[29] According to the first theorem, the electron density of the ground state of a many-electron system located in some external potential unambiguously determines this potential. According to the second theorem, for any positively determined trial electron density function ρ, such that $\int\rho(\mathbf{r})\mathrm{d}\mathbf{r} = N$, the energy of the system is the electron density functional; in this case, the relation $E[\rho] \geqslant E_0$ is satisfied. It follows from the first theorem that not only the arrangement of atomic nuclei determines the electron density distribution in the molecule (obtained, *e.g.*, by solving the Hartree – Fock equations, which include explicitly the interaction between electrons and nuclei), but also the arrangement of atomic nuclei itself can be found from the electron density function.

The computational scheme developed by Kohn and Sham and known as the Kohn – Sham equation is based on the Hohenberg – Kohn theorems.[30] The main point of this approach is that the exact electron density function of the ground state of many-electron system is replaced with the function for noninteracting particles; an auxiliary Hamiltonian is built, which contains a kinetic term for noninteracting electrons and, at the same time, an effective local potential that is responsible for the Coulomb interaction, electronic correlation and exchange interaction. The exact energy functional of the system can be written as:

$$E[\rho] = T[\rho] + V_{\mathrm{ext}}[\rho] + V_{\mathrm{ee}}[\rho] \tag{12}$$

where $T[\rho]$ is the kinetic term, $V_{\mathrm{ext}}[\rho]$ is the term responsible for the interaction with the external potential and $V_{\mathrm{ee}}[\rho]$ is the term responsible for the electron–electron interaction. Since the exact expression for the kinetic term is unknown, it is replaced with the expression for a system of N noninteracting electrons within the single-determinant wave function built from N orbitals ϕ_i:

$$T_{\mathrm{s}}[\rho] = -\frac{1}{2}\sum_{i}^{N}\langle\phi_i|\nabla^2|\phi_i\rangle \tag{13}$$

Having additionally selected the term responsible for the Coulomb interaction between electrons from the third term in expression (12),

$$V_{\mathrm{H}}[\rho] = \frac{1}{2}\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{14}$$

one can write the energy functional in the form

$$E[\rho] = T_{\mathrm{s}}[\rho] + V_{\mathrm{ext}}[\rho] + V_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho] \tag{15}$$

Expression (15) contains the so-called exchange-correlation functional $E_{\mathrm{xc}}[\rho]$, which is actually the sum of errors arising when the approximation of noninteracting electrons for kinetic energy and classical electron–electron interaction are used:

$$E_{\mathrm{xc}}[\rho] = (T[\rho] - T_{\mathrm{s}}[\rho]) + (V_{\mathrm{ee}}[\rho] - V_{\mathrm{H}}[\rho]) \tag{16}$$

Having applied the variational principle to expression (15), one obtains the following set of equations:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}' + V_{\mathrm{xc}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r}) \tag{17}$$

$$\rho(\mathbf{r}) = \sum_{i}^{N}|\phi_i(\mathbf{r})|^2 \tag{18}$$

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho} \tag{19}$$

This system of nonlinear equations describes the behaviour of noninteracting electrons in some effective local potential. If the exchange-correlation functional and, therefore, the local potential are exactly known, the orbitals obtained yield exact values for the electron density and energy of the ground state. The Kohn – Sham equations have the same structure as the Hartree – Fock equations, in which the exchange potential is replaced with the local exchange-correlation potential. Thus, the Kohn – Sham equations are solved using an iterative procedure similar to the scheme applied in the Hartree – Fock method.

The simplest approximation for describing the exchange-correlation interaction within the electron-density functional theory is the local-density approximation (LDA). Here, it is assumed that the electron density is a function slowly varying in space; *i.e.*, the initially inhomogeneous system is interpreted as locally homogeneous. The exchange-correlation functional in the LDA approximation is most often obtained by combining the Dirac – Slater exchange functional (S)[31, 32] with the Vosko – Wilk – Nusair (VWN) correlation functional.[33]

A higher order approximation is the generalized gradient approximation (GGA), which takes into account the change in the electron density at a transition to neighbour-

ing points of space; *i.e.*, introduces the dependence of energy on the electron density gradient. The three best-known exchange-correlation functionals within the GGA approximation are the combination of the Becke exchange functional[34, 35] with the Lee–Yang–Parr correlation functional (BLYP),[36] the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional,[37, 38] and the Perdew–Wang exchange-correlation functional (PW91).[39]

In addition, the so-called hybrid functionals, which combine GGA functionals with the exchange term within the Hartree–Fock theory, are currently widely used. In particular, one of the most popular hybrid functionals is the widely known three-parameter Becke–Lee–Yang–Parr functional (B3LYP).[40] Another well-known hybrid functional is the Perdew–Burke–Ernzerhof functional (PBE0).[41]

One of the first successful realizations of the Kohn–Sham theory in SSCC calculations was the method proposed by Malkin, Malkina and Salakhub in 1994[42, 43] at the level of the LDA and GGA approximations. It is noteworthy that in this method the spin–dipole contribution to the constant was not calculated and the paramagnetic spin–orbit contribution was approximated at the level of summation over states. The first completely analytical realization of the Kohn–Sham theory in SSCC calculations, which took into account all four contributions to the coupling constant, was presented in 2000 by Cremer and coworkers,[44] and (independently) by Helgaker *et al.*[45]

The methods based on the formalism of electron-density functional theory give fairly exact results in SSCC calculations for the systems that are difficult to study by more precise *ab initio* methods, for example, in large organic molecules or molecules containing transition metal atoms. For example, Peralta *et al.*[46] calculated the carbon–carbon constants in the C_{70} molecule at the B3LYP/cc-pCVDZ-sd level and obtained very good agreement with the experimental data. A good agreement with experiment was also achieved within using the electron density functional method in SSCC calculations for platinum complexes[47] and thymidines.[48]

However, despite the enviable and ever-growing popularity, all the methods of electron-density functional theory are parametric in their origin, and the accuracy of SSCC calculations is much worse than that of purely *ab initio* methods based on the formalism of wave function perturbation theory; the latter are considered below.

3. Methods based on configuration interaction theory

The configuration interaction (CI) method is the most precise *ab initio* method for taking into account the electronic correlation. Here, the complete wave function of the electronic system is written in the form of a linear combination of Slater determinants corresponding to different electronic configurations. Slater determinants are constructed using molecular orbitals obtained from the solution of the Hartree–Fock problem:

$$\Psi_{CI} = a_0\Phi_{HF} + \sum_S a_S\Phi_S + \sum_D a_D\Phi_D + \sum_T a_T\Phi_T + \ldots \quad (20)$$

$$+\ldots = \sum_{i=0} a_i\Phi_i$$

Here Ψ_{CI} is the complete wave function of the molecular system with allowance for the configuration interaction and Φ_i are the wave functions of the excited states of this system. The determinants of the configuration basis are constructed by replacing one or several occupied spin orbitals $\psi_\alpha, \psi_\beta, \ldots$ in the function $\Phi_0 = \Phi_{HF}$ with the same number of virtual unoccupied spin orbitals $\psi_a, \psi_b, \ldots$. These configurations are considered as a result of excitation of electrons from the orbitals $\psi_\alpha, \psi_\beta, \ldots$ to the orbitals $\psi_a, \psi_b, \ldots$ and the number of replacements of occupied orbitals with virtual ones is referred to as the excitation multiplicity. Configurations with single, double, triple, *etc.* excitations are denoted by symbols S, D, T, *etc.* The expansion coefficients a_i are found by applying the variational principle, as a result of which the problem is reduced to a problem on determining the eigenvalues of the Hamiltonian matrix $\hat{H}$ with matrix elements $\langle\Phi_i|\hat{H}|\Phi_j\rangle$.

The versions of the configuration-interaction method are classified with respect to the multiplicity of excited configurations included in expansion. The scheme with the configuration basis containing only singly excited configurations is referred to as the CIS method, the scheme containing both single and double excitations is called the CISD method, *etc.* The CIS method does not improve the calculation of the correlation energy in comparison with the Hartree–Fock method. In turn, CISD calculation makes it possible to take into account approximately 95% correlation energy.[49] The so-called full configuration interaction (FCI), in which all possible excitations are considered, occupies a particular place. The difference in the energies obtained by the FCI and Hartree–Fock methods yields the exact correlation energy for a given basis set. The FCI approach is the most exact method for taking into account the electronic correlation for a given basis; however, when the size of the basis set increases, the number of configurations used increases as the factorial of the number of basis functions; hence, the FCI method can be applied to only very simple systems. For example, the hydrogen fluoride molecule calculated by the FCI method in the DZ+P basis set calls for 944348 (!) configurations.[49] No wonder that there are only few studies devoted to SSCC calculations by the FCI method; among them, we should note interesting and exotic works aimed at calculating the helium–helium constant in helium dimer,[50] boron–proton constant in the hypothetical BH[51] molecule and the deuteron–proton constant in the HD molecule.[52]

Although the CI methods deal with a large number of determinants, they are constructed using one initial electron configuration, described by the Hartree–Fock determinant. This configuration is dominant; *i.e.*, the factor before Φ_0 in the representation of the complete wave function (20) is close to unity. Therefore, the above-considered methods are formally assigned to single-configuration ones. However, there are compounds whose ground state cannot be in principle described by a single electron configuration (*e.g.*, cyclobutadiene). Therefore, the further expansion of the configuration-interaction method was the model of multiconfiguration self-consistent field (MCSCF). This approach is a configuration-interaction method in which not only coefficients at different configurations are optimized according to the variational principle but the expansion coefficients of molecular orbitals in atomic orbitals, which are used to construct individual configurations, are also optimized within the self-consistent field theory. The coefficients at configurations depend on the molecular-orbital expansion coefficients; this dependence leads to an interde-

pendent system of equations, which should be solved using an iterative procedure. Formally the MCSCF method can be considered as a combination of the Hartree – Fock approach and the CI approximation.

According to the configuration interaction theory electrons can pass from any occupied orbital to any unoccupied one. However, the number of possible rearrangements is immense in this case, even for the simplest diatomic molecules, and calculations can hardly be carried out with such a complex wave function. At the same time, it is obvious from energy considerations that electronic transitions from higher occupied molecular orbitals to lower unoccupied ones are more likely. To simplify calculations, the so-called active configuration space is determined; *i.e.*, some set of higher occupied and lower unoccupied orbitals involved in electronic transitions. The main problem in the MCSCF method is to choose necessary configurations; *i.e.*, the size and shape of the active configuration space. One of the most popular approximations is the complete active space self-consistent field (CASSCF) method, in which configurations are chosen by dividing the entire space of molecular orbitals into active and inactive regions. Active molecular orbitals are generally a kind of a mixture of higher occupied and lower unoccupied orbitals, whereas inactive orbitals are the rest ones: either doubly occupied or unoccupied orbitals. The FCI equation is solved in the space of active molecular orbitals and the configurations obtained are included in the MCSCF optimization method.

A version of the CASSCF procedure is the method of restricted active space self-consistent field (RASSCF), which was proposed by Olsen *et al.*[53] In this method the active space is divided into three regions: the RAS1 space, which is composed of doubly occupied orbitals; the RAS2 space, which contains simultaneously occupied and unoccupied orbitals, and the RAS3 space, which is composed of unoccupied orbitals. Configurations in the RAS2 space are involved in full configuration interaction, as in the CASSCF procedure. Additional configurations are obtained upon excitation of some limited number of electrons from the RAS1 space to the RAS3 space. For example, if two electrons are excited from the RAS1 space to the RAS3 space, this situation is equivalent to the CISD method. Thus, the RASSCF procedure is a combination of the FCI method in some limited space of molecular orbitals (RAS2) and the CISD method in the expanded space (RAS1 and RAS3). The RASSCF method is not universal, because it requires manual fitting of the size of active regions and the number of excited electrons for specific molecular systems; in addition, this method is extremely difficult to be used by most of chemists who apply quantum chemical calculations in practice but are not experts in this field.

The resource intensity of MCSCF calculations is lower than that of the FCI method; nevertheless, the application of MCSCF in SSCC calculations is also restricted to very simple compounds. In particular, San Fabian and colleagues used the MCSCF (CAS and RAS) method in SSCC calculations for the hydrogen fluoride,[54] methane[55] and ethane[56] molecules. Specifically in these studies it was established that consideration of correlation effects related to inner electrons is of vital importance for SSCC calculations. Jaszuński and Ruud[57] applied the MCSCF method to calculate with a high accuracy (in comparison with experiment) the SSCCs in the acetylene molecule, which is known to be a very difficult and thankless object for any high-level *ab initio* calculations.

Ruud and co-workers[58, 59] used the MCSCF wave function in their SSCC calculations for the H_2Se, HF, H_2O and HCN molecules. Bryce and Wasylishen[60] calculated SSCCs for a large series of diatomic molecules by the MCSCF method and obtained good correspondence with the experiment. Helgaker and co-workers[61, 62] applied the MCSCF method to calculate SSCCs in the NH_3, HCN, CH_3CN and CH_2N_2 molecules. Pecul *et al.*[63, 64] carried out SSCC calculations at the RASSCF level for the ammonia dimer and ethane, methanol, methylamine molecules; they also obtained good agreement with experiment.

At the same time, we should note that the SSCC calculation methods based on the configuration interaction theory, FCI and MCSCF, have always been in disfavour, primarily in view of their extremely high resource intensity and technical complexity; even the researchers who were pioneers in application of these methods (Helgaker, Ruud, Jaszuński, Pecul, San Fabián, *et al.*) have eventually rejected them.

4. Methods based on the coupled-cluster theory

The coupled-cluster (CC) method is one of the most exact and reliable methods of quantum chemistry, which makes it possible to completely and efficiently take into account the electronic correlation effects. The CC method differs from the CI method by the way of constructing the wave function, which is also recorded as a linear combination of determinant functions.[65, 66] In the coupled-cluster method the excitation operator is presented in the exponential form:

$$\Psi_{CC} = e^{\hat{T}}\Phi_0 = (1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + ...)\Phi_0 \quad (21)$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \quad (22)$$

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{\tau}_i^a, \quad \hat{T}_2 = \sum_{i>j}\sum_{a>b} t_{ij}^{ab} \hat{\tau}_{ij}^{ab}, ... \quad (23)$$

where $\hat{\tau}$ are the operators of single, double, *etc.* excitations and t are coefficients, referred to as amplitudes. As in the CI method, classification is performed with respect to the multiplicity of excitations included in the operator $\hat{T}$. In particular, if $\hat{T} = \hat{T}_1 + \hat{T}_2$, one can speak about the coupled-cluster method with consideration of single and double excitations (CCSD),[65] which, as a matter of fact, is the best known and most often used method of the coupled-cluster theory. However, in contrast to the configuration-interaction method, due to the exponential presentation of the operator $\hat{T}$, the function of the CC method actually contains configurations corresponding to excitations of higher multiplicity with respect to those included in the operator $\hat{T}$. In particular, along with the singly and doubly excited configurations, the function of the CCSD method includes configurations obtained as a result of triple and quadruple excitations and even excitations of higher multiplicity. One can define similarly the method for triply excited configurations (CCSDT),[67, 68] which, however, is used much more rarely in practical calculations because of its much higher resource intensity in comparison with the CCSD method.

Since the excitation operator in the coupled-cluster method is represented in the exponential form, there are

some difficulties in determining the energies of the ground and excited CC states based on the variational principle. Instead of this, the ground-state energy in the coupled-cluster method is written in the form

$$E_{CC} = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle \quad (24)$$

The amplitudes t are found by constructing a system of equations obtained by multiplying both parts of the Schrödinger equation by excited configurations:

$$\langle\Phi_S|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0 \quad (25)$$

$$\langle\Phi_D|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

$$\langle\Phi_T|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

These equations are solved iteratively until the specified accuracy is reached. Note that the resource intensity of the coupled-cluster method corresponds approximately to that of the configuration-interaction method with the same excitation multiplicity. For example, the CCSD method, as well as the CISD method, scales as the sixth power of the number of basis functions used, whereas the CCSDT and CISDT methods scale as the eighth power (see Ref. 69, p. 144).

Intermediate mixed schemes are often used to reduce the resource intensity of the coupled-cluster method. For example, within the CC2 model,[70] single excitations are described at the CCSD level, whereas double excitations are considered within the perturbation theory. With respect to the theoretical level, the CC2 method is intermediate between the second-order Møller–Plesset perturbation theory (MP2) and the second-order CCSD theory; it scales as the fifth power of the number of basis functions. The CC3 approximation is constructed in the same way from the CCSDT level.[71, 72]

Another important approximation of the coupled-cluster theory is the CCSD(T) method,[73] in which single and double excitations are calculated within the coupled-cluster theory, whereas triple excitations are found from the perturbation theory. Currently, the CCSD(T) method is considered to be one of the best quantum chemical methods because it is a reasonable compromise between the calculation accuracy and resource intensity. This method scales as the seventh power of the number of basis functions; however, its calculation accuracy approaches that of the CCSDT method.

Within the coupled-cluster theory, the molecular properties that require knowledge of excited states, such as SSCCs, are often calculated using the equation-of-motion formalism (equation-of-motion coupled clusters, EOM-CC).[74–76] The EOM-CC method can be considered as a configuration interaction theory with a modified Hamiltonian in the form

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}$$

and parameterization according to the type of CI ground state, *i.e.*, expansion in the form of a series in excitation operators of different classes with corresponding coefficients. In this method the energy is varied in expansion coefficients in the configuration space, which leads to an asymmetric eigenvalue problem.

Two teams of American theoreticians, headed by Bartlett and Del Bene, played a key role in the development of high-precision SSCC calculations at the EOM-CC level, using primarily the EOM-CCSD method. In particular, Bartlett and co-workers[77] performed SSCC calculations for HF, CO, N_2, H_2O, NH_3 and HCl molecules by the EOM-CCSD method with a mean absolute error of only 13% with respect to the experimental values. At the same time, Del Bene *et al.*[78, 79] carried out SSCC calculations for single, double and triple bonds in a wide range of compounds at the EOM-CCSD level and also showed good agreement with the experimental data in comparison with other calculation methods.

Note that currently the EOM-CCSD method is widely used in SSCC calculations for various molecular systems of medium size by not only its founders but also many other research teams (see below). Thus, the coupled-cluster methods are of undoubted interest for practical high-precision SSCC calculations and form a reasonable alternative for the most efficient methods based on the polarization propagator theory.

5. Methods based on the polarization propagator theory

Another method for calculating SSCCs in molecules of medium size, which is also efficient, high-precision and important for practical applications, is the polarization propagator method, primarily in the second-order approximation of the perturbation theory.

Polarization propagator is the two-particle Green's function that describes the linear response of molecular system to external perturbation. In quantum mechanics, a polarization propagator $K(t_f, \mathbf{r}_f, t_m, \mathbf{r}_m; t_i, \mathbf{r}_i, t_j, \mathbf{r}_j)$ is a function relating the values of the two-particle wave function at two different spatio-temporal points through the expression

$$\psi(t_f, \mathbf{r}_f, t_m, \mathbf{r}_m) = \int K(t_f, \mathbf{r}_f, t_m, \mathbf{r}_m; t_i, \mathbf{r}_i, t_j, \mathbf{r}_j)\psi(t_i, \mathbf{r}_i, t_j, \mathbf{r}_j)\mathrm{d}\mathbf{r}_i\mathrm{d}\mathbf{r}_j$$

in which integration is over all possible paths connecting the initial and final points. For two time-dependent operators, $\mathbf{P}(t)$ and $\mathbf{Q}(t)$, the polarization propagator is determined by the expression[69, 80]

$$\langle\langle\mathbf{P}(t); \mathbf{Q}(t')\rangle\rangle = -i\hbar\,\theta(t - t')\langle 0|[\mathbf{P}(t), \mathbf{Q}(t')]|0\rangle \quad (26)$$

where $\theta(t - t')$ is the Heaviside function and $|0\rangle$ is the wave function of the ground state of the system. Expression (26) is referred to as the temporal representation of the polarization propagator, which passes (*via* the Fourier transform) to the so-called energy or frequency representation. The polarization propagator in the frequency representation for the frequency $\omega = 0$ can be written as

$$\langle\langle\mathbf{P}; \mathbf{Q}\rangle\rangle_{\omega=0} = 2\sum_{n\neq 0}\frac{\langle 0|\mathbf{P}|n\rangle\langle n|\mathbf{Q}|0\rangle}{E_0 - E_n} \quad (27)$$

Having compared expression (27) with expression (7), one can note that the polarization propagator in the frequency representation has the same form as the SSCC terms containing summation over states (*i.e.*, the paramagnetic spin–orbit and spin–dipole terms) and the term corresponding to the Fermi contact interaction in expression (7).

Despite the fact that the polarization propagator in the frequency representation has the form of a sum over states,

it is calculated in another way. The propagator is expressed in terms of the equation of motion, which is derived by applying the Heisenberg equation of motion to the time-dependent operators $\mathbf{P}(t)$ and $\mathbf{Q}(t)$ with subsequent Fourier transform, according to expression (28).[81]

$$\omega\langle\langle \mathbf{P};\mathbf{Q}\rangle\rangle_\omega = \langle 0|[\mathbf{P},\mathbf{Q}]|0\rangle + \langle\langle \mathbf{P};[\mathbf{H},\mathbf{Q}]\rangle\rangle_\omega \quad (28)$$

This expression shows that the propagator can be written as the sum of the commutator mean over the ground state of the system and the propagator containing a commutator with the Hamiltonian of the system. Thus, expression (28) can be written in the form of iteration:

$$\langle\langle \mathbf{P};\mathbf{Q}\rangle\rangle_\omega = \omega^{-1}\langle 0|[\mathbf{P},\mathbf{Q}]|0\rangle + \omega^{-2}\langle 0|[\mathbf{P};[\mathbf{H},\mathbf{Q}]]|0\rangle + \quad (29)$$
$$+ \omega^{-3}\langle 0|[\mathbf{P},[\mathbf{H},[\mathbf{H},\mathbf{Q}]]]|0\rangle + \ldots$$

The equation of motion for the polarization propagator is reduced to the final form by applying the superoperator algebra and internal projection on the complete set of excitation – deexcitation operators to expression (29):

$$\langle\langle \mathbf{P};\mathbf{Q}\rangle\rangle_\omega = (\mathbf{P}|\mathbf{h})(\mathbf{h}|\omega\mathbf{I} - \widehat{\mathbf{H}}|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{Q}) \quad (30)$$
$$(\mathbf{P}|\mathbf{Q}) = \langle 0|[\mathbf{P}^\dagger,\mathbf{Q}]|0\rangle$$
$$\widehat{\mathbf{H}}\mathbf{P} = [\mathbf{H},\mathbf{P}]$$

In these expressions **h** is a set of excitation operators, which can be used to describe the complete set of excited states based on the unexcited state $|0\rangle$; operators **P** and **Q** are also described in terms of excitation operators. When calculating time-independent second-order properties, such as SSCCs, the frequency ω in the expression for the polarization propagator (30) is assumed to be zero. Although the expression for the polarization propagator can be obtained in the form identical to the expression for the second-order properties with summation over all excited states, the final form of the polarization propagator contains only the ground-state function. Thus, the problem of determining SSCCs in polarization propagator methods is reduced to calculation of the matrix elements with Slater determinants and the problem of determining the inverse matrix; this approach is very efficient from the computational point of view.

In the existing calculation schemes based on the polarization propagator formalism the set of excitation operators is limited by certain maximum excitation multiplicity. For example, the random phase approximation (RPA) method[82] is restricted to consideration of only single excitations and the ground-state function is taken to be that of the Hartree – Fock problem. The RPA method is the first-order approximation within the polarization propagator theory and corresponds approximately to the level of CIS configuration interaction theory; *i.e.*, it insufficiently exactly takes into account electronic correlation effects. The RPA method can hardly be used in SSCC calculations because its error is too large in comparison with other techniques taking into consideration electronic correlation effects.[43, 83, 84]

The next popular approximation within the polarization propagator theory is the second-order polarization propagator approximation (SOPPA).[82, 85 – 87] This approach takes into account the operators of not only single but also double excitations, while the ground-state function contains additional corrections within the second-order Møller – Plesset perturbation theory with singly and doubly excited configurations. With regard to the account of electronic correlation, SOPPA is comparable with the CISD method and is considered to be at the level of the second-order perturbation theory. When used in calculations, SOPPA scales as the fifth power of the number of basis functions.

A further expansion of the computational approaches based on the second-order polarization propagator theory is the SOPPA(CCSD) method. Here, the Møller – Plesset coefficients of the ground-state function are replaced with the amplitudes of the coupled-cluster method for single and double excitations.[87, 88] Thus, this method calls for calculation at the CCSD level for the ground-state function, which scales SOPPA(CCSD) to the sixth power of the number of basis functions.

Sauer and co-workers[87] performed calculations of SSCCs over one, two and three bonds in HD, HF, H_2O, CH_4, C_2H_2, BH, AlH, CO and N_2 molecules within the SOPPA and SOPPA(CCSD) methods. Good agreement between the calculated and experimental data was demonstrated: the mean deviation from experiment was less than 2.5 Hz for both methods; the SOPPA(CCSD) results were slightly better than those obtained by the SOPPA method. Sauer and co-workers showed also (in their more recent study[89]) a high accuracy of SSCC calculations by the SOPPA(CCSD) method (as compared with other methods) for isotopomers of acetylene, which, as was noted above, is an extremely thankless object for high-level quantum chemical calculations. The SOPPA and SOPPA(CCSD) methods were also applied in SSCC calculations for some inorganic hydrides.[90, 91] Provasi *et al.*[92] studied the behaviour of vicinal SSCCs $^3J_{HH}$, calculated at the SOPPA level, in the series of substituted ethanes and also obtained good agreement with experiment.

Another approach within the second-order polarization propagator theory is the SOPPA(CC2) method,[93] in which the Møller – Plesset coefficients in the ground-state function are replaced with the amplitudes of the CC2 method for single and double excitations. This new method scales as the fifth power of the number of basis functions, as well as the original SOPPA method. Sauer *et al.* used SOPPA(CC2) in their fundamental study[93] to calculate SSCCs of different types in a wide series of small molecules and compared the SOPPA and SOPPA(CCSD) methods. They showed that in the absence of hydrogen bonds the SOPPA(CC2) results are on average somewhat better than the results obtained by the SOPPA method but worse than the SOPPA(CCSD) results (with the former of the same resource intensity as that of SOPPA method).

Recently another method has been proposed for calculating SSCCs, which is based on the second-order polarization propagator formalism within the model of algebraic diagrammatic construction (ADC): ADC(2);[94, 95] the authors of this review took part in the development of this method. In the ADC approach the polarization propagator is presented in the off-diagonal form, which is the result of transition to the basis of intermediate states and is expressed in terms of the effective parameters of the ADC method, expanded in perturbation-theory series with respect to the residual electron–electron interaction. These parameters are found by comparing the algebraic expansion

of excited polarization propagator and the propagator expansion in series within the many-particle theory of Feynman–Goldstone perturbation expansions (see Ref. 96, p. 92). The ADC(2) scheme takes into account both singly and doubly excited states and scales as the fifth power of the number of basis functions. Rusakova *et al.*[95] showed that the accuracy of the ADC(2) method in the SSCC calculations for a wide series of small molecules is intermediate between the SOPPA and SOPPA(CC2) methods. An advantage of the ADC approach is its high computational efficiency, which is based on the use of the intermediate state representation (ISR) and block Lanczos diagonalization.

IV. Main factors affecting the calculation accuracy of spin–spin coupling constants

The SSCC value is determined by a large number of various stereoelectronic factors, the most important of them are the hybridization of the coupled atoms and the s orders of the bonds involved in indirect spin–spin coupling transfer; the topology and geometry of the coupling path; the effects of substituents (electronic substitution effects) and the influence of the spatial orientation of neighbouring chemical bonds and lone pairs with respect to the spin–spin coupling path (steric effects); *i.e.*, all factors considered as 'stereoelectronic effects'. The dependences of SSCCs on these factors form the theoretical basis of their use in structural and stereochemical studies. All these stereoelectronic effects, which determine the magnitude and sign of experimental SSCCs, are reproduced to some extent (depending on the calculation method used) in the theoretical (calculated) SSCC values. In this context, when performing practical SSCC calculations, it is of key importance to understand what factors affect the calculation accuracy and the way they affect it, especially in comparison with the experimental data. Such factors include primarily the method chosen and the theoretical level of calculation (this factor was comprehensively analyzed above), the quality of the basis set chosen for the calculation, the influence of the environment, the influence of thermal vibrational corrections and (in some cases) relativistic effects. Let us consider the above-mentioned factors in more detail.

1. Basis set quality

The most important aspect of any *ab initio* calculation (when the theoretical level and calculation method are chosen) is the choice of atomic basis set. The basis set must be sufficiently large and flexible to characterize well the effects of perturbation used and take into account the electronic correlation; however, the size of the basis set is limited in practice by computational expenditures. Therefore, there is always a problem of compromise between the size of basis set and its adequacy and quality for a specific quantum chemical calculation. As will be shown below, this problem is especially urgent in SSCC calculations.

All modern *ab initio* calculations use basis sets where each atomic orbital is presented by several Gaussian functions of electron density distribution. Basis sets of the simplest type are STO-*n*GF bases, in which Slater-type atomic orbitals are approximated by *n* Gaussian-type functions. This means that each atomic orbital is set by a sum of *n* Gaussian-type functions; the coefficients of the Gaussian functions are chosen so as to make their linear combinations describe approximately Slater-type orbitals. This procedure increases the number of elementary basis functions; nevertheless, Gaussian-type functions much better fit real computations than Slater-type functions, and their use reduces computational expenditures in the long run.

The calculation quality can be improved by applying split basis sets, in which atomic orbitals are composed of two or more parts: internal (more compact) part and several external (more diffuse) parts. When constructing a molecular orbital in a self-consistent procedure, the coefficients of each part of the basis set can be varied independently. In split-valence basis sets only valence orbitals are divided into compact and diffuse components.

There are a very large number of basis sets, optimized for calculating particular molecular properties, both of the first and second orders. Currently SSCCs are often calculated using the scheme based on different basis sets for the atoms between which coupling constants are calculated and for all other atoms of the molecule. This approach, referred to as the approach of locally-dense basis sets,[92] is widely applied in practical SSCC calculations for relatively large molecules.

The following basis sets are used to set local bases for individual atoms between which coupling constants are not calculated: 6-31G and 6-311G[97,98] (the simplest standard doubly and triply, respectively, split-valence unpolarized Pople basis sets); 6-31G(d,p) and 6-311G(d,p)[97,99] (standard doubly and triply, respectively, split-valence polarized Pople basis sets using one p set of polarization functions for hydrogen atoms and one d set of polarization functions for atoms of the second and third periods); cc-pVXZ [X = 2(D), 3(T), 4(Q), 5, 6][100] (standard correlation-consistent X-multiple split polarized Dunning basis sets); aug-cc-pVXZ [X = 2(D), 3(T), 4(Q), 5, 6][101,102] (standard correlation-consistent X-multiple split polarized Dunning basis sets, augmented with diffuse functions).

Standard basis sets have been developed to describe flexibly the valence region of the electronic system; therefore, they not quite adequately take into account the inner electron shells, in particular, the electron density in the vicinity of nucleus. Thus, these basis sets are of little use for SSCC calculations.[2] Various special basis sets are applied for atoms between which SSCCs are calculated. For example, the cc-pCVXZ basis sets[100,103] are standard correlation-consistent X-multiple split polarized Dunning basis sets with core functions of all types added (one s set and one p set at X = 2; two s sets, two p sets and one d set at X = 3). The sad-J basis set[104] is a contracted (*i.e.*, containing several Gaussian functions with constant coefficients, combined into one orbital) correlation-consistent triply split dipole-polarized basis set, which has been specially optimized for calculating second-order properties by contracting the SADLEJ basis set with addition of four 1s-contracted tight functions for all elements. The aug-cc-pVTZ-J basis set[87,102,104,105] is a contracted correlation-consistent triply split polarized-diffuse basis set, specially optimized for calculations of second-order properties by contracting the aug-cc-pVTZ basis set, with the most diffuse d functions excluded and four 1s-contracted tight s functions added for all elements. We should clarify that core functions are the functions taking into account the electronic correlation with participation of inner electrons, while tight functions are those with large exponentials (increasing in geometric progression), which are necessary

for correct description of the electron density distribution directly on the nucleus surface. This approach is of major importance when calculating the contribution of Fermi contact interaction to SSCC.

Helgaker *et al.*[59] studied in detail the influence of the basis set quality on the accuracy of *ab initio* SSCC calculations for three simple molecules: HF, H_2O and HCN. At the MCSCF level the constants were calculated with application of the correlation-consistent cc-pVXZ, cc-pCVXZ, aug-cc-pVXZ (X = D, T, Q, 5, 6) and aug-cc-pCVXZ (X = D, T, Q, 5, 6) basis sets, in which core and diffuse functions are simultaneously added. They completely decontracted the s-functions of the cc-pVXZ basis sets in the basis sets of cc-pVXZ-su0 series. Then tight s functions were successively added to the sets of the cc-pVXZ-su0 series to improve them. The thus obtained sets were denoted as cc-pVXZ-su*n* (su indicates the use of non-contracted s functions, and *n* is the number of tight s functions.[59]

A series of cc-pVXZ-Cs basis sets was obtained in this study from cc-pVXZ basis sets by adding only core s-type functions, which correspond to cc-pCVXZ bases. The basis sets of the cc-pVXZ-Cs series are much smaller than the complete cc-pCVXZ basis sets, due to which the computational resource intensity is significantly reduced; note that the accuracy of the data obtained in the cc-pVXZ-Cs basis sets is not worse than that of the data obtained in the complete cc-pCVXZ basis sets. The results of study[59] showed that the basis sets constructed based on cc-pVDZ are too small to provide the required accuracy of SSCC calculations. However, the calculation results are improved with an increase in the number of atomic orbitals in the basis set and approach the best results beginning with X = 4. It was also established that the standard correlation-consistent sets are not good for calculating the constants, because the s functions used in them are not sufficiently flexible, and this circumstance affects the accuracy of calculating the contributions of Fermi contact interaction.[59] It was also proposed in this study to modify standard Dunning basis sets by decontracting all s functions and augmenting them with a set of tight s functions with large values of exponential coefficients. Indeed, some researchers indicated high sensitivity of the contribution of Fermi contact interaction to the addition of s functions with very large exponentials.[87, 92, 106]

Åstrand *et al.*[107] investigated a series of basis sets using HF and CASSCF methods for calculating SSCCs in the hydrogen fluoride molecule; in particular, correlation-consistent cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5) sets were used. It was found that the type of basis set affects most strongly the FC contribution, although significant changes were also observed for other contributions.

Krivdin *et al.*[84] studied the carbon–carbon SSCCs in the cyclopropane, aziridine and oxirane molecules by the RPA, SOPPA and DFT-B3LYP methods using the basis sets of the following five types: 6-31G(d,p), cc-pVTZ, cc-pCVDZ, cc-pCVTZ and aug-cc-pVTZ-J. The results obtained showed that at each level of the theory the calculated full values of the constants depend quite differently on the basis set used. This dependence is most pronounced at the SOPPA level, where the discrepancy between the data obtained in the smallest and largest basis sets [6-31G(d, p) and aug-cc-pVTZ-J, respectively] is about 12 Hz. At the RPA and DFT levels, the results obtained with the same basis sets differ by 8 and 4 Hz, respectively. It was also shown[84] that the correlation effects and the influence of basis sets on the accuracy of SSCC calculations are not additive. It was concluded that successive increase in the complexity and size of the correlation-consistent basis sets improves the calculation quality and that the standard 6-31G(d, p) basis, which proved to be good for calculations of the total energy and optimization of geometric parameters, yields incorrect results in SSCC calculations. It was established that addition of the functions taking into account the internal electronic correlation to the basis set sharply increases the calculation accuracy with a slight increase in the basis size.[84]

Recently Jensen[108] proposed a series of polarization-consistent pcJ-*n* basis sets, specially optimized for SSCC calculations at the level of electron-density functional theory. This series is based on the pc-*n*,[109, 110] basis sets, in which the symbol *n* is the number of additional polarization functions. For example, the pc-0 basis set contains only s and p functions; the pc-1 basis set is the DZP basis with with d function added; the pc-2 basis set is the TZP basis with d and f functions added, *etc*. To improve the convergence of SSCC calculation results, the pcJ-*n* basis set was augmented with dense s, p, d and f functions. It is noteworthy that tight s functions are necessary for more exact calculation of the contribution of Fermi contact interaction to the coupling constant, tight p-functions are required for calculating the paramagnetic spin–orbit contribution, and tight d and f functions are used to calculate more accurately the spin–dipole contribution to SSCC.[108]

Kupka *et al.*[111] studied in detail the convergence of the pcJ-*n* basis sets in calculations of different SSCCs at the level of electron-density functional theory using 40 (!) different functionals in nine molecules. Their SSCC calculations with the aid of pcJ-*n* basis sets for some functionals showed an average accuracy from 5% to 20% with respect to the experimental values; this is a fairly good result for the DFT level.

The Huz-X-su*n* (X = I, II, III, IV),[45] basis sets, which are modified standard Huzinaga's Huz-X basis sets,[112, 113] are widely used for the calculation of SSCs. These basis sets are derived from standard Huz-X bases by complete decontracting of the s part and adding *n* tight s functions. Note that the Huz-X-su*n* basis sets are not correlation-consistent in the general case; hence, one must use fairly large basis sets (X = III, IV) to ensure correct SSCC calculations. However, the calculations with these basis sets often demonstrate very good agreement with experimental values of constants. For example, Bryce[114] studied in detail the nitrogen–nitrogen SSCCs in polynitrogen chains using the Huz-III-su3 basis set and showed good correspondence between the calculated coupling constants and the experimental data. Ruden *et al.*[115] also performed high-precision calculations of SSCCs of different types in allene, cyclopropane and cyclopropene molecules using the Huz-II-su2 basis sets.

Based on the aforesaid, one can conclude that certain, fairly stringent requirements are imposed on the basis sets used in SSCC calculations. These basis sets must be optimized for correlated calculations (*i.e.*, calculations taking into account electronic correlation effects); a factor of key importance is the use of special functions to take into account electronic correlation with participation of inner electrons. Basis sets must be optimized for calculating

second-order molecular properties; *i.e.*, they must be expanded using special functions, which describe correctly the electron density distribution on the nucleus surface. Finally, the basis sets must be multiply split in their valence part and contain a necessary number of polarized and diffuse functions to describe correctly the valence shell in high-level correlated calculations.

2. Vibrational corrections

The SSCC value is extremely sensitive to the mutual arrangement of atomic nuclei in molecules. On the one hand, this SSCC property provides a rather efficient analytical tool in structural studies of molecules; at the same time, this property means that the SSCC value should depend on vibrations of atomic nuclei, *i.e.*, be temperature-dependent.

One of the most important factors affecting the SSCC value is the effect of zero-point vibrations (ZPVs) of atomic nuclei. The nature of this effect is that atomic nuclei vibrate in the electric field of the molecule at absolute zero temperature. This is a purely quantum effect, which has no analogues in classical physics. It was shown that ZPV corrections to SSCC can be found through the quantum mean value over the ground state.[116, 117] Generally, SSCCs are expanded in Taylor series over mean deviations of the internal coordinates of atomic nuclei from the equilibrium geometric value, obtained from the Born–Oppenheimer approximation in calculation of the electron energy of molecule. The derivatives of the constants with respect to internal coordinates in this expansion are found by numerical differentiation methods. The desired mean values of internal coordinates in calculations of the ZPV correction are most often determined using the values of the force constants and harmonic frequencies of molecular vibrations. The temperature dependence of SSCC is generally obtained by averaging internal coordinates, with application of Boltzmann distribution over molecular vibrational levels.

The influence of the isotope effect on the SSCC value is based on the fact that the vibrational energy of atomic nuclei depends on not only the electric field distribution in the molecule but also on the mass of vibrating nuclei. Generally, the value of the isotope effect for SSCCs is extremely small. For example, Sergeyev *et al.*[118, 119] studied the influence of the isotope effect of the replacement of hydrogen with deuterium on the carbon–proton constant in methane derivatives $CH_{2-n}D_nCl_2$ ($n = 0, 1, 2$) and $CH_mD_nX_{4-m-n}$ (X = Cl, Br, I).[120] They showed that the influence of isotope effect on the ^1J(C,H) constant does not exceed 0.5 Hz or 0.3% of the SSCC value. According to the results obtained by Novak *et al.*,[121] the isotope effect for the ^1J(C,H) constant in benzaldehyde is 0.34 Hz.

Note that the calculation of vibrational and thermal corrections to the SSCC value is a fairly time-consuming problem. High-precision calculation of all derivatives of SSCC with respect to coordinates in polyatomic molecules by methods of numerical differentiation requires multiply repeated calculations of SSCC values for a large number of different molecular geometries. According to our estimates, currently the effect of nuclear motion on the SSCC value can be investigated at a high nonempirical level for only molecules containing no more than ten atoms.

A situation often occurs when the difference between the calculated and experimental SSCC values is smaller than the vibrational correction. For example, when calculating the carbon–carbon constant in the acetylene molecule, the deviation of the calculated value from the experimental result was found to be about 2–3 Hz,[57] whereas the vibrational correction for this constant exceeds 10 Hz.[89] What conclusions should be drawn based on these results? One can speak about systematic underestimation or, *vice versa*, overestimation of the chosen calculation method in view of the so-called 'fortuitous cancellation of errors'. Another possible reason is inaccurate calculation of vibrational corrections. Both explanations appear to be reasonable; however most researchers blame the accuracy of calculations of vibrational corrections and generally disregard them.

Vibrational corrections to SSCCs were calculated at different times using different methods and different theoretical levels. For example, an extremely large value of the ZPV correction (−25 Hz) for the SSCC in hydrogen fluoride molecule was calculated by Åstrand *et al.*[107] at the MCSCF level. In a similar study Wigglesworth *et al.*[89] calculated vibrational corrections for acetylene at the SOPPA(CCSD) level. At the same time, Sneskov and Stanton[122] calculated recently vibrational corrections to different spin–spin coupling constants at the CCSD level for acetylene, ethylene, ethane and cyclopropane. According to their results, the values of vibrational corrections were in the range from 8% to 32% for carbon–proton constants and from 1% to 7% for carbon–carbon constants. Kirpekar *et al.*[123] calculated vibrational and thermal corrections for one-bond SSCCs in XH_4 molecules (X = C, Si, Ge, Sn) at the RPA, SOPPA and CASSCF levels. The average value of vibrational corrections to one-bond SSCCs was found to be 1%–3% of the SSCC value. Del Bene and co-workers[124] calculated the vibrational corrections for nitrogen–nitrogen SSCCs through the hydrogen bond N–H···N at the EOM-CCSD level. Despite the fact that only two vibrational modes were considered, the SSCC value was recalculated for 108 different molecular geometries, which illustrates the extremely high resource intensity of the calculation of vibrational corrections.

A reasonable alternative to high-level *ab initio* methods for calculating vibrational corrections is the methods based on the electron density functional formalism, which are widely used by Helgaker and co-workers.[115, 116] Thus, a kind of compromise between the computational expenditures and SSCC calculation accuracy is the scheme where the SSCC value for equilibrium geometry is calculated at a high theoretical level, using a large basis set, while the vibrational corrections to the SSCC value are calculated at the DFT level, applying simplified basis sets.

Norwegian researchers,[116] who are trendsetters in the field of calculation of vibrational corrections, performed detailed comparison of the vibrational corrections to a number of SSCC values calculated at the DFT and MCSCF levels. It was found that the DFT vibrational corrections for small molecules are in good correspondence with the corrections calculated previously at higher nonempirical levels. In the further study Ruden *et al.*[115] reported systematic comparison of the vibrational corrections calculated by three high-level methods, CCSD, SOPPA and MCSCF, along with calculations of SSCCs in allene, cyclopropane, cyclopropene and cyclobutane at the DFTDFT-B3LYP level. It was demonstrated in this study that the vibrational corrections for the SSCCs under con-

sideration had generally the same value as the difference between the theoretical and experimental SSCC values.

Sauer and co-workers [125] studied in detail the vibrational and thermal corrections to the one-bond and geminal SSCCs in ammonia isotopomers. It was shown that the total value of vibrational and thermal corrections at 300 K is 0.36 Hz (or 0.6% of the SSCC value) for the one-bond N–H constants and 0.56 Hz (or 5.0%) for geminal H–H constants.

Generally, the thermal correction to the SSCC value may vary in a fairly wide range, depending on the specific types of compounds studied. For example, Thorshaug *et al.*[126] investigated in detail the temperature dependence of Si–H SSCCs in chlorosilanes. They revealed a linear decrease in the SSCC values with an increase in temperature. In particular, the change in the ^1J(Si,H) constant in unsubstituted silane SiH_4 in the temperature range from 213 to 273 K was only 0.36 Hz or 0.2% of the SSCC value, whereas the change in the ^1J(Si,H) constant in dichlorosilane SiH_2Cl_2 in the same temperature range was 14.82 Hz, *i.e.*, 3.9% of the SSCC value.[126]

The results presented in this section demonstrate that the vibrational corrections to SSCCs must be calculated in some cases. Nevertheless, in most series SSCC calculations one can either neglect vibrational corrections or use known data in the literature, which can be found, *e.g.*, in the papers by Ruden *et al.*[115–117]

3. Solvation effects

Another important factor affecting the calculated SSCC values is the chemical environment of molecule, *i.e.*, the solvation effect (the influence of the medium). Solvation effects are generally taken into account in SSCC calculations using the following three best-proven techniques: continuum model of the medium, supermolecule model and dynamic simulation model. The continuum model implies quantum chemical consideration of a single molecule surrounded by a continuous homogeneous dielectric medium. In the supermolecule method, which is more resource-intensive, intermolecular complexes composed of the molecule under consideration and several solvent molecules interacting with it are explicitly calculated. Finally, the dynamic simulation model is basically a kind of the supermolecule method; the difference is that the spatial arrangement of the solvent molecules around the molecule under study in the dynamic simulation model is set by the Monte Carlo simulation or molecular dynamics methods.

The influence of the environment in practical SSCC calculations is most often taken into account using the polarizable continuum model (PCM) [127–129] within the continuum model of medium. In this approach the molecule under study is placed in some cavity, which is most often composed of spheres centred at the atoms of the molecule. This cavity is surrounded by an isotropic medium, which is either dielectric or partially conducting (depending on the specific model used). The molecular charges, differently distributed between the atoms of the molecule, induce some charge distribution on the cavity surface, and the electrostatic interaction energy of the molecular and induced charges is introduced as an additional term into the Hamiltonian of the system. The following models have been developed for practical SSCC calculations taking into account the solvation effects: the integral equation formalism polarizable continuum model (IEF-PCM) [130, 131] and the conductor-like screening model (COSMO).[132, 133] The PCM model was preceded by reaction-field model [134, 135] (which is still rather popular); within this model a molecule under study is placed in a spherical cavity surrounded by a dielectric medium.

Pecul and Ruud [136] performed detailed comparison of the influence of solvent effects, calculated at the DFT and CASSCF levels, on the SSCC value in acetylene by the PCM method in six solvents: cyclohexane, benzene, chloroform, acetone, water and acetonitrile. The largest correction due to the solvent effect was found for the ^1J(C,C) SSCC in acetone, acetonitrile and water. In these solvents the solvation corrections turned out to be approximately the same and equal to $\sim$10 Hz (!), which is 5% of this constant in an isolated molecule. For the ^1J(C,H) constant the maximum value of the correction was found to be surprisingly small: only 0.8 Hz (0.3% of the SSCC value); similar small solvation effects were calculated for the geminal and vicinal constants [^2J(C,H) and ^3J(H,H)], which were found to be 0.8% and 0.2%, respectively, of the corresponding constants in isolated molecules.[136]

Contreras and co-workers [137] performed a comprehensive study of the influence of solvent on the carbon–proton SSCCs in acetaldehyde at the DFT level using the PCM model. They revealed that the correction for the ^1J(C,H) constant at the carbonyl carbon atom in DMSO is approximately 2.5 Hz, *i.e.*, 1.4% of the constant value in an isolated molecule. For the ^2J(C,H) constant in DMSO the correction was found to be much larger: 2.2 Hz or 6.8% of the SSCC.[137] Contreras and his colleagues showed in another study [138] that the ^1J(C,H) SSCC value increases in the simplest imine $HN{=}CH_2$ when going from an isolated molecule to a DMSO solution within the PCM model. The correction to the ^1J(C,H) constant was almost 6 Hz or 3.8% of the SSCC value for an isolated molecule.

Thus, SSCC value depends on the solvent type; however, the solvent effect can be neglected in many cases (what is generally done in practice). The correction introduced by taking into account the solvent type rarely exceeds few percent of the SSCC value in an isolated molecule; therefore, consideration of the solvent influence in SSCC calculations is not generally of major importance.

4. Relativistic effects

Most of the computational methods of quantum chemistry are based on solutions to the Schrödinger equation, *i.e.*, on nonrelativistic approximations of the theory; however, to calculate molecular properties more correctly, one must consider relativistic corrections in some cases. Relativistic effects influence most significantly the electrons of the inner shells that are spatially adjacent to atomic nuclei. Since it is the inner electron shells that determine most SSCCs, the SSCC values should therefore contain relativistic corrections, at least to some extent.

As was noted in Autschbach's review,[139] the theory based on the formalism of four-component single-electron Dirac equation is the most complete relativistic approximation for SSCC calculations. It were Pyykko [140] and later (independently) Aucar and Oddershede [141] who proposed for the first time to use the four-component formalism in SSCC calculations. The SSCC calculations according to the four-component relativistic scheme are extremely resource-intensive; therefore, SSCC values are often calculated at the uncorrelated level of the Dirac–Hartree–Fock theory

using the the two-electron Dirac–Coulomb Hamiltonian.[142, 143]

In the approximation of the relativistic Breit–Pauli theory,[139] which is based on simplified consideration of the Dirac equation, the main relativistic effects that directly affect the SSCC value are determined by three corrections to the nonrelativistic Hamiltonian: the correction for the dependence of the electron mass on electron velocity, the Darwin correction and the correction for the spin–orbit interaction. The first correction is due to the increase in the electron mass when the electron velocity is comparable with the speed of light. The Darwin correction changes the effective nucleus potential; it is often considered as quantum oscillatory motion of electron. The spin–orbit correction is determined by the interaction of the electron spin with the magnetic field induced by the electron motion. The Darwin correction and the correction for the dependence of the electron mass on velocity are often combined into the so-called scalar relativistic corrections, because, in contrast to the spin–orbit correction, they both are independent of the electron spin. Generally the SSCC value is most strongly affected by specifically the scalar relativistic corrections, which manifests itself in the increased electron density in the immediate vicinity of atomic nuclei. The Darwin correction and the correction for the dependence of the electron mass on velocity can be rather large for heavy atoms (which we consider to be elements of the fourth and next periods). As a result, the perturbation theory is often inadequate for SSCC calculations in studies of scalar relativistic effects.

In view of the significant resource intensity of SSCC calculations by four-component methods, several approximations with transformation of the four-component Dirac–Coulomb Hamiltonian into the two-component form have been developed by different authors. These are primarily the zero-order regular approximation (ZORA),[144] the infinite-order regular approximation with modified metric method (IORAmm)[145] and the Douglas–Kroll–Hess (DKH) transformation.[146]

Aucar and co-workers[147] calculated the relativistic corrections to the one-bond and geminal SSCCs in the series of XH_3 (X = N, P, As, Sb, Bi) and XH_2 (X = O, S, Se, Te, Po) molecules at the level of four-component Dirac–Hartree–Fock theory using the RPA calculation scheme. They found that the relativistic correction for the one-bond X–H constants (X is an element of the second or third period) does not exceed 0.8% of the SSCC value calculated at the nonrelativistic level. At the same time, the relativistic correction was found to be 13.6% for the one-bond ^1J(As,H) constant and even 45.3% for the ^1J(Se,H) constant. This example shows a considerable increase in the relativistic correction, depending on the atomic number of the atom involved in the spin–spin coupling.

Oddershede and co-workers[142, 143] studied in detail the influence of relativistic effects on the values of the one-bond SSCCs in the series of XH_4 (X = C, Si, Ge, Sn, Pb) and XH (X = F, Cl, Br, I) molecules at the level of four-component RPA approximation. They found the relativistic correction to the one-bond ^1J(Ge,H) constant to amount to 12% of the nonrelativistic value, whereas the relativistic corrections for the ^1J(Sn,H) and ^1J(Pb,H) constants were 37% and 156%, respectively. At the same time, the relativistic corrections for the constants involving carbon and silicon nuclei did not exceed 2%. Based on the results of these studies, it was concluded that the main component of the relativistic correction for the SSCCs under study is the scalar relativistic contraction of s orbitals. Similar results were obtained in another work by Oddershede and co-workers,[148] who showed that, even for the ^1J(Sn,H) SSCC, the spin–orbit relativistic correction calculated at the RPA level is only 1% of the SSCC value calculated at the nonrelativistic level of the theory.

Argentine researchers[146] applied the DKH technique at the level of Hartree–Fock theory and DFT to calculate the one-bond SSCCs in the series of XH_4 (X = C, Si, Ge, Sn) molecules. They also noted that the relativistic corrections for the SSCCs of proton with atoms of the second- and third-period elements do not exceed 1%, while for the ^1J(Ge,H) constant the relativistic correction is 13% of the nonrelativistic SSCC value.

Recently Bryce and Autschbach[149] studied the influence of relativistic effects on the SSCC value in a wide series of alkali metal halides, halogen fluorides and xenon fluorides by the ZORA method at the DFT level. They obtained good agreement between the calculated SSCC values and experimental data and showed that the consideration of relativistic corrections is especially important for the elements beginning with the fifth period. Bagno *et al.*[150] used the ZORA method at the DFT level to calculate the relativistic corrections to SSCCs in different tin compounds. They showed that the results of SSCC calculations within the ZORA approximation correlate with experimental data with good accuracy. According to their results, the relativistic correction for the vicinal constant ^3J(Sn,H) in $Me_3SnSnMe_3$ molecules was only 9.8% of the experimental SSCC value.

Summing up the discussion of this section, we can draw the following general conclusion. The consideration of relativistic effects in SSCC calculations is of major importance for only the elements of the fifth and higher periods. At the same time, the relativistic corrections for the elements of the first three periods and, to a great extent, the fourth-period elements, are negligible and can be disregarded in practical calculations.

5. Programme realization

SSCC calculations have been implemented in many quantum chemical software packages at different theoretical levels. We list below the most popular packages allowing for SSCC calculations. Since these programme codes are continuously developed, their computational possibilities and characteristics may change from version to version. It is noteworthy that most calculations are carried out using Gaussian-type basis sets in almost all of these packages.

ACES[151] makes it possible to calculate SSCCs at the level of the Hartree–Fock theory and by the EOM-CCSD method.

ADF[152] allows one to calculate SSCCs at the DFT level applying original Slater basis sets. Relativistic effects for SSCCs are taken into account by the ZORA method. There is a possibility of using the polarized-medium model COSMO to take into account the solvent effects in this package.

CFOUR[153] makes it possible to calculate SSCCs at the levels of the Hartree–Fock theory and CCSD. This package also allows one to take into account vibrational corrections to the SSCC value.

The latest version of DALTON[154] makes it possible to calculate SSCCs at the Hartree–Fock theory, DFT, MCSCF, SOPPA, SOPPA(CC2) and SOPPA(CCSD) levels.

Using this package, one can also calculate the vibrational corrections to SSCCs and take into account the solvent effects within the PCM and reaction-field models.

DIRAC[155] allows one to calculate SSCCs at the level of the four-component relativistic Dirac–Hartree–Fock theory.

GAUSSIAN[156] makes it possible to calculate SSCCs at the levels of Hartree–Fock theory and DFT. This package allows one to take into account the solvent effects within the PCM model.

V. Structural and stereochemical applications of modern quantum chemical methods for calculating spin–spin coupling constants

Calculation of spin–spin coupling constants is a versatile tool for solving various structural problems related to the structure and chemical properties of organic and inorganic compounds. In particular, calculation of SSCCs, in combination with analysis of their experimental values, makes it possible to solve very sophisticated stereochemical problems of modern organic chemistry and biochemistry. Comprehensive discussion of numerous structural applications of quantum chemical methods for calculating SSCCs is beyond the scope of this review; this subject was considered more or less comprehensively in the recent review by Krivdin and Contreras.[9] In this section we will only dwell on few most characteristic examples (including mostly our own results) to illustrate the power of modern quantum chemical tools aimed at solving fundamental structural and stereochemical problems by calculating spin–spin coupling constants and focus on the *ab initio* methods based on the formalism of the wave function perturbation theory. We are deeply convinced that the DFT methods, although exceptionally popular today, will gradually (with the development of computational tools) give way to more exact and reliable, purely *ab initio* methods for calculating SSCCs, primarily the techniques based on the polarization propagator approach and coupled-cluster theory.

1. Studies of the nature of chemical bonding and steric strain effects

We should primarily note the series of studies of steric strain effects and the nature of chemical bonding based on the calculations of $^{13}C-^{13}C$ SSCCs for sterically strained carbocyclic compounds: cycloalkanes,[84,157] bicycloalkanes,[158] condensed bicycloalkanes,[159,160] spiroalkanes,[161,162] propellanes,[163,164] polyhedranes[165] and cage carbocycles.[166,167] These compound are exceptionally interesting for studying the chemical bonding nature, which has an unusual character as a result of striking manifestation of the steric strain effects in their carbon framework. Systematic calculation of $^{13}C-^{13}C$ SSCCs in carbocyclic compounds[168,169] and their heteroanalogues[170–173] showed that these parameters contain unique structural information about the nature of carbon–carbon bonds, reflecting the unusual character of chemical bonding and the influence of steric strain on the unprecedently high reactivity of, *e.g.*, bicycloalkanes and propellanes. At the same time, the $^{13}C-^{13}C$ SSCCs are a relatively new (and previously hard-to-reach) NMR spectroscopic parameter, which contains unique structural information about such factors of chemical structure as the stereoelectronic nature of carbon–carbon bond and the electronic influence of substituents. However, measurement of the $^{13}C-^{13}C$ SSCCs in the series of polycycloalkanes is far from being always possible because of the low stability or high molecular symmetry of these compounds; therefore, in some cases they can be studied only theoretically, in particular, by *ab initio* calculation of $^{13}C-^{13}C$ SSCCs.[168] Among the variety of the results obtained in this field, we will focus on the following three most interesting and illustrative examples: small carbo- and heterocycles, condensed bicycloalkanes (exemplified with bicyclobutane and propellane) and polyhedranes.

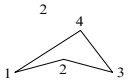
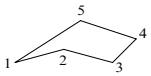
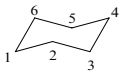
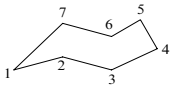
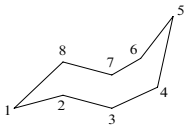
a. Small carbo- and heterocycles

One of the first examples of application of high-precision high-level nonempirical methods for calculating $^{13}C-^{13}C$ SSCCs in real organic molecules is the two works by Krivdin *et al.*,[84,170] devoted to the calculation of coupling constants by the SOPPA method (in comparison with the RPA and DFT-B3LYP methods) in cyclopropane, cyclobutane and their heteroanalogues (Table 1).[84,170] Good correspondence of the results of these studies with the existing experimental data proved a key role of electronic correlation effects; hence, it was concluded that uncorrelated RPA methods are totally unacceptable for SSCC calculations. A short time later Ruden *et al.*[115] performed comprehensive comparative analysis of the accuracy of calculations of the $^{1}H-^{1}H$, $^{13}C-^{1}H$ and $^{13}C-^{13}C$ SSCCs in cyclopropane and cyclopropene by the MCSCF, SOPPA, CCSD and DFT-B3LYP methods. According to these data, the electronic correlation effects turned out to be obviously underestimated in the MCSCF method. SOPPA gave much better results and the CCSD method turned out to be the best. Calculation by the DFT-B3LYP method also showed

Table 1. $^{13}C-^{13}C$ spin–spin coupling constants (Hz) in cycloalkanes and their heterocyclic analogues, calculated by the SOPPA method.[173]

Compound	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
	0.15	−0.57	−0.14	14.75	14.19	12.4
	0.16	−0.51	−0.29	22.55	21.91	21.0
	0.18	−0.52	−0.42	28.48	27.72	28.0
	0.18	−0.16	0.35	10.63	11.00	–
	0.19	−0.63	−0.01	26.89	25.45	–
	0.20	−1.90	0.00	29.75	28.05	–
	0.19	1.20	1.26	27.88	30.54	28.4
	0.20	0.83	1.14	28.66	30.83	–
	0.21	0.97	1.21	28.22	30.60	29.54
	0.20	0.95	1.21	26.47	28.83	24.6
	0.21	0.67	1.15	30.40	32.43	–
	0.22	1.05	1.30	30.80	33.37	31.52

Table 2. $^{13}C-{}^{13}C$ spin–spin coupling constants (Hz) in monocycloalkanes, calculated by the SOPPA method.[157]

Atom number	SSCC	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
	*J*(C-1,C-2)	0.15	−0.46	−0.09	14.61	14.21	12.4
	*J*(C-1,C-2)	0.19	1.11	1.15	27.13	29.57	28.4
	J(C-1,C-3)	0.02	−0.21	−0.21	−11.09	−11.36	(−)8.1
	*J*(C-1,C-2)	0.21	−0.19	1.00	32.38	33.50	32.6
	J(C-1,C-3)	0.02	−0.18	−0.04	0.62	0.42	(+)2.8
	*J*(C-1,C-2)	0.22	−0.08	1.01	32.82	33.97	33.10
	J(C-1,C-3)	0.03	−0.14	−0.04	−2.78	−2.93	(−)2.12
	J(C-1,C-4)	0.01	−0.07	−0.01	2.10	2.03	(+)2.05
	*J*(C-1,C-2)	0.22	−0.07	0.99	33.51	34.65	34.0
	J(C-1,C-3)	0.03	−0.23	−0.04	−2.13	−2.37	–
	J(C-1,C-4)	−0.01	−0.00	−0.01	0.00	−0.02	–
	*J*(C-1,C-2)	0.22	−0.06	0.97	34.35	35.48	–
	J(C-1,C-3)	0.03	−0.18	−0.03	−2.34	−2.52	–
	J(C-1,C-4)	−0.01	0.00	−0.01	0.21	0.10	–
	J(C-1,C-5)	0.02	−0.21	−0.01	−0.14	−0.14	–

Note. Here, as in Table 3, the sign before SSCC is in parentheses if it was not determined experimentally but assigned based on calculations.

good results with adequate description of electronic correlation effects. In the forthcoming study, Sauer and Krivdin [157] calculated the $^{13}C-{}^{13}C$ SSCCs by the SOPPA and SOPPA(CCSD) methods (in comparison with the RPA method) for the series of monocycloalkanes (from cyclopropane through cyclooctane) taking into account the specific features of the conformational structure of these compounds (Table 2). They demonstrated again the key role of consideration of electronic correlation effects at least at the second order of the perturbation theory.

The $^{13}C-{}^{13}C$ spin–spin coupling constants are widely used for empirical estimation of the s orders of carbon–carbon bonds, which is especially important for sterically strained carbocycles (compounds with unusual hybridization of carbon atoms).[174, 175] Well-known correlations relate experimental and theoretical $^{13}C-{}^{13}C$ SSCC values with the product of the s characters of hybrid orbitals, which form the corresponding carbon–carbon bonds. Nevertheless, one must take into account the mechanism of spin–spin coupling transfer through several independent paths (in other words, splitting of spin–spin coupling transfer into different ways) in carbocyclic compounds. In the opposite case the use of the correlation of the 'constant–hybridization' type may lead to significant errors in estimating the s characters of hybrid orbitals. Specifically the existence of two independent transfer paths for the $^{13}C-{}^{13}C$ coupling explains the small experimental value J(C,C) = 12.4 Hz in cyclopropane (due to the negative geminal contribution) and large (in comparison with cyclopropane) value J(C,C) = 28.4 Hz in cyclobutane (due to the positive vicinal contribution), which is well reproduced in theoretical calculations [84, 157, 170] at the SOPPA level. Nevertheless, separation of the $^{13}C-{}^{13}C$ coupling paths in sterically strained carbocycles is far from unambiguous; moreover, the concept of spin–spin coupling transfer *via* several independent paths does not seem self-evident.[175]

As follows from the data of Table 1, the entire range of variation in the J(C,C) values in the series of heterocyclopropanes is almost 17 Hz. The least J(C,C) value (11 Hz) is observed for silirane (which contains an electropositive silicon atom), while the largest values are observed for thiirane (27 Hz) and oxirane (28 Hz), which contain, correspondingly, sulfur and oxygen atoms. The main changes are due to the FC contribution, which is positive throughout the entire series of compounds; at the same time, the orbital paramagnetic and spin–dipole contributions are negative. The orbital diamagnetic contribution is barely sensitive to the nature of the heteroatom and is only 0.15–0.2 Hz. As follows from the results obtained, the decisive factor for changes in $^{13}C-{}^{13}C$ SSCCs in heterocyclopropanes is the heteroatom electronegativity, the increase in which is accompanied by an increase in the coupling constant and a decrease in the carbon–carbon bond length. It is noteworthy that the calculated value J(C,C) = 14.2 Hz in cyclopropane is much smaller than the value J(C,C) = 28.1 Hz in thiirane, although the electronegativities of carbon and sulfur atoms (2.5 and 2.4, respectively) are very close. This should be primarily attributed to the significant shortening of the carbon–carbon bond in thiirane. Thus, the change in $^{13}C-{}^{13}C$ SSCCs in monoheterocyclopropanes is determined by the joint effect of two factors: heteroatom electronegativity and the carbon–carbon bond length. The calculated $^{13}C-{}^{13}C$ SSCC values for small heterocycles coincide with the experimental data within 1–2 Hz. Krivdin and Kuznetsova [170] showed that in the case of heterocycles containing third-period atoms (Si, P, S) with diffuse lone pairs and unoccupied d orbitals, the calculation quality can be significantly improved using the triplet-split correlation-consistent polarization aug-cc-pVTZ basis set augmented with diffuse functions of s, p, d and f types) for these atoms.

The range of variation in the $^{13}C-{}^{13}C$ SSCC values in the heterocyclobutane series is 29–34 Hz (see Table 1). The orbital diamagnetic, orbital paramagnetic and spin–dipole

contributions are positive in these heterocycles and amount to no more than 3 Hz in sum. The increase in the heteroatom electronegativity in the ring leads to larger positive values of calculated J(C,C) constants. However, the dependence of J(C,C) on the nature of heteroatom in four-membered heterocycles is not so obvious as in three-membered rings. The total contribution of the non-contact terms in all compounds does not exceed 10% of the total SSCC value. The main changes in the $^{13}C-^{13}C$ SSCC values in the series of heterocycles under study are determined by the contribution of the Fermi contact interaction, which is highly sensitive to the heteroatom nature and ring size. It is noteworthy that this pioneering *ab initio* calculation of $^{13}C-^{13}C$ SSCCs in the series of three- and four-membered saturated heterocycles at the SOPPA level made it possible to predict for the first time the $^{13}C-^{13}C$ SSCCs in silirane (12 Hz), phosphirane (24 Hz), thiirane (27 Hz) and phosphetane (32 Hz); these data need experimental confirmation.[170]

The $^{13}C-^{13}C$ SSCCs in small heterocycles were also decomposed[170] into the components corresponding to the one-bond, geminal and vicinal coupling pathways. As follows from the data obtained, all contributions from the one-bond paths are positive and amount to 20–25 Hz on average, which indicates a significantly reduced s order of carbon–carbon bonds in both three-membered and four-membered heterocycles, if we take into account that the $^{13}C-^{13}C$ SSCCs for the carbon–carbon bond in related onen-chain compounds are on average of about 35 Hz: 33.0 Hz in propane, 35.8 Hz in ethylamine and 37.4 Hz in ethyl alcohol. The 'heavy-atom effect' is well-pronounced for geminal coupling paths. Indeed, a replacement of a second-period element by its isoelectronic analog from the third period in a geminal path doubles the magnitude of the corresponding increment (−8.5 and −14.9 Hz for the C/Si pair; −7.2 and −15.6 Hz for N/P; −6.3 and −14.6 Hz for O/S). The small total $^{13}C-^{13}C$ SSCCs values in the cyclopropane heteroanalogues containing third-period atoms (silirane, phosphirane and thiirane), are thus determined, along with the low s-bond order, by the large negative contribution of geminal coupling paths. At the same time, all contributions of vicinal coupling paths are positive (as well as all vicinal $^{13}C-^{13}C$ SSCCs in open-chain compounds), amounting on average to 10–12 Hz.

In the series of cycloalkanes (Table 2)[157] the values of the one-bond $^{13}C-^{13}C$ SSCCs calculated by the SOPPA method, rapidly increase in magnitude with an increase in the ring size: from 14 Hz in cyclopropane and 30 Hz in cyclobutane to 35 Hz in cyclooctane. Note that the range of 33–35 Hz is a characteristic range of $^{13}C-^{13}C$ SSCC values in sterically unstrained aliphatic compounds. Obviously, the unusually small $^{13}C-^{13}C$ SSCC values in cyclopropane and cyclobutane are related to the steric strain effects, which lead to significantly underestimated s characters of the carbon hybrid orbitals forming endocyclic carbon–carbon bonds. Nevertheless, a key point of this interpretation is the necessity of taking into account the spin–spin coupling transfer *via* two independent paths, as was noted above.

b. Bicyclobutane and propellane

The electronic structures of bicyclobutane and propellane are highly unordinary and diverse, despite the seeming similarity of their structural formulas. This circumstance once caused a barrage of theoretical studies; they continue even now. In particular, the central bicyclobutane bond, which is formally assigned to the aliphatic sp^3-sp^3 type, possesses in reality almost 100% p character. At the same time, the central propellane bond has a highly nonbonding character, which is because its bonding electron density is inverted, being concentrated basically in the external part of the molecule. For this reason the central propellane bond is referred to as a 'phantom bond', and many researchers even doubt its existence. Estimates of the orbital hybridization of this bond are also highly contradictory: from $sp^{0.5}-sp^{0.5}$ to sp^5-sp^5.[174] Figure 1 shows the electron density distribution for the highest occupied molecular orbitals (HOMOs) of bicyclobutane and propellane, which mainly contain contributions of outer atomic orbitals of the bridgehead carbon atoms; this pattern describes to some extent the character of their electronic bonding, which was considered above.[158]

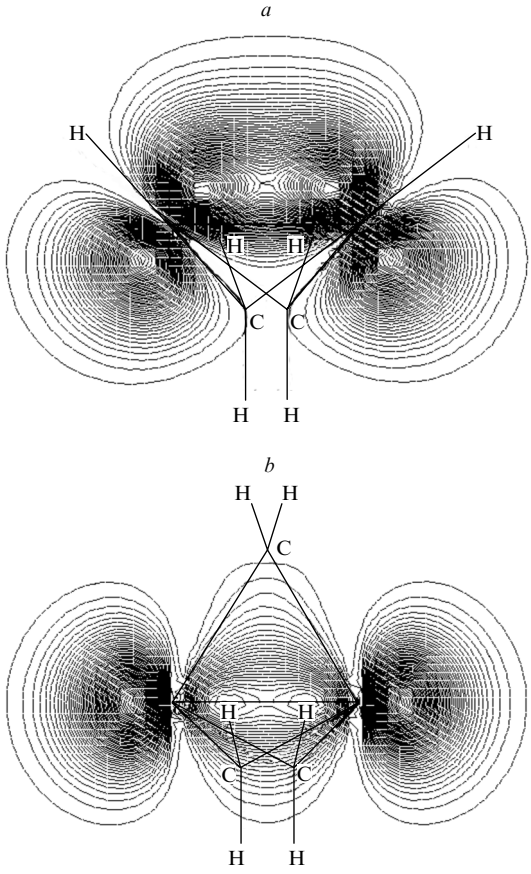


Figure 1. Distribution of HOMO electron density for (*a*) bicyclobutane and (*b*) propellane.[158]

The unusual character of bonding between the bridgehead carbon atoms in bicyclobutane and propellane also manifests itself in the unusual values of their $^{13}C-^{13}C$ SSCCs, which yield a direct estimate of the s characters of the corresponding bonds, *i.e.* their orbital hybridization. The most intriguing fact is the negative sign of the coupling constant between the bridgehead carbon atoms in the 2,2,4,4-tetramethylbicyclobutane molecule, which was measured by Finkelmeier and Luettke.[176] It is noteworthy that bicyclobutane and its derivatives yield the only known

example of negative spin–spin coupling constant between covalently bound carbon atoms.

High-level nonempirical calculations confirm the negative sign of $^{13}C-^{13}C$ SSCCs between the bridgehead carbon atoms in bicyclobutane: the SSCC values calculated by the MCSCF and SOPPA methods turned out to be -15.52 Hz[177] and -14.51 Hz,[158] respectively, in very good agreement with the experimental value: -17.49 Hz. With the use of the well-known correlations of the constant–hybridization type[174, 175] and with allowance for the additive model of spin–spin coupling transfer in bicyclobutane, the s character of the bond between its bridgehead carbon atoms was estimated (based on $^{13}C-^{13}C$ SSCCs) to be sp^9-sp^9 in the formal sp^n representation; this estimation gives evidence of extremely high involvement of the p orbitals of bridgehead atoms in the formation of this unique bond.[158]

On the contrary, the central bond in propellane, according to the results of many theoretical studies, does not exhibit any extraordinary dominant p character, which also manifests itself in the value of $^{13}C-^{13}C$ SSCC between the bridgehead carbon atoms. The spin–spin coupling constants between the bridgehead carbon atoms in propellane cannot be experimentally measured for symmetry considerations; thus, one should rely on only the calculation results.

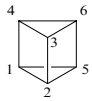
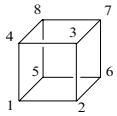
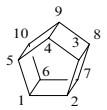
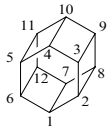
Semiempirical calculation by the SCPT INDO method leads to an obviously inadequate result (213.8 Hz);[178] low-level *ab initio* calculations, such as HF-SCF (130 Hz)[158] or EOM (2 Hz),[179] also deserve little credit. Obviously, in this case the electronic correlation effects for unusual bridgehead carbon atoms are dramatically underestimated. And only high-level *ab initio* calculation yields more realistic results: $+21.84$ Hz[180] (MCSCF-CCSD method) and $+17.46$ Hz[158] (SOPPA method). As was noted above, this SSCC cannot be experimentally measured; therefore, high-level calculations are the only tool providing a more or less realistic estimate of its value. According to this estimate ($+20$ Hz), the 'phantom bond' does physically exist in propellane, being involved in indirect spin–spin coupling transfer between bridgehead carbon atoms; concerning its hybridization characteristics, it approximately corresponds (strange as it may seem) to the ordinary aliphatic carbon–carbon bond.

c. Polyhedranes

These compounds are another fair example illustrating the prospects of *ab initio* quantum chemical SSCC calculations for studying the nature of chemical bonding. The SOPPA method was used to calculate the $^{13}C-^{13}C$ SSCCs in the classical series of polyhedranes: tetrahedrane, prismane, cubane, pentaprismane and hexaprismane (Table 3).[165, 167] We should primarily note that the use of some very efficient procedures (such as setting locally dense basis sets and explicit consideration of point symmetry groups) makes it possible to perform high-precision high-level *ab initio* calculations (to which the SOPPA approach belongs) of spin–spin coupling constants in molecular systems of up to C_{12} (hexaprismane) and even C_{14} (diamantane), which in principle cannot be done in direct calculations (*i.e.*, without the aforementioned procedures).

In view of the high molecular symmetry of polyhedranes (T_d for tetrahedran, O_h for cubane, D_{3h} for prismane, D_{5h} and D_{6h} for pentaprismane and hexaprismane, respectively) and for some other reasons (primarily, the instability of compounds), it is fairly difficult or even impossible to experimentally measure their $^{13}C-^{13}C$ SSCCs; therefore,

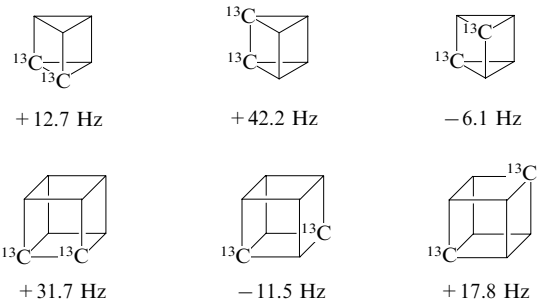
Table 3. $^{13}C-^{13}C$ spin–spin coupling constants (Hz) in polyhedranes, calculated by the SOPPA method.[165, 167]

Compound	SSCC	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
	*J*(C-1,C-2)	0.17	−0.22	−0.78	13.55	12.72	(+)9.2
	*J*(C-1,C-2)	0.24	−0.25	−0.21	12.88	12.66	–
	J(C-1,C-4)	0.26	2.29	1.18	38.46	42.19	–
	J(C-1,C-3)	0.03	−0.23	−0.01	−5.85	−6.06	–
	*J*(C-1,C-2)	0.28	1.77	1.30	28.32	31.67	29.4
	J(C-1,C-6)	0.08	−0.32	−0.12	−11.15	−11.51	–
	J(C-1,C-7)	−0.02	−0.07	−0.04	17.89	17.76	–
	*J*(C-1,C-2)	0.31	0.63	1.01	29.20	31.15	–
	J(C-1,C-6)	0.30	1.87	1.31	26.40	29.94	–
	J(C-1,C-3)	0.07	−0.23	−0.04	0.19	−0.01	–
	J(C-1,C-7)	0.10	−0.22	−0.10	−10.51	−10.73	–
	*J*(C-1,C-2)	0.32	0.89	1.00	30.05	32.26	–
	J(C-1,C-7)	0.30	1.79	1.40	27.40	30.89	–
	J(C-1,C-3)	0.06	0.02	0.00	−4.26	−4.18	–
	J(C-1,C-4)	0.05	−0.12	0.01	8.64	8.58	–
	J(C-1,C-8)	0.11	−0.19	−0.10	−12.51	−12.69	–

calculation of these constants at the high nonempirical level is often the only possible tool to estimate them.

Coming back to the data of Table 3, we should note that all formally one-bond $^{13}C-^{13}C$ SSCCs (*i.e.*, the spin–spin coupling constants between covalently bound carbon atoms) are positive and vary in the ranges of 11–13 Hz in cyclopropane fragments and 30–40 Hz in cyclobutane, cyclopentane and cyclohexane moieties. The calculated $^{13}C-^{13}C$ SSCCs values are in good agreement with the existing (unfortuanately, very few) experimental data. The total values of the calculated constants of this type in all compounds are completely determined by the dominant contribution of Fermi contact interaction, whereas the total contribution of the non-contact terms, as follows from the data of Table 3, is negligible.

As was noted above, the main factor affecting the change in $^{13}C-^{13}C$ SSCCs in cyclic compounds is the multipath coupling transfer, which is illustrated below for prismane and cubane. The negative values, J(C-1,C-3) = −6.1 Hz in prismane and J(C-1,C-6) = −11.5 Hz in cubane, should undoubtedly be related to the presence of two negative geminal spin–spin coupling paths, as in the case of related cyclobutane, where this constant amounts to −8.1 Hz.



A peculiar case is the simplest member of the polyhedrane series: tetrahedrane. The experimental value of the $^{13}C-^{13}C$ SSCC in tetrahedrane (measured in its tetra-*tret*-butyl derivative) was published [181] back in 1983; however, the sign of this constant remained undetermined for a long time. Indeed, based on the undoubted negative sign of the $^{13}C-^{13}C$ SSCCs between the bridgehead carbons in bicyclobutane, one should reasonably expect the corresponding constant in tetrahedrane (composed of seemingly 'connected' bicyclobutane fragments) be also negative. This question can be unambiguously answered by carrying out high-precision *ab initio* calculations at the SOPPA level; according to these calculations, this constant is positive (+12.72 Hz) due to the dominant positive FC contribution (+13.55 Hz).[165, 167]

2. Configuration assigment of azomethines

Determination of the configuration of azomethines using the $^{13}C-^{13}C$ SSCCs is based on the orientational lone pair effect (LPE) of nitrogen atom, which is one from main stereoelectronic effects influencing the change in the $^{13}C-^{13}C$ SSCCs involving heteroatoms of organic molecules; it is most pronounced specifically in imine nitrogen compounds, amounting to 20% of the SSCC value. Historically oximes were the first objects where the main concepts about the nature of this effect were formulated and the methods of the configurational assignment of azomethines using $^{13}C-^{13}C$ SSCCs were developed; they were published for the first time in the pioneering papers by Krivdin *et al.*[182, 183] This configuration assignment is based on the significant difference in the $^{13}C-^{13}C$ SSCCs for the configurational isomers of azomethines, which is related, first, to the spatial interaction of the nitrogen lone pair with the neighbouring bond, which is in the *cis*-position to the lone pair under consideration. This interaction opens an additional channel of spin–spin coupling transfer, thus providing a positive contribution to the total value of the coupling constant between the carbon atoms of the corresponding bond. Second, electron density is transferred from the nitrogen lone pair to the antibonding orbital, which is in the *trans*-position to this lone pair ($n_\sigma-\sigma^*$-interaction). Due to this, the this carbon–carbon bond is elongated, thus reducing the corresponding spin–spin coupling, and the coupling constant for the carbon atoms of this bond decreases; as a result, a negative contribution to the total value of this constant arises.[184, 185] The mutual contribution of the two aforementioned stereoelectronic effects gives rise to this sharp difference in the $^{13}C-^{13}C$ SSCCs of the azomethine configurational isomers.

This method performs very well when one can measure the $^{13}C-^{13}C$ SSCCs in both azomethine isomers; however, this often cannot be done for a number of reasons (for example, when the azomethine under study is isolated and exists in the form of only one configurational isomer). As a result, one has to be relied on the corresponding constant for only one isomer. Specifically in this case high-precision nonempirical SSCC calculation provides an inestimable help: it predicts (with an accuracy close to the measurement accuracy) this constant for both isomers of azomethine with unknown structure and thus allows one to unambiguously assign its configurations based on one experimental and two calculated $^{13}C-^{13}C$ SSCCs.

A cycle of studies was devoted to SOPPA calculations of $^{13}C-^{13}C$ SSCCs in aliphatic, alicyclic,[186, 187] aromatic, heteroaromatic,[188] carbonyl- and carboxyl-containing[189] oximes. As a result, the ranges of variation in the $^{13}C-^{13}C$ SSCCs for the carbon–carbon bond of the oxime function located in *cis* (J_{cis}) and *trans* (J_{trans}) positions with respect to the nitrogen lone pair were established, which makes it possible to assign configurations of oximes and any their derivatives. As an example we report below the SOPPA-calculated J_{cis} and J_{trans} in acetone oxime, which are in excellent agreement with the experimental values; the latter differ by 8.6 Hz for different conformers, *i.e.*, ~20% of the SSCC value.[186]

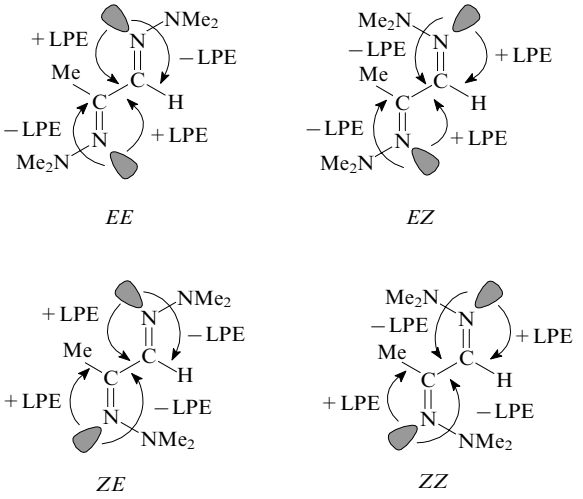
SSCC	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
J_{cis}	0.2	−1.1	0.7	51.8	51.6	49.8
J_{trans}	0.2	−1.1	0.7	41.7	41.5	41.2

The method for establishing oxime configuration based on experimental measurement in combination with high-precision *ab initio* calculation of $^{13}C-^{13}C$ SSCCs, being universal, was further used to determine the configuration at the C=N double bond in molecules of a large number of compounds of the azomethine series with most diverse structures: allenylthioimidates,[190] azomethines of α,β-unsaturated aldehydes,[191] iminodihydrofuranes[192] and their functionilized derivatives,[193] iminopyrrolizins,[194] oximes of silicon- and germanium-containing propynals,[195] aminosul-

fonylamidines,[196] *N*-arenesulfonylimines of polychloraldehydes[197] and N-arenesulfonylformamidines,[198] and methylglyoxal bis(dimethylhydrazones).[199]

It is of interest that in the last example we had to establish simultaneously configurations at two C=N bonds in four theoretically possible configurational isomers of one compound, which was isolated as a mixture of two isomers of unknown structures. SOPPA calculation[199] was used to determine all LPE contributions (+LPE and −LPE) to the corresponding $^{13}C-^{13}C$ SSCCs in four possible isomers of methylglyoxal bis(dimethylhydrazone), as shown in Scheme 1.

Scheme 1



Measurement of $^{13}C-^{13}C$ SSCCs from ^{13}C-satellite ^{13}C NMR spectra of the two isomers obtained (Fig. 2) in combination with calculation of these constants in all four possible isomers by the SOPPA method made it possible to unambiguously assign the isolated methylglyoxal bis(dimethylhydrazone) isomers as *EE* and *ZE*.[199]

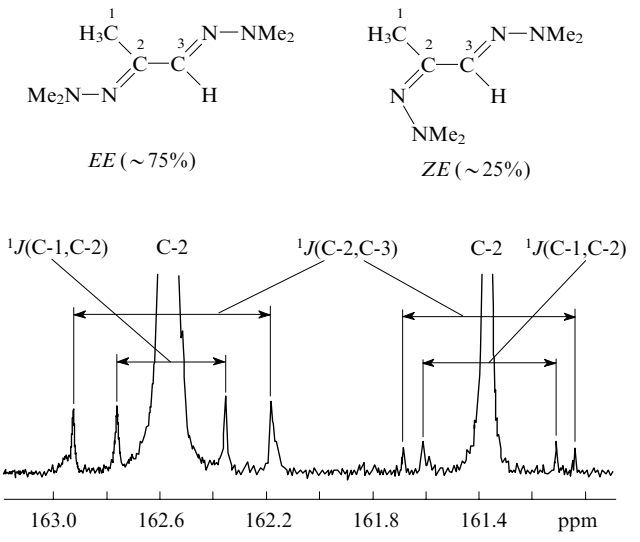


Figure 2. ^{13}C-Satellite ^{13}C NMR spectrum of bis(dimethylhydrazone) methylglyoxal in $CDCl_3$.[199]

3. Conformational analysis of organic compounds

No less important is the role of SSCC calculations (both at the DFT level and with the use of more exact, purely *ab initio* methods) in the conformational analysis of organic compounds. A classical example in this field is the work by Wu and Cremer,[200] dealing with the conformational analysis of tetrahydrofuran based on calculations of the angular dependence of $^{1}H-^{1}H$, $^{13}C-^{1}H$ and $^{13}C-^{13}C$ SSCCs within the electron-density functional theory by the B3LYP method. They obtained 26 theoretical angular dependences of SSCCs of different types related to the internal pseudorotation of tetrahydrofuran molecule and found a good agreement between the calculated constants, averaged over conformational states of the molecules, and their experimental values. In another similar study Wu *et al.*[201] performed detailed analysis of the conformational structure of cyclopentane based on calculated angular dependences of the $^{1}H-^{1}H$ and $^{13}C-^{1}H$ SSCCs by the B3LYP method. They derived and thoroughly studied the angular dependences of SSCCs upon internal pseudorotation of cyclopentane molecule; this approach, in combination with analysis of experimental SSCC values, made it possible to perform complete conformational analysis of the cyclopentane molecule.[201]

In the three recent studies Contreras *et al.* compared the results of calculating the $^{1}H-^{1}H$, $^{13}C-^{1}H$ and $^{13}C-^{13}C$ SSCCs by the B3LYP method with experimental data to perform conformational analysis of 5-substituted furan-2-carbaldehydes,[202] 2-hydroxypyridines[203] and 2-substituted 4-*tert*-butylcyclohexanones.[204] Afonin *et al.*[205] used theoretical calculations of different SSCC values to perform configuration and conformational analysis of pyrrole-2-carbaldehyde oxime. The SSCC calculations were performed at the B3LYP level using the 6-311G++(3df,p) and aug-cc-pVDZ basis sets. Analysis of the calculated and experimental SSCC values revealed that the pyrrole-2-carbaldehyde oxime molecule has a preferred *syn*-orientation of the oxime group in both *E* and *Z* isomers.[205] Pecul *et al.*[206] performed theoretical calculations of $^{1}J(P,X)$ (X = H, O, S, Se, C and N) SSCCs in different phosphorinanes at the B3LYP level using the aug-cc-pVTZ-J and aug-pcJ-1 basis sets and thoroughly studied the stereoelectronic substitution effects at the phosphorus atom. They revealed a significant difference in the $^{1}J(P,H)$ values for the axial and equatorial hydrogen atoms in 1,3,2-dioxophosphorinane, which reaches 90 Hz(!); such a large difference can be used as a reliable tool for identifying diastereoisomers in the series of compounds under study.

Ambati and Rankin[207] performed a systematic study of $^{2}J(Si,H)$ and $^{3}J(Si,H)$ SSCCs in a wide series of alkoxysilanes. The SSCC calculations were carried out at the DFT/B3LYP level using the 6-31G, cc-pVTZ and 6-311G+(d,p) basis sets. They calculated the Karplus angular dependences for internal rotation in molecules of some representatives of the alkoxysilane series for the $^{3}J(Si,H)$ vicinal constants; this approach, in combination with the analysis of the cross sections of energy surfaces, made it possible to thermally average the SSCCs under consideration and carry out conformational analysis in this series.

There is a large cycle of studies devoted to calculations of the angular dependences of SSCCs of different types, caused by the orientational LPE of heteroatoms (primarily, nitrogen, oxygen, phosphorus and selenium). The value of this effect is determined by the spatial orientation of the lone pair with respect to the spin–spin coupling path; this

circumstance can be used in the conformational analysis of various heteroatomic compounds. In the early studies these calculations were performed at the semiempirical level.[208, 209] Being qualitative to a great extent, they, nevertheless, affected significantly the application of more precise *ab initio* calculation methods for solving stereochemical problems based on SSCCs.

Here, we should primarily note a large number of studies devoted to calculation of $^{1}H-^{1}H$, $^{13}C-^{1}H$, $^{15}N-^{1}H$, $^{29}Si-^{1}H$ and $^{13}C-^{13}C$ SSCCs by the SOPPA method in order to gain insight into the conformational structure of a large series of heteroatomic compounds, in which the heteroatom bearing lone pair is formally not included in the spin–spin coupling path. The compounds studied from this point of view contain a large number of heterocycles of the pyrrole series: *N*-vinylpyrroles,[210–213] including arylazo-*N*-vinylpyrroles,[214] iminopyrrolizines,[215, 216] pyrrolylpyridines[217] and related heterocycles and open-chain heteroatomic compounds, for example, vinylfurfuryl ethers,[218] *O*-vinyloximes of acetophenone[219] and unsaturated chlorosilanes with a double bond at the silicon atom.[220, 221]

The basic concept of these studies is as follows: upon internal rotation of individual molecular fragments, SSCCs of different types demonstrate pronounced angular dependences due to the change in either the contribution from the lone pairs of neighbouring heteroatoms or stereospecific contributions of steric interactions; hence, they can be used for conformational analysis and other stereochemical studies. The latter situation (*i.e.*, the change in stereospecific contributions of steric interactions upon internal rotation) is shown in Fig. 3 for the case of one geminal and two vicinal $^{13}C-^{1}H$ SSCC in 1-vinyl-2-methylpyrrole. According to the results of SOPPA calculations, these coupling constants exhibit a pronounced angular dependence upon rotation of the vinyl group with respect to the N–C bond.[211]

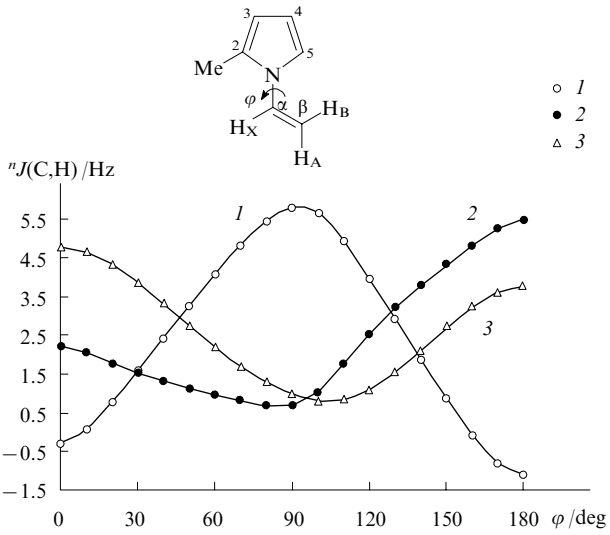


Figure 3. Angular dependences of the ^{2}J(C,H) and ^{3}J(C,H) spin–spin coupling constants in 1-vinyl-2-methylpyrrole upon internal rotation of vinyl group with respect to the N–C bond, calculated by the SOPPA method.[211]
(*1*) $^{2}J(C_{\beta},H_X)$, (*2*) $^{3}J(C\text{-}2,H_X)$, (*3*) $^{3}J(C\text{-}5,H_X)$.

As the analysis of spin–spin coupling with the use of natural bond orbitals (Natural J-Coupling, NJC)[222, 223] showed, the stereospecificity of geminal and vicinal $^{29}Si-^{1}H$ SSCCs in vinylsilane[221] is determined by three main contributions: the steric interaction between the Si–C and C–H bonds ($\sigma_{SiC}+\sigma_{CH}$), hyperconjugation electron density transfer from the bonding Si–C orbital to the antibonding C–H orbital ($\sigma_{SiC}\rightarrow\sigma^{*}_{CH}$) and, *vice versa*, the electron density transfer from the bonding C–H orbital to the antibonding Si–C orbital ($\sigma_{CH}\rightarrow\sigma^{*}_{SiC}$) (Fig. 4). Based

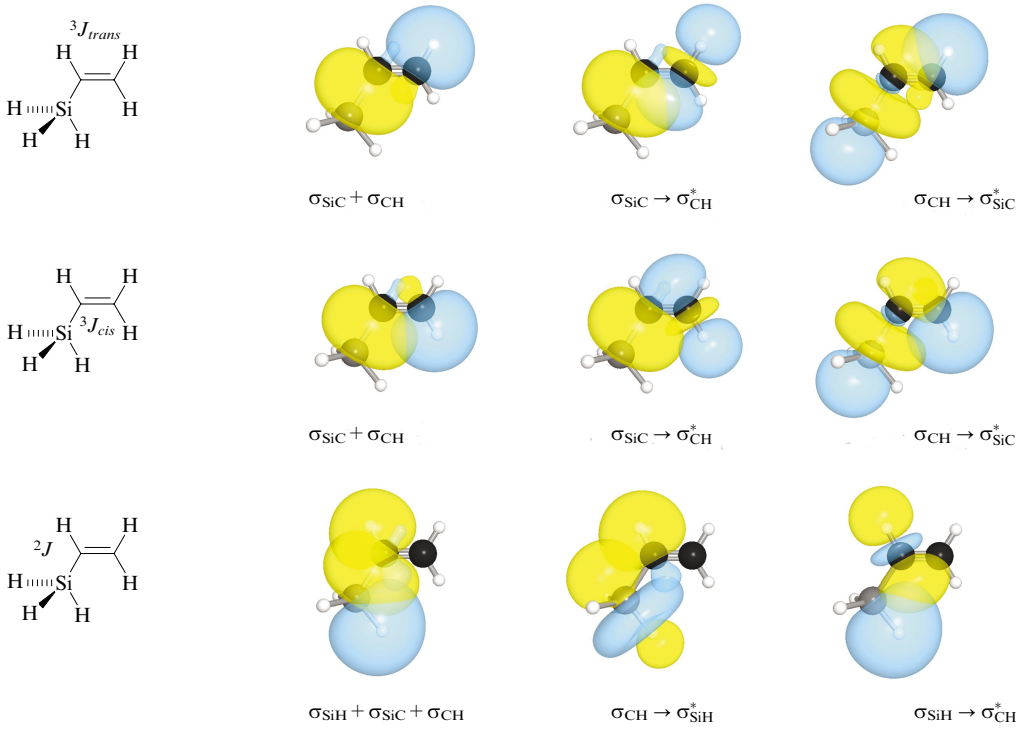


Figure 4. Main NJC contributions determining the stereospecificity of the $^{29}Si-^{1}H$ SSCC in vinylsilane.[221]

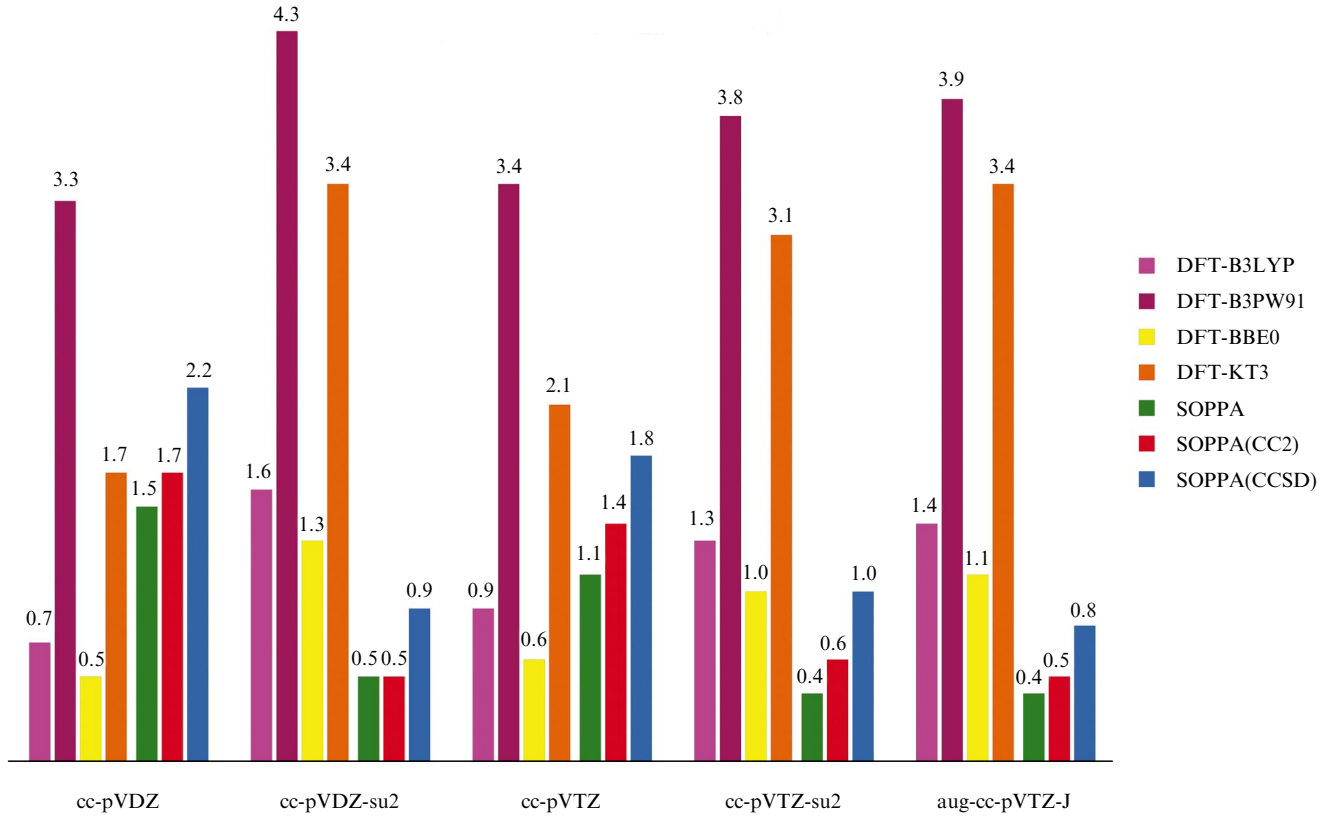


Figure 5. Mean absolute errors of the density functional theory and polarization propagator methods in combination with different basis sets in calculations of $^{29}Si-{}^{1}H$ SSCCs in unsaturated chlorosilanes.[220]
The mean absolute errors (in Hz) are given above the bars.

on these data, the vicinal $^{29}Si-{}^{1}H$ SSCCs, both measured and calculated by the SOPPA method, were used for the configuration assignment of isomers in a wide series of chlorovinylsilanes.[221]

Shown in Fig. 5 are the results on the relative accuracy of different DFT and SOPPA methods used in combination with different basis sets for the calculation of silicon-hydrogen coupling constants in the series of unsaturated chlorosilanes. It was established that the DFT methods provide an acceptable calculation accuracy, which is, however, lower than that of the second-order polarization propagator approach.[220]

A systematic study of the stereospecificity of $^{31}P-{}^{1}H$ SSCCs in unsaturated phosphines, phosphine oxides, phosphine sulfides and phosphine selenides, which is due to the internal rotation of vinyl groups with respect to the P–C bonds, was performed in three fundamental studies by Fedorov *et al.*[224–226] using the SOPPA method. Somewhat later Hersh *et al.* published a paper,[227] where very similar results on the angular dependence of the vicinal $^{31}P-{}^{1}H$ SSCC through the double bond in phosphines were obtained at the DFT level. Here, the case in point is the angular dependences (induced by the orientational LPE) of the SSCCs where the heteroatom bearing lone pair is formally included in the spin–spin coupling path. As the SOPPA calculations showed, these dependences are highly pronounced, and the range of variation in the SSCC values, determined by the internal rotation of molecular fragment with respect to the heteroatom with lone pair, may reach several dozens of hertz.[224, 226] In particular, upon rotation of vinyl group around the P–C bond in trivinylphosphine by 180°, the geminal $^{2}J(P,H)$ constant increases by 70 Hz as the $C-H_X$ bond turns toward the phosphorus lone pair, as

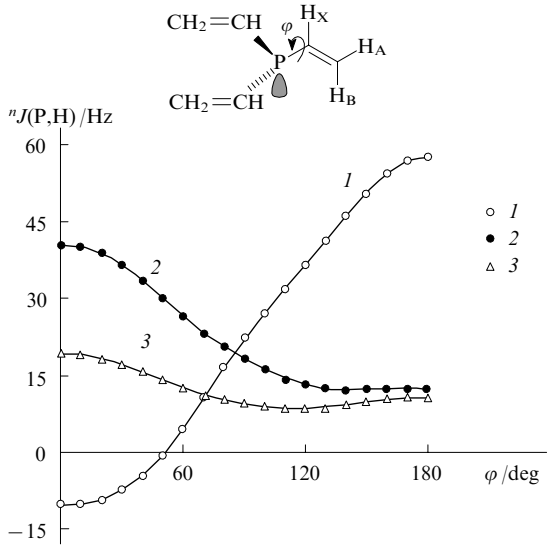


Figure 6. Angular dependences of the $^{2}J(P,H)$ and $^{3}J(P,H)$ spin–spin coupling constants of trivinylphosphine upon rotation of vinyl group around the P–C bond, calculated by the SOPPA method.[224]
(*1*) $^{2}J(P,H_X)$, (*2*) $^{3}J(P,H_A)$, (*3*) $^{3}J(P,H_B)$.

shown in Fig. 6. The pronounced angular dependences of the $^{31}P-{}^{1}H$ SSCC, related to the stereospecific influence of the phosphorus lone pair, can be used in stereochemistry and conformational analysis of organophosphorus compounds.[224, 226, 227]

The large cycle of recent studies by Rusakov *et al.*[228–235] is devoted to the conformational analysis of various organoselenium compounds based on high-level *ab initio* calculations (SOPPA, SOPPA(CC2) and SOPPA(CCSD) methods) of $^{77}Se-{}^{1}H$ spin–spin coupling constants in combination with experimental measurements. It turned out that the $^{77}Se-{}^{1}H$ SSCCs exhibit extremely pronounced stereospecificity, which is bound to the orientational effect of the selenium lone pair; this property is excellently reproduced in *ab initio* calculations at the SOPPA level for such compounds as the parent divinyl selenide,[229] and its derivatives: sterically hindered phenylselanylalkenes [230] and alkenylselanyl sulfides with open chain,[231] saturated selenium-containing heterocycles — derivatives of 1,3-diselenane and 1,2- diselenolane,[232] and aromatic and unsaturated selenium-containing heterocycles, including 2-substituted selenophenes [233, 234] and, on the other hand, thiaselenetane, selenasilole, thiaselenole, thiaselenolane and dihydrothiaselenine derivatives.[235]

Our theoretical study [236] was devoted to comprehensive analysis (at the SOPPA level) of the stereospecificity of geminal and vicinal $^{77}Se-{}^{1}H$ SSCCs in diethyl selenide, which is due to the effect of selenium lone pair. In particular, in the case of vicinal ^{3}J(Se,H) constant, we used the SOPPA method to calculate the three-dimensional surface for the $^{77}Se-{}^{1}H$ SSCC in diethyl selenide for simultaneous internal rotation around two bonds: C–C (φ_1) and Se–C (φ_2) (Fig. 7). One can see that this surface is characterized by a global maximum **A** (38 Hz) at $\varphi_1 = \varphi_2 = 180°$, two degenerate maxima **B** (27 Hz) at $\varphi_1 = 0°(360°)$, $\varphi_2 = 180°$ and two degenerate minima **C** (−2 Hz) at $\varphi_1 = 90°(270°)$, $\varphi_2 = 180°$. A characteristic feature is that the two-dimensional slice of the surface under consideration at a fixed value of one of the angles ($\varphi_2 = 180°$) yields a classical Karplus dependence for ^{3}J(Se,H) with a pronounced global minimum (−2 Hz) at $\varphi_1 = 90°$ and two maxima (27 and 38 Hz) at $\varphi_1 = 0$ and 180°, respectively; this fact makes vicinal $^{77}Se-{}^{1}H$ SSCCs promising in conformational analysis of organoselenium compounds.

An elegant example of solving complex stereochemical problems applying high-precision *ab initio* SSCC calculations is the assignment of diastereotopic protons of selenium-containing heterocycles based on experimental measurement and SOPPA calculation of the $^{77}Se-{}^{1}H$ spin–spin coupling constants involving a diastereotopic proton pair.[235] The experimental values of these constants turned out to be significantly different, and this difference is excellently reproduced in SOPPA calculations with averaging over localized conformational states. This approach served a basis for carrying out conformational analysis and unambiguous assignment of diastereotopic protons in the series of selenium-containing heterocycles under consideration.[235]

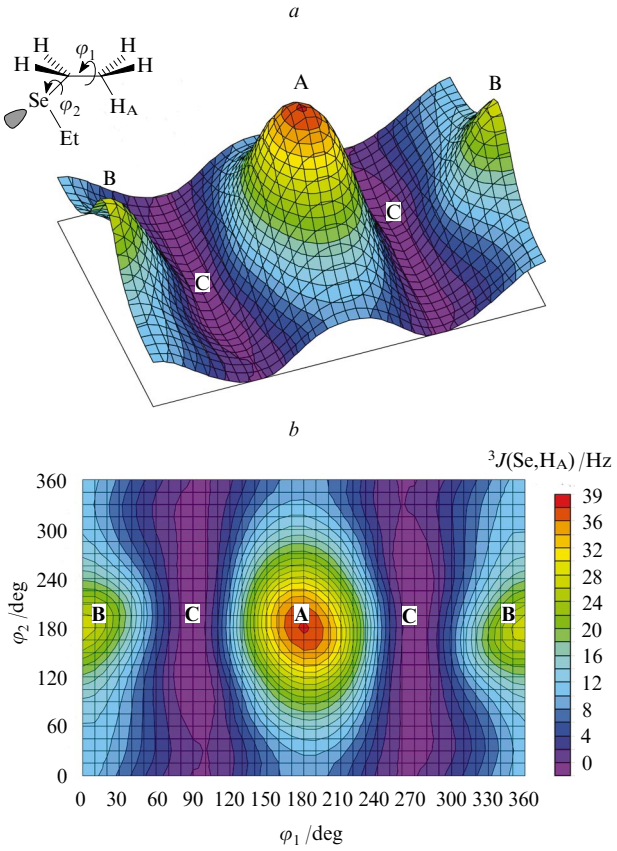


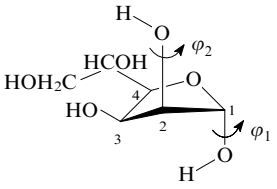
Figure 7. Surface of the $^{77}Se-{}^{1}H$ spin–spin coupling constant (*a*) and its two-dimensional projection (*b*) in diethyl selenide for rotation around the C–C (φ_1) and Se–C (φ_2) bonds, calculated by the SOPPA method.[236]

4. Stereochemical studies of biomolecules

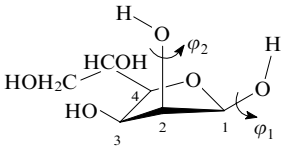
The establishment of configuration and conformational structures of sugar residues in carbohydrates, nucleosides, nucleotides, nucleic acids and products of their metabolism is of exceptional importance for studying and predicting their biological activity. Stereochemical analysis of biological molecules with carbohydrate rings is based on a wide use of different physicochemical analytical methods and on a number of calculation and theoretical methods of computer and quantum chemistry. In the last years, in view of rapid development of NMR spectroscopy, much attention has been paid to spin–spin coupling constants, which contain unique information about the stereochemical and electronic structures of biomolecules, primarily carbohydrates. The accumulated experimental data on $^{1}H-{}^{1}H$, $^{13}C-{}^{1}H$ SSCCs in carbohydrates (see, *e.g.*, Marshall's review [237]) suggest that they are sensitive to stereochemical effects, exhibiting dependence on the configuration of anomeric centre, conformation of carbohydrate ring, and the rotational conformations of hydroxyl groups.

These dependences were also established in the theoretical studies devoted to the stereospecificity of SSCCs in sugars: furanoses,[238–240] pyranoses,[241–245] septanoses [246, 247] and more complex biological objects, including carbohydrate fragments.[248–250] Those studies (as well as many others that are not reviewed here), which gain insight into the nature of SSCC stereospecificity, were performed either at the DFT level, or using low-level *ab initio* methods (HF-SCF, RPA) or applying semiempirical methods, such as SCPT (or FPT) INDO.

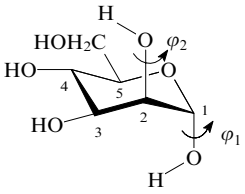
Scheme 2



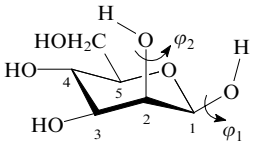
α-D-Mannofuranose



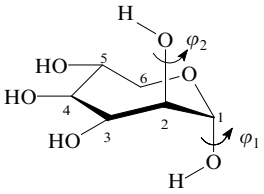
β-D-Mannofuranose



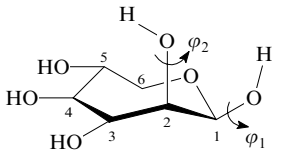
α-D-Mannopyranose



β-D-Mannopyranose



α-D-Mannoseptanose



β-D-Mannoseptanose

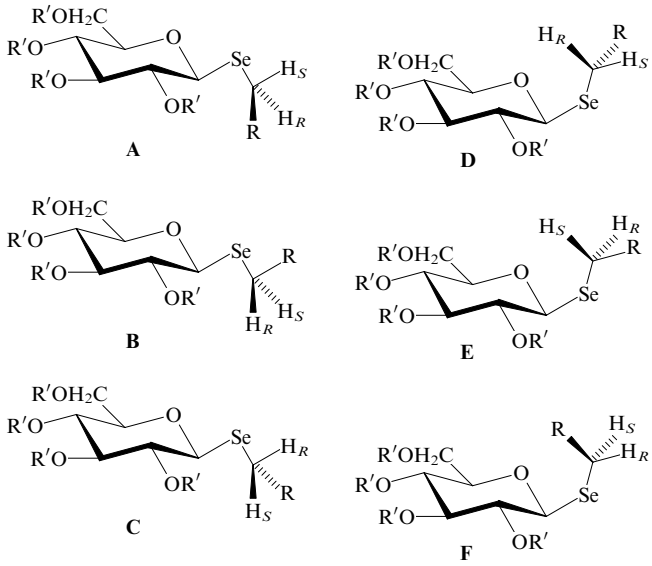
For example, Cloran *et al.*[248] studied in detail the specific features of the conformational structure of 2-deoxy-β-D-*erythro*-pentafuranose based on calculations of different one-bond, geminal and vicinal $^{1}H-{}^{1}H$, $^{13}C-{}^{1}H$ and $^{13}C-{}^{13}C$ SSCCs. The SSCC calculations were performed at the DFT level applying the B3LYP functional. They derived theoretical angular dependences of different constants upon internal pseudorotation of pentafuranose ring, which made it possible to study different conformational features of this molecule. Helgaker and co-workers[251] performed systematic study of the specific features of conformational structure of glycolaldehyde with calculation of all possible SSCCs in this molecule. The constants were calculated at the DFT and CCSD levels using the Huz-II, Huz-III and Huz-III-su3 basis sets. The dependences of SSCCs on different torsion angles upon internal rotation in the glycolaldehyde molecule were derived, analyzed and approximated by Fourier series. These dependences can be used to determine the conformational structure of various carbohydrates and their derivatives.

The results of SCPT INDO calculations with specific parameterization for a number of carbohydrates were used to formulate straightforward rules for determining the configuration of anomeric centre and the conformational structure of furanose, pyranose and septanose rings based on $^{13}C-{}^{13}C$ SSCCs and establish the preferred rotational conformations of ring hydroxyl groups, related to rotation around the C(1)–O and C(2)–O bonds.[239, 241, 246, 247] Scheme 2 exemplifies the existence of the possible mannose isomers and conformers.[247]

We should focus upon two studies devoted to high-precision *ab initio* SOPPA calculation of the geminal $^{77}Se-{}^{1}H$ SSCCs in six localized conformers **A**–**F** of the selenoglycoside series (Scheme 3).[252, 253]

The results of these calculations are illustrated for the parent representative of this series of selenocarbohydrates (R = Me, R′ = H) in Table 4. One can see that there is

Scheme 3



R = Me, Ar; R′ = H, Ac

Table 4. ^{2}J(Se, H) spin–spin coupling constants (Hz) in selenoglycoside, calculated by the SOPPA method.[253]

SSCC	Conformer	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	J^{a}_{av}	Experiment
^{2}J(Se, H_R)	**A**	−0.01	−0.34	−0.5	−4.22	−5.07	4.3	6.6
	B	−0.02	−0.51	−0.4	−1.07	−2.00		
	C	−0.01	1.40	−0.8	30.17	30.76		
	D	0.01	−0.07	−0.7	−3.33	−4.09		
	E	0.02	−0.28	−0.2	−1.16	−1.62		
	F	−0.01	−0.06	−0.6	24.24	23.57		
^{2}J(Se, H_S)	**A**	−0.01	1.20	−0.7	25.91	26.40	11.2	9.8
	B	−0.01	−0.23	−0.3	−1.51	−2.05		
	C	−0.01	−0.65	−0.9	−3.41	−4.97		
	D	0.01	1.00	−0.5	29.12	29.63		
	E	−0.01	−0.39	−0.1	−1.42	−1.92		
	F	0.04	1.05	−0.6	−4.10	−3.61		

[a] Averaged over six localized conformers with allowance for their occupancies.

excellent agreement between the theoretical (SOPPA calculated) conformationally averaged geminal $^{77}Se-^{1}H$ SSCCs and the experiment values. Based on these results, the authors of study [253] could not only establish preferred rotational conformations with respect to the Se–C bonds but also unambiguously assign diastereotopic protons in the side chain of the selenocarbohydrates under study. In addition, this is one of examples (still rare) of purely high-level *ab initio* calculation of SSCCs in biological molecules.

5. Study of hydrogen bonds and intermolecular complexes

A very large number of studies are devoted to the analysis of intra- and intermolecular hydrogen bonds and various intermolecular complexes with the aid of theoretical SSCC calculations; some of them are systematized, for example, in the review by Alkorta and Elguero.[254] We refer the readers to this review and to the review by Krivdin and Contreras [9] and restrict ourselves to only the most illustrative examples.

A large cycle of works by Del Bene, Alkorta, Elguero *et al.* is devoted to the large-scale study of hydrogen bonds and intermolecular complexes based on high-precision calculation of SSCCs of different types, including the SSCCs through hydrogen bond (SSCCs of this type have been intensively studied in the last years). In particular, we should indicate the comprehensive theoretical analysis of the vicinal constants $^{3h}J(N,P)$ through the hydrogen N–H···O–P bond in different model cationic and anionic complexes, including the NH_4^+, NF_nH_{3-n} ($n = 0-2$), OPH, O_nPH_{4-n} ($n = 1, 2$) systems.[255] The $^{3h}J(N,P)$ constant was calculated by the EOM-CCSD method. This study revealed in particular that the $^{3h}J(N,P)$ constant is highly sensitive to the distance between the nitrogen and phosphorus atoms in linear anionic and cation complexes; this fact can be used to find the interatomic distance from the experimental values of this constant. In addition, the geminal $^{2h}J(N,N)$ constant through the N–H···N hydrogen bond in the series of cationic complexes was investigated by Del Bene *et al.*[256] They calculated the $^{2h}J(N,N)$ constant by the EOM-CCSD method and, based on the results obtained, derived the dependence of the $^{2h}J(N,N)$ constant on the distance between nitrogen atoms. The same research team [257] systematically studied (at the EOM-CCSD level) the behaviour of the geminal $^{2h}J(F,N)$ constant in 13 different complexes stabilized by the F–H···N hydrogen bond. It was found that the change in the $^{2h}J(F,N)$ constant in the complexes under study can be approximated by only the FC contribution to the constant. The contribution of the Fermi contact interaction and, correspondingly, the $^{2h}J(F,N)$ constant exhibit a strong dependence on the distance between fluorine and nitrogen atoms: the constant linearly decreases with an increase in this distance. A correlation between the $^{2h}J(F,N)$ constant and the electron charge density of the F–H···N hydrogen bond was also obtained in work.[257]

A number of studies were devoted to comprehensive investigation of different constants, $^{1h}J(N,H)$, $^{2h}J(N,N)$ and $^{2h}J(C,N)$, through N–H···N and C–H···N hydrogen bonds in a large series of neutral, cationic and anionic molecular complexes.[258–260] The SSCCs were calculated in these studies at the DFT, SOPPA and EOM-CCSD levels. As a result, it was found that both one-bond and geminal constants systematically decrease with an increase in the distance between nitrogen atoms of the N–H···N hydrogen bond and the nitrogen and carbon atoms of the C–H···N hydrogen bond. It was also noted that the SSCC value is significantly affected by the hybridization state of the donor atom in the hydrogen bond and, to a smaller extent, the hybridization of the acceptor atom. A decrease in the linearity of the C–H···N hydrogen bond, *i.e.*, an increase in the C–H–N angle, leads to a systematic decrease in the $^{2h}J(C,N)$ constant.

Among further publications of this research team (Del Bene, Alkorta, Elguero *et al.*), we should primarily note the studies of hydrogen bonds and intermolecular interactions in terms of high-level theoretical calculation of SSCCs of different types by the EOM-CCSD, SOPPA and DFT methods. The SSCCs were calculated for lithium-based molecular complexes,[261, 262] tetrafluoroethylene π-complexes,[263] 2-fluorobenzamide,[264] weak intermolecular complexes of molecular hydrogen with a number of molecules (HC≡CH, HC≡CLi, HC≡CF, HCN, HOH, HCl, HNC, HF),[265] $X \cdot BH_nF_{3-n}$ complexes (X = N_2, NCH, NCLi, H_2CNH, NF_3, NH_3; $n = 0-3$),[266] fluoro-substituted 1,3-diborate-2,4-diphosphoniocyclobutanes [267, 268] and some other halogen-containing complexes based on nitrogen and phosphorus.[269–272]

Afonin *et al.*[273–275] showed that one-bond $^{13}C-^{1}H$ SSCCs coud serve as an indicator of the formation of intramolecular C–H···N hydrogen bonds. Indeed, the formation of these bonds in ketoximes,[273] pyrroles [274] and hetaryl vinyl ethers [275] is accompanied by an increase in the $^{1}J(C,H)$ constant by 3–6 Hz. In the early stage of the theoretical study the influence of intra- and intermolecular C–H···N(O) bonding on one-bond $^{13}C-^{1}H$ SSCCs was investigated within the semiempirical SCPT INDO method. In particular, Afonin *et al.*[276, 277] showed that the intra- and intermolecular hydrogen bonds of this type in vinyl derivatives of heterocycles lead to an increase in the one-bond $^{13}C-^{1}H$ SSCCs for the β hydrogen atom of the vinyl group, which is directly involved in the coupling; in addition, the direct $^{13}C-^{1}H$ SSCC for the second β hydrogen atom of the vinyl group, which is not involved in hydrogen bonding, is significantly reduced. A decrease in the geminal $^{1}H-^{1}H$ and $^{31}P-^{1}H$ SSCCs due to the formation of intramolecular C–H···N(O) hydrogen bonds was also predicted.[278]

The next works of this series were devoted to the systematic study of intramolecular hydrogen bonds using SSCC calculations at the DFT/B3LYP level in a wide series of nitrogen-containing unsaturated and heteroaromatic compounds. A combined study, including analysis of experimental and theoretical data, made it possible to reveal with a high reliability the influence of intramolecular C–H···N(O) hydrogen bonds on the $^{1}J(C,H)$ constants in configurational isomers of 1-vinyl-2-carbaldehyde oxime and bis(methylhydrazone) methylglyoxal.[279, 280] It was shown that the $^{1}J(C,H)$ significantly increases in all cases when intramolecular hydrogen bonds are formed. At the same time, the effect of intramolecular N–H···N(O) hydrogen bonds on the one-bond $^{15}N-^{1}H$ SSCCs is multidirectional. In particular, the DFT/B3LYP calculation, in combination with the experimental data for the series of 2-substituted pyrroles, revealed that strong intramolecular N–H···N(O) hydrogen bonds reduce the corresponding $^{1}J(N,H)$ constant, whereas weak hydrogen bonds, in contrast, increase the latter.[281]

In elaboration of the concepts about the influence of intramolecular hydrogen bonds on SSCCs, Afonin *et al.*[282, 283] performed DFT/B3LYP calculations in order

to study theoretically the influence of bifurcation hydrogen bonds on the SSCCs with participation of ^{15}N nucleus in 2,5-disubstituted pyrroles. They showed that, in the case of weak intramolecular bifurcation hydrogen bonds, the changes in the $^{1}J(N,H)$ SSCC of the pyrrole fragment, caused by three-centre interaction with participation of pyrrole NH proton, are almost additive.[282] At the same time, in the case of strong bifurcation hydrogen bonding, this additivity is violated. In particular, the one-bond $^{1}J(N,H)$ constant through the N–H covalent bond increases in this case, whereas the $^{15}N-{}^{1}H$ and $^{15}N-{}^{15}N$ SSCCs through the hydrogen bond decrease.[283] It was shown in some studies[284, 285] that the effects of intramolecular hydrogen bonds on $^{1}J(N,H)$ SSCCs can be successfully analyzed within Bader's general quantum theory of atoms in molecules[286] and using Weinhold's method of natural bond orbitals.[287] Indeed, it turned out that the topological and energetic parameters of the intramolecular hydrogen bonds obtained within these approaches correlate well with the experimental and calculated values of the hydrogen bonding effect on the one-bond $^{15}N-{}^{1}H$ SSCCs.[284, 285]

We should also note the study by Freitas and co-workers,[288] who thoroughly studied the mechanism of spin–spin coupling transfer through the intramolecular F···HO hydrogen bond in 2′-fluoroflavonol. The $^{1h}J(F,H)$ SSCC was calculated at the DFT level applying the B3LYP and PBE0 functionals. These researchers studied in detail the effect of intramolecular hydrogen bonds of two different types (specifically, F···H–O and C=O···H–O) on the $^{1h}J(F,H)$ SSCC. The calculations for different conformers showed that this constant is extremely sensitive to the presence or absence of hydrogen bond. In the authors' opinion, this can be a good tool for determining the presence of F···H–O hydrogen bond in such compounds. For example, in the most energetically favourable conformer of 2′-fluoroflavonol, where the intramolecular F···H–O hydrogen bond is absent, the $^{1h}J(F,H)$ constant amounts to <1 Hz, whereas in the conformer containing the F···H–O hydrogen bond this constant reaches about -32 Hz.

VI. Conclusion

The material discussed in this review convincingly demonstrates evident progress of the last years in the theoretical calculations of spin–spin coupling constants. At the same time, one can see obviously increasing importance of these calculations for the structural and stereochemical investigations of the nature of chemical bonding and stereoelectronic effects, configuration assignment and conformational analysis of organic molecules, stereochemical study of biological molecules, analysis of intra- and intermolecular bonds and molecular complexes. Modern exact and reliable *ab initio* methods, which are primarily based on the formalism of polarization propagator approach and coupled-cluster theory, make it possible to calculate SSCCs almost with the same accuracy as the measurement accuracy; thus, these methods can be widely used in chemistry. The landmark of the last decade is the fact that, despite the large resource intensity of purely *ab initio* methods for calculating SSCCs and the great popularity of much less resource-intensive methods of electron-density functional theory, the range of application of high-level nonempirical methods for calculating SSCCs in practical structural studies of organic and even biological molecules constantly increases.

Summing up, we will also dwell on some purely practical considerations and recommendations on the SSCC calculations at the modern quantum chemical level. The examples reported in this review clearly demonstrate the importance of high-precision SSCC calculations in combination with experiment for solving urgent stereochemical problems. The main concept of this combined approach is as follows: performing high-precision calculations of SSCCs in different configurational isomers or conformers of molecule and comparing the results with experiment, one can determine the molecular configuration, establish the preference of conformers, and sometimes solve even finer stereochemical problems, such as the establishment of the configuration of anomeric centre in carbohydrates or carrying out diastereotopic assignment at asymmetric centres. All these procedures require SSCC calculations as exact as possible, best of all, with accuracy close to the measurement accuracy. The following questions arise: what method should be used to calculate SSCCs, what basis sets must be applied, is it necessary to take into account the influence of the chemical environment (solvation effects), vibrational corrections and relativistic effects, what programme should be used and what computational resources are required to this end?

Primarily, the SSCC calculation method must be chosen. To increase the calculation accuracy, one should obviously use *ab initio* calculations of possibly higher level, for example, the polarization propagator methods or coupled-cluster theory. But this is far from being always possible, primarily, because of the size of molecular system. In this case, one has to use DFT methods, which can also give acceptable accuracy. The relative error of different calculation methods and the quality of basis sets were discussed above by the example of calculation of the $^{29}Si-{}^{1}H$ SSCCs.

If a molecule contains more than 20 atoms (let alone hydrogen atoms), it is necessary to use one of DFT methods. These calculations are generally based on the B3LYP, B3PW91 and PBE0 functionals; cc-pVTZ, cc-pCVTZ, aug-cc-pVTZ and aug-cc-pVTZ-J can be recommended as basis sets. Obviously, the most appropriate programme for these purposes is GAUSSIAN 09, which is generally applied in these calculations; the DALTON programme can be recommended for more advanced users.

If a molecular system contains less than 20 atoms or a real molecule can reasonably be reduced to required size (for example, by replacing a long alkyl fragment with a methyl group), one can try to perform more exact *ab initio* calculation using one of the polarization propagator methods or coupled-cluster theory. Incidentally, we should note that the the 'reduction' of molecule may lead to obviously unacceptable results, and it must be performed very carefully, clearly understanding what stereoelectronic effects may arise in this case and how they may affect the calculated SSCC values.

As was noted above, three polarization propagator methods have been computationally implemented to date: SOPPA, SOPPA(CC2) and SOPPA(CCSD). According to our experience, the SOPPA(CC2) and SOPPA(CCSD) methods only slightly improve the calculation accuracy in comparison with the basic SOPPA method, whereas their resource intensity [especially that of SOPPA(CCSD)] is

much higher. Therefore, SOPPA is optimal for routine calculations. When choosing basis sets, it is of key importance to set basis sets separately, *i.e.*, use special high-quality basis sets for the atoms for which SSCCs are calculated and standard basis sets of satisfactory quality for other atoms. A characteristic point is that specifically separate setting of basis sets made it possible to expand exact *ab initio* calculations from 2 – 3-atom molecules to real organic molecules. We can recommend cc-pVTZ-Cs, aug-cc-pVTZ-J, sad-J and pcJ-*n* ($n = 2, 3$) as basis sets for the atoms between which SSCCs are calculated and the standard Dunning sets cc-pVXZ (X = D, T) for other atoms. All the aforementioned polarization propagator methods for calculating SSCCs are implemented in the recently released version of the DALTON package. The SSCC calculation within the coupled-cluster theory in combination with the equation-of-motion formalism, EOM-CCSD, is implemented, for example, in the CFOUR and ACES packages. Here, we can recommend the same basis sets as for SOPPA calculations.

Should one take into account the influence of the solvation effects, vibrational corrections and relativistic effects in routine SSCC calculations? Generally not; however, according to the experimental data, consideration of these factors may significantly increase the accuracy and reliability of SSCC calculations in some cases. This is primarily true for the influence of the chemical environment (solvent), especially at the stages of localization of stationary points on the potential surface and geometry optimization, which precede direct SSCC calculations. Consideration of the solvent effect at the stage of SSCC calculation generally does not lead to significant changes in the calculation results. The same holds true for vibrational corrections. In addition, consideration of the influence of the environment and vibrational corrections at the stage of SSCC calculation greatly increases the calculation resource intensity; therefore, these effects are neglected in most cases (although in each specific case one must at least conceive the possible contribution of environment and vibrational corrections, for example, using the known data in the literature). The effect of the environment and vibrational corrections can be taken into account at the stage of SSCC calculations at the DFT level in some available programme package, *e.g.*, DALTON or ADF.

Concerning relativistic effects, as was noted above, their consideration is of reasonable importance for only the elements of the fifth and higher periods, whereas for the elements of the first three periods and, to a great extent, the fourth-period elements the relativistic corrections are negligible and can be disregarded with full confidence in practical calculations. The relativistic effects in SSCC calculations for heavy atoms are most fully taken into account in the DIRAC and ADF packages, especially the former.

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