Russian Chemical Reviews **74** (11) 1027 – 1038 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n11ABEH001175

Quantum-chemical methods for the construction of wave functions of many-electron systems alternative to the Hartree – Fock approximation

N D Chuvylkin, E A Smolenskii, N S Zefirov

Contents

I.	Introduction	1027
II.	Retrospective view on the development of *ab initio* methods in quantum chemistry	1028
III.	Many-electron wave functions	1032
IV.	Testing of many-electron wave functions	1034
V.	Conclusion	1036

Abstract. Modern quantum-chemical methods for the construction of approximate many-electron wave functions differing from the traditional Hartree – Fock approximation are considered. Attention is focused on the methods based on the use of symmetric groups and nodal surfaces of many-electron wave functions. A new interpretation of the Pauli exclusion principle is discussed. The bibliography includes 75 references.

I. Introduction

The latest achievements in theoretical chemistry are largely related to quantum chemistry. The advent of computers with vector processors such as CRAY and CYBER in the late-1970s – early-1980s affected appreciably the status of quantum-chemical calculation.[1] Even more pronounced changes in computational quantum chemistry were induced by the appearance of computers with parallel processors.

The applications of computational quantum-chemical methods have now gone far beyond the limits of traditional fields of chemistry (organic, inorganic, physical) and have extended into many fields of physics, biology, pharmacology, materials science, *etc*. The range of these applications is being extended because more and more problems can be tackled by the techniques of computational chemistry, which has become a generally recognised source of valuable information. Computers can supplement (and in some cases replace) conventional laboratory techniques if experimental information is either insufficient or cannot be gained due to temperature, concentration or procedural restrictions.

Reliable quantum-chemical predictions of the electronic structure and physicochemical parameters of molecular systems are based on *ab initio* methods, which are more rigorous than the single-electron Hartree – Fock (HF) approximation and take into account electron correlation. The development of these methods receives most attention.[1 – 5] Numerous computer programmes taking account of the electron correlation effects, to some extent, have now been developed.

N D Chuvylkin, E A Smolenskii, N S Zefirov N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp 47, 117913 Moscow, Russian Federation. Fax (7- 495) 135 53 28, tel. (7- 495) 135 90 89 (N D Chuvylkin, E A Smolenskii), e-mail: smolensk@cacr.ioc.ac.ru (E A Smolenskii), tel. (7- 495) 939 16 20 (N D Zefirov)

Received 9 March 2005
Uspekhi Khimii **74** (11) 1118 – 1131 (2005); translated by Z P Bobkova

Owing to all-round computerisation and the availability of major quantum-chemical software programmes to chemists, some of these programmes have lately been regarded as routine. Whereas 30 years ago the predictions of quantum chemists were met, at best, with scepticism, now there is rather a risk of overestimating the reliability of quantum-chemical results. It should be borne in mind that the magical words *ab initio* do not always ensure high accuracy computations.

One can hardly be confident that quantum-chemical predictions are correct, if, for example, the errors in determining the system energy, which are involved in any *ab initio* computation due to the neglecting of or incomplete allowance for the electron correlation effects, prove to be much greater than the estimated activation energies, barriers to internal rotation and inversion, chemical bond dissociation energies, *etc*. Therefore, to obtain reliable physicochemical information using *ab initio* methods, effective ways of taking account the electron correlation are required. It is not by chance that the problems of accurately calculating correlation effects based on primary principles are regarded as highly important in quantum chemistry.

Unfortunately, computational procedures for the elimination of correlation errors are not embedded in all routine quantum-chemical programmes. Until chemists who run modern computing machinery realise its limited scope, even the most expensive *ab initio* computations will be fraught with artifacts and illegitimate conclusions.

A critical analysis[1 – 3] of the trends and prospects for the development of modern quantum chemistry has shown that traditional *ab initio* calculations have reached a sort of limit. This calls for searching for new ways of solving the Schrödinger equation for many-electron systems, other than those based on the HF approximation. While working along this line, we proposed an approximate method for solving this equation and called it the many-electron wave function (MWF) method.[6]

The MWF technique is based on in-depth mathematical analysis of the generally accepted interpretation of the fundamental Pauli exclusion principle, which actually forbids not only 'trivial', but also many other seemingly quite allowable electron configurations. A specific feature of the proposed method is that, in conformity with the views of the founders of quantum mechanics — W Heisenberg, P Dirac and E Schrödinger — paramount importance is ascribed to analysis of the properties of the nodal surfaces of antisymmetric MWFs.

The foundation of the MWF method is composed of two fundamental statements.

1. Generalisation[7] of the Courant–Hilbert theorem for the case of precise non-relativistic many-electron wave function Ψ for the electronic state with a specified spin.

2. An original hypothesis,[8] according to which the Pauli exclusion principle should be interpreted as the prohibition for two electrons with identical spins to occur on the same equipotential surface in a given configuration space.

The MWF method has now been tested using a number of 'test systems' most representative of quantum mechanics.

II. Retrospective view on the development of *ab initio* methods in quantum chemistry

Since the HF method in *ab initio* approximation is free from experimental or adjustable parameters, and allows a simple and vivid interpretation of the calculated properties, many quantum chemists do not see the point in developing alternative approaches, referring to the sharp increase in the degree of computerisation of theoretical investigations observed in the last decade and to the progress in computer engineering already attained (and expected in the future). Indeed, the last ~ 50 years have seen the transition from scalar computers (three successive generations) to modern vector computers and computing potential has sharply increased.

Chemists already have powerful computers of a new architecture at their disposal. Perhaps, not only supercomputers but also sets of computers operating in parallel with hundreds or thousands of simultaneously operating units could play an important role in the further development of quantum chemistry and could initiate a new avalanche of more accurate *ab initio* calculations based on the HF approximation. However, most likely, this would have an adverse effect on the development of theoretical quantum chemistry, as it is much easier to apply well-developed theoretical methods to new systems than to develop absolutely new approaches.

One should bear in mind that apart from the obvious advantages, the Hartree–Fock approximation has substantial drawbacks. These drawbacks are due to the fact that in the use of this approximation, the number of two-electron integrals grows as $m(m+1)/2$, where $m = n(n+1)/2$, and n is the number of the basis functions. This sharp ($\sim n^4$) dependence imposes natural restrictions on high-precision *ab initio* calculations for large molecular systems. In addition, the electron correlation effects are often great. For example, the HF approximation does not describe adequately the dissociation of even diatomic molecules, especially Be_2 and F_2 (Table 1). Usually, such drawbacks can be eliminated only partially on switching to Configuration Interaction (CI) methods, despite the impressive number ($\sim 10^6$) of configurations additionally taken into account.

However, the popularity of the CI methods is held up by the fact that the *ab initio* calculation, which reaches in accuracy the 'Schrödinger' limit, is not physically obvious, its results requiring interpretation like experimental data. The point is that in high-precision *ab initio* methods, taking into account the configurational interaction, the total wave function is 'smeared' over many thousand determinants, whose clear interpretation is impossible. It is noteworthy that the implementation of CI methods for complex molecular systems currently does not provide even a 90% allowance for the electron correlation energy.

Table 1. Dissociation energy (in eV) of diatomic molecules.[1]

Molecule	HF calculation	Experiment
H_2	3.64	4.75
Li_2	0.17	1.07
Be_2	see [a]	0.10
B_2	0.89	3.09
C_2	0.79	6.32
N_2	5.20	9.91
O_2	1.28	5.22
F_2	−1.37	1.66
LiH	1.49	2.52
HF	4.38	6.10

[a] The HF approximation gives a purely 'repulsive' curve for the dependence of energy on the distance between the nuclei.

At first glance, this is surprising. Indeed, for $N = 2$ (N is the number of electrons) for example, for a helium atom or a hydrogen molecule, the problem is solved by a high-precision *ab initio* method using an advanced computer with an accuracy in energy down to 10^{-8} a.u. in fractions of a second. Meanwhile, for $N = 3$ (Li atom) or $N = 4$ (LiH molecule), the same computer can ensure, at best, an accuracy of ~ 0.001 a.u. after running for several hours, *i.e.*, the duration of an equivalent high-precision calculation increases on passing from $N = 2$ to $N = 4$ by approximately ten (!) orders of magnitude. This is accompanied by a catastrophic complication of the problem, to such an extent that equally high-precision *ab initio* calculations are absolutely impracticable for complex electron systems

This means that on passing to systems with $N = 3$, the computational situation changes in principle. This brings about the viewpoint that, due to the substantial growth of the number of mathematical operations involved in the use of the Self Consistent Field (SCF) scheme, even for an insignificant increase in the number of electrons, high-precision *ab initio* calculations have no prospects in most fields of chemistry and materials science, because they are forcibly meant for relatively small molecules. Therefore, researchers still pay considerable attention to further development of semi-empirical methods. However, this is not a priority line of research, although it is still important. At present, the problem of searching for fundamentally new methods to solve the Schrödinger equation for many-electron systems is being brought to the forefront.[1]

The specialists engaged in quantum chemistry refuse more and more often basis concepts related to the model of independent particles, which are fairly well known to most of physical chemists. Instead, they have started to borrow diverse theories from solid-state physics, nuclear physics and related fields,[1–3] in which N-particle problems are solved for $N \to \infty$. The mathematical apparatus used to solve these problems, which had been developed for ideal translationally invariant systems, was modified in the last decade; first of all, the simplifications related by translational symmetry were eliminated, because this is not inherent in finite molecular systems.

Ab initio methods using the concept of Atomic Pseudopotential or Effective Core Potential (ECP) have been developed. The introduction of this notion made the computation much simpler and reduced it to considering only valence electrons. Due to the 'passivity' of the core electrons of the inner electron shells, their influence on the valence electrons is often not taken into account explicitly, but is modelled by the ECP. Therefore, the work content of *ab initio* quantum-chemical calculations sharply decreases. In addition, it becomes possible to include, without much difficulty, the relativistic effects created mainly by the core electrons.[9]

Many pseudo-potential methods imply the presence of N_v valence active and N_c core passive electrons. The full Hamiltonian (in atomic units) for a system of $N = N_v + N_c$ electrons is represented in the form

$$\hat{H}_v = \sum_{i=1}^{N_v}\left[-\frac{1}{2}\nabla_i^2 + \sum_A \hat{W}^A(r_i)\right] + \sum_{i<j}^{N_v}\frac{1}{r_{ij}} + \sum_{A<B}\frac{Z_v^A Z_v^B}{R_{AB}}, \qquad (1)$$

where $\hat{W}^A(r_i)$ is the model pseudo-potential describing the interaction of valence electrons with the nucleus and with core electrons of atom A; r is the distance between the electrons, Z_v^A is the shielded charge of the atomic nucleus ($Z_v^A = Z^A - N_c^A$), R is the distance between the nuclei; A and B are the numbers of atom

nuclei, and i, and j are the numbers of electrons. For any chemical element, $\hat{W}^A(r_i)$ is a fixed and transferable operator that is usually determined from calculations of atomic wave functions in the HF approximation.

The authors of many publications have used, not without success, by analogy with ECP, schemes of effective single-fragment potentials that simulate the presence of chemically inactive functional groups in molecular systems. The intuitive reasons in favour of these schemes look rather convincing, although they can hardly be called substantiated.

In view of the above, one can plainly see why some researchers [10–20] have started bringing Density Functional Theory (DFT) to the forefront of quantum chemistry. The idea of using DFT to calculate the ground-state total energies of many-electron systems was put forward by Thomas and Fermi.[21,22] Their model implies a completely uncorrelated electron motion. A real N-electron object is matched to some fictitious system of non-interacting electrons, which is not identical but equivalent to this object. This system has the same electron density $\rho(\boldsymbol{r})$ as the initial system, consisting of interacting electrons.

Initially, the Thomas – Fermi model was perceived as a useful simplification based on the assumption that the energy of this quantum system can be expressed in terms of the electron density. This hypothesis has been formally proven by the Hohenberg – Kohn theorem,[10] according to which the ground-state energy of a system of electrons in an external field is the functional (moreover, the only) of the single-particle density $\rho(\boldsymbol{r})$. After the appearance of this theorem, the interest of researchers in the DFT has sharply grown.

Modifications of DFT have been described in numerous publications (see, for example, the studies [12–14]). It is worthy to note that the early Slater model, borrowed from the solid-state physics, actually reduces the problem of solving the many-particle Schrödinger equation to the solution of the one-particle differential equation

$$\left[-\frac{1}{2}\nabla_i^2 + V_c^{X_\alpha}(\boldsymbol{r}) + V_e^{X_\alpha}(\boldsymbol{r})\right]\Psi_i^{X_\alpha}(\boldsymbol{r}) = \varepsilon_i^{X_\alpha}\Psi_i^{X_\alpha}(\boldsymbol{r}), \tag{2}$$

where $V_c^{X_\alpha}(\boldsymbol{r})$ is the Coulomb potential (including the contribution of the electron self-action), $V_e^{X_\alpha}(\boldsymbol{r})$ is the exchange Slater potential

$$V_e^{X_\alpha}(\boldsymbol{r}) = -3\alpha\left[\frac{3}{4\pi}\rho(\boldsymbol{r})\right]^{1/3} = \alpha V_e^S(\boldsymbol{r}), \tag{3}$$

$\Psi_i^{X_\alpha}$ is a single-electron orbital and $\varepsilon_i^{X_\alpha}$ is its energy.

Expressions (2) and (3) reflect the essence of the so-called X_α method. A scaling parameter α appeared historically during the development of the X_α method and is included in its name. An α value, chosen from the 2/3 to 1 range, is usually accepted for the calculations.

The Slater potential has been successfully used in quantum chemistry for many years, despite the lack of a strict theoretical substantiation of its use for inhomogeneous electron density. A lot of effort was concentrated on the problem of improving of potential (3), which favoured to a considerable extent the successful development of general DFT methods involving the exchange-correlation potential

$$V_{ec} = \frac{dE_{ec}}{d\rho}, \tag{4}$$

where E_{ec} is the exchange-correlation energy functional.

Among the variants of DFT, the Kohn – Sham (KS) variant is currently the most popular and best developed.[11] This version can, in principle, be considered as a quantum-mechanical generalisation of the Thomas – Fermi model. In this scheme, the solution of the many-electron Schrödinger equation is reduced to the solution of a single-electron equation of type (2), in which the full effective potential is the sum of three potentials: nuclear $V_{nuc}(\boldsymbol{r})$, the classical Coulomb electron $V_{el}(\boldsymbol{r})$, and the exchange-correlation $V_{ec}(\boldsymbol{r})$ potentials. The magnitude of the exchange-correlation potential at point $\boldsymbol{r}$ is assumed to depend only on the electron density $\rho(\boldsymbol{r})$ at this point. The resulting single-electron equation is solved by iterations; hence, this scheme is self-consistent.

The KS equation closely resembles the Hartree – Fock equation. The difference is that in the KS equation, the orbital-dependent exchange HF operator is formally replaced by the exchange-correlation (taking into account the electron correlation) operator $V_{ec}(\boldsymbol{r})$, which depends on $\rho(\boldsymbol{r})$ (and on the spin density in the spin-polarised DFT versions). Therefore, the form of the matrix elements of the 'modified Fockian' become simpler and, in practice, single-electron molecular orbitals (MO) ψ_i can be represented by linear combinations of not only Gaussian type functions (GTF) but also other functions such as Slater type orbitals (STO), numerical Hartree – Fock atomic orbitals, planar waves, *etc*. The use of GTF in the KS, as in the Hartree – Fock theory, accelerates the computation of multicentre integrals, opens up the way for constructing efficient and precise basis sets that are still relatively small, simplifies the analytical determination of the energy gradients, *etc*. Moreover, all the experience accumulated in the HF theory regarding the selection of basis sets can be used in the DFT calculation of molecular systems.

As applied to molecules with large numbers of atoms, some variants of the SCF approach based on DFT prove to be much more attractive than *ab initio* methods, because the number of arithmetic operations in DFT increases as $\sim N^3$, rather than $\sim N^4$ as in the HF approximation or $\sim N^5$ as in the CI scheme. At present, DFT is a rapidly developing field of quantum chemistry. The popularity of DFT is largely determined by the fact that it allows one to study complicated and real rather than model objects, while requiring much fewer resources and less computer time than the HF calculations. Moreover, DFT usually provides much better agreement with experiment, especially for transition element compounds.[15]

In the KS model, the equality of the densities $\rho(\boldsymbol{r})$ in the real and equivalent systems is provided by the functional $V_{KS}(\boldsymbol{r})$. If this functional was known exactly, it would be possible to determine the energy of a real system by solving a model single-particle KS equation. Unfortunately, the exact form of this functional is most often unknown; therefore, the only way forward than is to use model forms.

The exchange-correlation functional should be defined in such a way as to ensure the required accuracy of property calculations. As a rule, it exhibits an appreciable dependence on the accepted geometry of the system and the set of basis functions chosen; the convergence of the results is often deteriorated upon increasing the size of the basis set.[23] Therefore, it is not always clear whether the recommended functionals tested for determination of particular characteristics would be suitable for accurate prediction of other, qualitatively different characteristics of chemical compounds.

A number of expressions for $V_{ec}(\boldsymbol{r})$ have now been proposed within the framework of the Local Density (LD) approximation.[12–15] Almost all these expressions can formally be reduced to the following formula

$$V_{ec}(\boldsymbol{r}) = \alpha(\boldsymbol{r})V_e^S(\boldsymbol{r}), \tag{5}$$

whose form emphasises the relationship between the LD approximation and the X_α method [*cf*. Eqn (3)]. Note also that numerous Local Spin Density (LSD) and Gradient-Corrected Local Spin Density (GCLSD) functionals have been developed; in addition to the spin densities ρ^α and ρ^β, these contain their gradients $\bigtriangledown\rho^\alpha$ and $\bigtriangledown\rho^\beta$, which take into account the non-uniformity of spin distributions in real systems compared to the spin distributions in the homogeneous electron gas models, in which the motion of electrons is uncorrelated.[18] Gradient-corrected functionals have markedly increased the reliability of the DFT-based methods.

It should be especially emphasised that the LD approximation plays more or less the same role in modern DFT as ascribed to the HF approximation in the theory of many-electron systems. Meanwhile, the LD approach has a substantial benefit as it is less

labour-consuming, despite the partial allowance for electron correlation (within the electron gas model). The main difficulty in using LD approximation is the lack of strict systematic methods for correcting errors, *i.e.*, the corrections applied often rely on the researcher's flair.

Apart from the inclusion of gradient corrections into the energy functional, the idea of combining the HF and LD approximations has been implemented beyond the LD scheme,[19] giving rise to a more labour-consuming but more efficient method. This method makes use of a special three-parameter hybrid B3LYP functional (Becke – Lee – Yang – Parr) that contains three semiempirical coefficients ($a_0 = 0.80$, $a_e = 0.72$, $a_c = 0.81$), selected by experimental data adjustment of 56 atomisation energy, 42 ionisation potential, 8 proton affinity and 10 atomic energy values for a specially selected set of molecules. Currently, the B3LYP approximation is universally used to perform high-precision calculations of thermochemical and spectroscopic parameters for relatively simple molecular systems. The B3LYP functional in combination with specially constructed basis sets of a moderate size have also proved applicable for studying structure – property relationships (see the references cited in Ref. 23).

Analysis of the use of local approximation for the exchange contribution [24, 25] has shown that the most serious errors are due to the changes that take place to the 'angular' nodal surfaces of wave functions.

The Quantum Monte Carlo (QMC) methods brought to quantum chemistry in the 1970s – 1980s from nuclear physics may appear quite promising.[26–28] The most widely used QMC approaches are the Variational Quantum Monte Carlo (VQMC), Diffusion Quantum Monte Carlo (DQMC) and Green's Function Quantum Monte Carlo (GFQMC) methods. These methods are closely related to one another, but each has its own specific features, advantages and disadvantages.

The main approximations of VQMC are, in principle, the same as those of the traditional analytical variational approach; however, the required integrals should be found using special Monte Carlo methods. In this approximation, the expected total electron energy $\langle E \rangle$ is estimated using the local energies ($E_{loc} = \hat{H}\Psi_0/\Psi_0$) for the trial wave function Ψ_t and using its square as the weight factor

$$\langle E \rangle = \frac{\int \Psi_t^2(\hat{H}\Psi_t/\Psi_t)\mathrm{d}\tau}{\int \Psi_t^2 \mathrm{d}\tau} = \lim_{n\to\infty} \frac{\sum_{i=1}^{n} \Psi_t^2(\hat{H}\Psi_t/\Psi_t)}{\sum_{i,=1}^{n} \Psi_t{}^2}. \quad (6)$$

In expression (6), summation is usually carried out over the arbitrary points in the electron configuration space, which is characterised by probabilities proportional to Ψ_t^2. As in analytical variational computations, the $\langle E \rangle$ value is an upper estimate of the Schrödinger energy.

With this approach there is no need to carry out numerical integration; to determine E_{loc}, one only has to calculate the $\hat{H}\Psi_t/\Psi_t$ values at specified points. Therefore, this function can acquire any form and even contain the electron – electron distances r_{ij} in an explicit form. Hence, by using relatively simple trial functions, one can take into account the electron correlation effects with much higher accuracy, which would result in a much lower expected energy for a molecular system than that corresponding to the Hartree – Fock limit.[26, 27]

The so-called diffusion version of the QMC method is physically explicit and provides high accuracy to the energetic characteristics of atoms and molecules, because the correlation energy is often taken into account to 80% – 100%. The expediency of using the DQMC method to solve the stationary Schrödinger equation

$$-\sum_i \frac{\mathrm{h}^2}{2m_e}\nabla_i^2\Psi(\boldsymbol{R}) + \hat{V}\Psi(\boldsymbol{R}) = E\Psi(\boldsymbol{R}) \quad (7)$$

can be easily understood by paying attention to the formal similarity between the non-stationary Schrödinger equation for a single electron of mass m_e in imaginary time $\tau = it$

$$h\frac{\partial\Psi(\boldsymbol{r},\tau)}{\partial\tau} = \frac{\mathrm{h}^2}{2m_e}\nabla^2\Psi(\boldsymbol{r},\tau) - \hat{V}(\boldsymbol{r})\Psi(\boldsymbol{r},\tau) \quad (8)$$

and the branching diffusion equation

$$\frac{\partial C(\boldsymbol{R},t)}{\partial t} = D\nabla^2 C(\boldsymbol{R},t) - kC(\boldsymbol{R},t), \quad (9)$$

where R is a $3N$-dimensional vector that specifies the coordinates of N electrons in a molecular system. The potential energy operator for the system has the form

$$\hat{V}(\boldsymbol{R}) = \sum_{i>j}^{N}\sum^{N}\frac{e^2}{r_{ij}} - \sum_{i=1}^{N}\sum_{\mathrm{A}=1}^{M}\frac{Z_A e^2}{r_{iA}} + \sum_{\mathrm{A}>\mathrm{B}}^{M}\sum^{M}\frac{Z_A Z_B e^2}{r_{AB}}. \quad (10)$$

As previously, the i and j subscripts designate the electrons, A and B correspond to the nuclei, e is the charge of the electron and Z_A is the charge of nucleus A. The second term in the right-hand part of Eqn (9) describes the concentration C of particles that diffuse with probability k (the first-order rate constant for a chemical reaction), the random path Δr they effectively travel in time Δt being determined through the diffusion coefficient D using the Einstein relation

$$D = \frac{1}{2}\frac{(\Delta r)^2}{\Delta t}. \quad (11)$$

It is assumed that the $\Psi(\boldsymbol{R},\tau)$ value corresponds to $C(\boldsymbol{R},t)$, $V(\boldsymbol{R})$ to k and $h^2/2m_e$ to D.

In the diffusion version of the QMC method, the function $\Psi(\boldsymbol{R},\tau)$ acquires the meaning of the density of imaginary 'walkers,' the search for the solution of stationary Eqn (7) is equivalent to the search for the solution of a type (8) equation for an equilibrium stable state. When simulating the Schrödinger equation in imaginary time, Δr and Δt in relation (11) are chosen in such a way as to ensure that D is close to $h^2/2m_e$. In particular, for the H_2 molecule with fixed A and B nuclei (the Born – Oppenheimer approximation), the Schrödinger equation in imaginary time has the following form (in atomic units):

$$\frac{\partial\Psi}{\partial\tau} = \frac{1}{2}\nabla_1^2\Psi + \frac{1}{2}\nabla_2^2\Psi - V\Psi, \quad (12)$$

the potential energy operator ($\hat{V}$), without allowance for the internuclear repulsion, being determined using the formula

$$\hat{V} = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}}, \quad (13)$$

where r_{1A} is the distance between electron 1 and the proton A, and r_{12} is the interelectron distance. Then, in designations of the diffusion equation, we have $D = 1/2$ and $k = V$.

Along with DQMC, the GFQMC technique is often used;[26] this is underlain by the fact that the time-independent Schrödinger equation can be written in the form

$$-\sum_i \nabla_i^2\Psi(\boldsymbol{R}) + k^2\Psi(\boldsymbol{R}) = k^2\frac{V(\boldsymbol{R})}{E}\Psi(\boldsymbol{R}), \quad (14)$$

where $k^2 = -2mE/h^2$. For the k^2 value to be positive, the energy value should be negative. Hence, it is necessary to specify an appropriate reference level of the potential energy. The Green function for Eqn (14) that satisfies the required boundary conditions ($\Psi \to 0$ for $\boldsymbol{R} \to \infty$) can be represented as follows

$$G(\boldsymbol{R} \to \boldsymbol{R}') = \frac{K_{3N/2-1}}{(2\pi)^{3N/2}}\frac{k|\boldsymbol{R}' - \boldsymbol{R}|}{k|\boldsymbol{R}' - \boldsymbol{R}|^{3N/2-1}}, \quad (15)$$

where K is the modified Bessel function and N is the number of electrons.

The search for $\Psi(\boldsymbol{R})$ within the framework of the GFQMC method is accomplished by iterations using the arbitrary initial wave function $\Psi_0(\boldsymbol{R})$

$$\Psi_{n+1}(\boldsymbol{R}') = \int G(\boldsymbol{R} \to \boldsymbol{R}') \frac{V(\boldsymbol{R})}{E} \Psi_n(\boldsymbol{R}) \mathrm{d}\boldsymbol{R}. \quad (16)$$

The iteration procedure is carried out until the verification shows that the process convergence has been attained. In essence, $G(\boldsymbol{R} \to \boldsymbol{R}')$ in Eqn (16) is the probability of transforming one electron configuration ($\boldsymbol{R}$) into the other ($\boldsymbol{R}'$) through arbitrary motion of each electron.

The solution of the Schrödinger equation for molecules by the GFQMC method is faced with substantial difficulties caused, first of all, by the properties of the Coulomb potential and the antisymmetry requirement. The time-dependent many-electron wave function $\Psi(\boldsymbol{R},t)$ is represented at the initial instant [$\Psi(\boldsymbol{R},0)$] as a set of $3N$ coordinates of electrons. For example, for LiH, this ensemble would consist of 12 Cartesian coordinates that determine the spatial arrangement of each of the four electrons. Any specified electron configuration defines one point ($\boldsymbol{R}$) in a $3N$-coordinate space, the set of these allowed configurations is considered as a configurational ensemble.

If the second addend in the right-hand part of Eqn (8) were missing, this would correspond to the usual diffusion equation with coefficient D, and would describe particle 'walk' in the configuration space. However, only in the presence of this addend, is Eqn (8) applicable to branching processes, for example radioactive decay, or the exponential development of populations. This branching is due to a decrease in the probability density in the regions with greater values for the $V(\boldsymbol{R})$ potential and its increase in the regions with a low potential energy.

The interpretation of Eqn (8) as a diffusion equation implies that the 'walker' density [*i.e.*, $\Psi(\boldsymbol{R},t)$] should always be positive. Since the phase of the function $\Psi(\boldsymbol{R},t)$ is arbitrary, the function can also always be negative; it must have one sign. This requirement is equivalent to the absence of nodes in the $\Psi(\boldsymbol{R},t)$ function.

However, in the case of Fermi systems, the MWF can have nodes or a change in the sign. Therefore, to retain the analogy with the diffusion equation, the regions of positive and negative MWF values should be considered separately. The exclusion of the 'walk' between these regions is called the fixed-node approximation of the QMC method. Equation (8) is solved by the variational method separately for each node-free region, with application of the conditions $\Psi(\boldsymbol{R},t) = 0$ only at the boundary of this region. As applied to the branching diffusion process, this means that as soon as a 'walker' reaches the boundary of its region, it is destroyed.

Until recently, researchers have paid relatively little attention to the topological structure and other properties of MWF nodal hypersurfaces. In practice, the QMC method was used most often to upgrade the existing MWFs with known nodal hypersurfaces.

The trial function $\Psi_t(\boldsymbol{R}, t)$ should possess the following properties:

(1) be rather simple, which would allow fast calculation of the value of the function and its derivatives;

(2) be a smooth and well-defined function of the argument $\boldsymbol{R}$, in order to avoid difficulties in the calculation of the local energies $(\hat{H}\Psi_t/\Psi_t)$;

(3) have nodal surfaces close to the Schrödinger ones, in order to ensure a sufficiently high accuracy calculated to the energy.

The last two requirements are better fulfilled when Ψ_t is close to the exact solution of the Schrödinger equation. Therefore, when determining Ψ_t, it is expedient to invoke everything that is known about the sought-after exact solution (symmetry conditions, boundary conditions, *etc.*).

It has been recommended [27, 28] to divide the electron configuration space into two parts by means of a hypersurface in which $\Psi(\boldsymbol{R}) = 0$ for any electron pair with parallel spins. Then, the resulting MWF would possess the required antisymmetry if it is specified to be positive on one side and negative on the other side of the nodal hypersurface. For describing excited electron states, a larger number of such hypersurfaces are required.

However, it is no confidence that the above arbitrary division of the electron configuration space would give a wave function corresponding to the ground state. Moreover, a mathematically feasible solution of the Schrödinger equation does not always have a physical meaning. Without strict rules for defining the nodal hypersurfaces, finding a sufficiently accurate upper estimate of the desired energy may require variation of the chosen nodal hypersurfaces.

The application of Eqn (8) to the branching walk is faced with certain difficulties. The point being that the branching rate, proportional to the Coulomb potential, can become very high when the 'walkers' closely approach each other, which would entail a pronounced fluctuation of their number. However, such fluctuations and hence the statistical uncertainty in solving equations such as Eqn (8), can be substantially reduced by using the so-called Importance Sampling (IS) procedure proposed $\sim$35 years ago.[29] The essence of IS is the use of preliminary knowledge of the properties of MWF in order to make quantum-chemical calculations more accurate; the procedure involves the introduction of a 'controlling' function $g(\boldsymbol{R})$, meant to meet the symmetry requirements of the desired function $\Psi(\boldsymbol{R},t)$. This allows one to operate with $\Phi(\boldsymbol{R},t) = \Psi(\boldsymbol{R},t)g(\boldsymbol{R})$ rather than with $\Psi(\boldsymbol{R},t)$. This markedly enhances the accuracy of QMC estimates of the mean values of physical quantities.[26–28]

In order to be interpretable as the probability density corresponding to the Schrödinger equation, the function $\Phi(\boldsymbol{R},t)$ should be non-negative [$\Phi(\boldsymbol{R},t) \geqslant 0$]. This means that the functions $\Psi(\boldsymbol{R},t)$ and $g(\boldsymbol{R})$ have identical signs. However, they change the sign on permutation of electrons with identical spins, *i.e.*, they are positive in some regions of the configuration space and negative in other regions; the dimensions and shapes of these regions being entirely determined by the nodal surfaces. Thus, the requirement for non-negative definiteness of the function $\Phi(\boldsymbol{R},t)$ is equivalent to the requirement of coincidence for the nodal surfaces of $\Psi(\boldsymbol{R},t)$ and $g(\boldsymbol{R})$.

The condition of the presence of identical nodes for MWF and $g(\boldsymbol{R})$ restricts the arbitrariness in choosing the function $\Psi(\boldsymbol{R},t)$. Due to the use of the fixed-node approximation, any electron configuration should be excluded from the configuration ensemble (see above) if it crosses the nodal surface for Ψ $(\boldsymbol{R},t)$ upon shifting from $\boldsymbol{R}$. This requirement is equivalent to the presence of an infinitely high barrier (potential) at $g(\boldsymbol{R}) = 0$. With this formalism, the 'controlling' function $g(\boldsymbol{R})$ fixes the nodes of the MWF and thus influences the accuracy of calculations. The closer the nodal surfaces of the 'controlling' and the proper (exact) functions, the more accurate the obtained solution of the Schrödinger equation.[26–28]

The choice of optimal trial MWF is dictated by a compromise between two criteria. On the one hand, it is desirable that the function Ψ_t in the QMC calculation be as simple as possible, because this markedly shortens the time it takes to calculate its first and second derivatives at points $\boldsymbol{R}$ of the spinless configuration space (this computation has to be repeated up to 10^7 times).[26–28] On the other hand, it would be better if the trial function Ψ_t were as close as possible to the Schrödinger one, because in this case, the statistical deviations decrease and the MWF nodes are located more correctly.

The results of particular computations (see the references cited in Ref. 26) have shown that a plausible compromise results from using an expression for Ψ_t equal to the product of the Slater determinant $\det(Q_{kl})$ (k, l are the numbers of lines and columns in the determinant), and the electron–electron and electron–nuclear Jastrow's factors (see the references in Refs 26, 28), which impose the required conditions on Ψ_t for $r_{ij} \to 0$ and $r_{iA} \to 0$,

$$\Psi_t(\boldsymbol{R}) = \det(Q_{kl}) \exp\left(\sum_{i>j} \frac{a_{ij} r_{ij}}{1 + b r_{ij}} - \sum_{i,A} \frac{Z_A a_{i,A} r_{i,A}}{1 + b r_{i,A}} \right). \quad (17)$$

Jastrow's factors allow one to explicitly take into account the correlation in the electron motion. Usually, it is taken that $a_{ij} = 1/8D$ for electrons i and j with parallel spins, $a_{ij} = 1/4D$ in the case of antiparallel spins and $a_{i,A} = 1/2D$; the parameter b is considered as a variable parameter during energy minimisation [D is the diffusion coefficient, see expression (11)].

Since the Jastrow's factors are positive, they do not affect the trial function (17) nodes, which are totally dictated by the Slater determinant. The molecular orbitals $\varphi_k(\boldsymbol{r})$ are usually linear combinations of exponential functions (linear combinations of atomic orbitals), determined by the SCF procedure. Attempts at using multideterminant SCF trial functions instead of one Slater determinant are still few and far between.[26–28]

The energy characteristics calculated by the QMC method for both small and large molecules and for clusters are usually much more accurate than those obtained when using other quantum-chemical approaches. During recent years, substantial progress has been made by using QMC methods.[28] QMC methods have proved highly efficient in studies of rather complex molecules, electron–positron systems, vibronic effects and so on. However, the difficulties encountered in their use are still great, especially for many-electron compounds containing atoms heavier than fluorine. In these cases, the accuracy of the QMC methods decreases sharply. The statistical error inherent in QMC calculations is, most often, proportional to $t^{-1/2}$ (t is the computer time spent).[30]

Currently, QMC methods are used most of all, for the improvement of the existing wave functions of which the nodal hypersurfaces are known. Unfortunately, a strict definition of MWF nodal hypersurfaces is problematic.

The testing of various QMC versions (see the references cited in Ref. 31) has shown that most of them are unstable. This accounts for the inadmissible expenses of computer provision needed to attain high accuracy. Among the innovations discussed in detail in the literature, mention should be made of the uncoupled node procedure with subspace design [32] and a version of the mirror potential method [33] meant for electron systems. Some known approaches have been modified rather successfully.[34, 35]

Unfortunately, in most cases, it is only possible to evaluate the correctness of choice of MWF nodal hypersurfaces that separate the configuration space into the regions with constant sign by solving the Schrödinger equation with a plausible accuracy. To have physical meaning, the MWF thus found should satisfy the general principles of quantum mechanics (spin and symmetry ones), which were defined back in 1925–1926 by Pauli, Dirac and Heisenberg.[36–38] In 1927–1928, Wigner, Hund and Heitler formulated these principles in terms of group theory.[39–41] In the 1920s, researchers paid much attention to a thorough investigation into the properties of MWF nodal surfaces.

After Slater [42] had introduced (in 1929) a determinant representation for the MWF, the problem of nodal surfaces receded into the background for a long period. Indeed, when Slater determinants are used, the antisymmetry of trial many-electron functions is ensured automatically. In addition, according to the theorem proven by Levdin,[43] an exact MWF for the ground or excited state of an N-electron system can be represented as a linear combination of all sorts of Slater determinants (with $N \times N$ dimensionality), which include single-electron spin orbitals that constitute the mathematically full set of basis functions.

Probably, due to the above, the interest in detailed investigations of the structures of MWFs in solving the Schrödinger equation by the variational method has been lost. In the MWF method being developed, this problem has acquired again a prime importance (thus illustrating the well-known proverb that new is well-forgotten old).

III. Many-electron wave functions

Antisymmetry and diversity of the nodal surfaces are fundamental characteristics of the MWF. If the potential possesses the symmetry property, the Hamiltonian eigen functions Ψ_i (solutions of the stationary Schrödinger equation $\hat{H}\Psi = E\Psi$) can be classified according to irreducible representations of an appropriate symmetry group. Unlike single-electron orbitals, a physically acceptable MWF reflects not only the point symmetry of the Hamiltonian but also its invariance with respect to permutations of the spin and space electron coordinates; in addition, it vanishes on nodal surfaces predetermined by permutation symmetry. It is obvious that even for $N = 3$ and for the ground state of an N-electron system, it is impossible to construct a many-electron wave function Ψ_0 without nodes.

The nodal surfaces divide the whole coordinate space in which the MWF is specified into the regions in which its sign is constant (positive on one side and negative on the other side of each nodal surface). Since the MWF is $3N$-dimensional, one can hardly rely on intuition in attempts to visualise the nodal hypersurfaces. Visual representation of these, even for very simple systems (He and H_3), is possible only by constructing 3D cross-sections of the $3N$-dimensional space with fixed positions for all particles, except for one electron.[44, 45]

The antisymmetry requirements of the function Ψ_i relative to the permutations of the spatial coordinates of electrons with parallel spins, except for systems such as He (^{3}S), do not suffice for correct determination of the coordinates of the nodal surfaces, although this strongly restricts the arbitrariness of the *a priori* selection of the shape of these surfaces.[31] In essence, the Wigner approach (discussed in a publication [46]) is unable to provide efficient assistance, as it does not contain any practical recommendations on constructing the coordinate (spinless) MWF with the required symmetry properties. The method outlined below takes into account the limitations of the generally accepted interpretation of the fundamental Pauli exclusion principle.

The canonical interpretation of the Pauli principle for a many-electron atom states that two electrons with identical spins cannot exist in the same state specified by four quantum numbers. In the HF approximation, the sought-after MWF is represented by the Slater determinant, thus ensuring fulfilment of the Pauli principle and antisymmetry with respect to the corresponding electron permutations.

The antisymmetry requirement for the MWF means the presence of a definite set of nodal surfaces in the multidimensional configuration space. The probability of finding an electron configuration on this surface is equal to zero. It is beyond doubt that for any many-electron system, solution of the stationary Schrödinger equation should vanish on a nodal surface. Among the possible diverse multidimensional nodal surfaces, there exist some that determine the configurations corresponding to the occurrence of a pair of electrons with the same orientation of spins at the same point in space. The exclusion of such configurations by the Pauli principle is taken into account automatically when the antisymmetric MWF is constructed. However, in reality, apart from these configurations, the Pauli principle forbids a multitude of other, seemingly quite acceptable configurations.[47]

The main feature distinguishing this approach from the Hartree–Fock one is the investigation of the possible form of nodal surfaces. This essentially narrows down the excessively broad set of acceptable antisymmetric functions by distinguishing the functions that satisfy the boundary conditions derived from the modern interpretation [47] of the Pauli principle. It can be demonstrated, for example, that the Slater determinants corresponding to different electron configurations turn to zero on non-coincident surfaces. Therefore, the CI calculations converge slowly, as one has to consider a very large number of determinants with different nodal surfaces in order to approach the true (Schrödinger) MWF and corresponding nodal surface. If it was possible to determine *a priori* the nodal surfaces and use them for constructing the trial MWF, the convergence of quantum-chemical calculations would be substantially faster and the accuracy higher.

In addition, owing to the use of a symmetric group in the MWF construction, the computational procedure becomes much simpler, because for a system of N electrons, the initial problem is finally reduced, without loss of accuracy, to $N!$ identical problems, but with a smaller integration region.[47,48] Indeed, if a system with spin S has $K = (N/2)+S$ electrons with the spin coordinates $s_i = +1/2$ (set I) and $N-\mathrm{K} = (N/2)-S$ electrons with $s_j = -1/2$ (set J), then among the total group of permutations S_N, one can distinguish the subgroups S_K and $S_{N-\mathrm{K}}$ acting on the elements of sets I and J, respectively. The direct product of these subgroups $S_K \times S_{N-\mathrm{K}} \equiv S(I,J)$ can be reasonably termed as a 'spin-invariant subgroup', as its elements act only on the electrons with the same projections of the spin.[49]

The use of 'spin-invariant subgroups' for solving the Schrödinger equation allows one to handle only the part of the wave function which is antisymmetric with respect to electron permutations contained in $S(I,J)$ rather than the whole many-electron wave function $\Psi(\boldsymbol{r}_1, \mathrm{s}_1; ...; \boldsymbol{r}_N, \mathrm{s}_N)$. The full MWF is easily restored from this part by means of appropriate symmetry operations. With this approach, the number of integrals needed to calculate the matrix elements of the Hamiltonian decreases by a factor of $M = N!/\{[(N/2)+S]![(N/2)-S]!\}$.

The problem of methods suitable for the practical construction of the functions $\Psi(\boldsymbol{r}_1, \mathrm{s}_1; ...; \boldsymbol{r}_N, \mathrm{s}_N)$ having a different physical meaning from spinless functions, which depend only on spatial coordinates $\boldsymbol{r}_i$ and possess the required symmetry properties, has been studied comprehensively by Fok.[46] Both the Pauli principle and the equation for the full spin angular momentum

$$\hat{S}^2 \Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_N) = S(S+1)\Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_N) \tag{18}$$

($\boldsymbol{x}_i$ designates the set of spatial coordinates and the spin variable for ith electron) were taken into account [46] by strict mathematical techniques. By representing the operator $\hat{S}^2$ as

$$\hat{S}^2 = N - \frac{N^2}{4} + \sum_{i<j} \hat{P}_{ij}\,, \tag{19}$$

where $\hat{P}_{ij}$ is the permutation operator for spin variables s_i and s_j, Fok expressed the full MWF for a system of N electrons through only the spinless wave function [for k electrons with parallel spins and $(N-k)$ electrons with antiparallel spins]

$$\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_k | \boldsymbol{r}_{k+1}, \boldsymbol{r}_{k+2}, ..., \boldsymbol{r}_N) \tag{20}$$

and formulated the following necessary and sufficient symmetry properties for the latter:

(1) antisymmetry with respect to k arguments on the left of the vertical line in series (20), for example,

$$\Psi(\boldsymbol{r}_2, \boldsymbol{r}_1, ..., \boldsymbol{r}_k | \boldsymbol{r}_{k+1}, ..., \boldsymbol{r}_N) = -\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_k | \boldsymbol{r}_{k+1}, ..., \boldsymbol{r}_N);$$

(2) antisymmetry with respect to $(N-k)$ arguments on the right of the vertical line in series (20), for example

$$\Psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_k | \boldsymbol{r}_{k+2}, \boldsymbol{r}_{k+1}, ..., \boldsymbol{r}_N) = -\Psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_k | \boldsymbol{r}_{k+1}, \boldsymbol{r}_{k+2}, ..., \boldsymbol{r}_N);$$

(3) so-called cyclic symmetry, expressed by the following equalities:
when $(N-k)$ is even

$$(1 + P + P^2 + ... + P^{N-k})\Psi = 0, \tag{21}$$

when $(N-k)$ is odd

$$(1 - P + P^2 - ... - P^{N-k})\Psi = 0, \tag{22}$$

where P designates the cyclic permutation of the arguments $(\boldsymbol{r}_k, \boldsymbol{r}_{k+1}, ..., \boldsymbol{r}_N)$, *i.e.*, the permutation in which each term of the cycle $(\boldsymbol{r}_k, \boldsymbol{r}_{k+1}, ..., \boldsymbol{r}_N)$ is replaced by the next one, and the last term by the first one.

It follows from expressions (21) and (22) that a system of two electrons with a total spin of zero ($S = 0$, $N = 2$, $k = 1$) is described by a symmetric Schrödinger function, while its triplet state ($S = 1$, $N = 2$, $k = 0$) is described by an antisymmetric function relative to the spatial coordinates of the electrons. The Schrödinger wave function does not depend on spin variables; however, in this case, the resultant spin is reflected in its properties by governing the symmetry and the nodal surface.

An example of a many-electron function that satisfies the three above-indicated conditions of symmetry, exceptionally important for quantum chemistry, is the product of two determinants [46]

$$\Psi = |A| \times |B|, \tag{23}$$

where

$$|\mathrm{A}| = \begin{vmatrix} \varphi_1(\boldsymbol{r}_{k+1}) & ... & \varphi_{N-k}(\boldsymbol{r}_{k+1}) \\ ... & ... & ... \\ \varphi_1(\boldsymbol{r}_N) & ... & \varphi_{N-k}(\boldsymbol{r}_N) \end{vmatrix}, \quad |\mathrm{B}| = \begin{vmatrix} \varphi_1(\boldsymbol{r}_1) & ... & \varphi_k(\boldsymbol{r}_1) \\ ... & ... & ... \\ \varphi_1(\boldsymbol{r}_k) & ... & \varphi_k(\boldsymbol{r}_k) \end{vmatrix}$$

and $2k \leqslant N$.

These determinants are composed of one set of single-electron orbitals $\{\varphi_1(\boldsymbol{r}), \varphi_2(\boldsymbol{r}), ..., \varphi_{N-k}(\boldsymbol{r})\}$, the greater of them containing all $(N-k)$ orbitals, and the smaller of them containing only the first k wave functions present in the set.

A similar consideration [48,50–55] of the symmetry properties and nodal MWF having a physical meaning, and taking into account the most meaningful properties of nodal surfaces, has resulted in the formulation of a theorem [7] that is a generalisation of the Courant – Hilbert [56] theorem, concerning the nodes of the eigen functions of elliptical operators, and the theorem proven by Zhislin [57] on the nodes of the eigen functions of the Schrödinger operator, without the requirement of their permutation antisymmetry. According to the formulation of this theorem in the study,[7] there exists an eigen function $\Psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N)$ of an N-electron Schrödinger operator

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{A=1}^{M}\sum_{i=1}^{N} \frac{Z_A}{r_{Ai}}\,, \tag{24}$$

that corresponds to the ground electronic state with the spin S, and whose nodal surfaces divide the Euclidean space $|\boldsymbol{R}^{3N} = \{\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N\}$ into at least

$$L = (N/2+S)!\ (N/2-S)!$$

regions $\Omega_1, ..., \Omega_L$ with constant sign. Any of these Ω_i regions can be regarded as fundamental, while the others are regarded as its copies. The total many-electron wave function Ψ_0 can be restored, based on the distinguished part, by using symmetry operations.

The continuous function Ψ_0 within each constant-sign region is not equal to zero but becomes zero at the boundary. Due to the splitting of the whole space $|\boldsymbol{R}^{3N}$ into L Ω_i regions, the determination of MWF becomes $\sim L$ times simpler, without a loss of accuracy due to the transition from the integration over $|\boldsymbol{R}^{3N}$ to the Ω_i region. In the case of a large value of N, the number L is great. Moreover, in this case, there is no need to consider the symmetry of the desired function or its spin part, isolated as a multiplier; instead, it is sufficient that the function is equal to zero at the boundary of the fundamental region.

The possibility of restoring the full MWF by means of symmetry operations should certainly facilitate high-precision calculation of the observed values and the construction of a trial MWF for the stationary states of given multiplicity. In view of the possibility of replacing the antisymmetrisation over the whole group of permutations S_N by antisymmetrisation over the spin-invariant subgroup $S(I,J)$ of this group (see above), strictly substantiated mathematically, the degree of computation involved in the numerical solution of the Schrödinger equation is expected to be reduced by a factor of $L \times M = N!$. For example, for the molecule LiH ($N = 4$), one can expect a 24-fold increase in the calculation performance compared to that used traditionally; for the CH_4 molecule ($N = 10$), this increase may be up to 3 628 800-fold.

For any atomic or molecular system, each electronic state is matched by the MWF nodal surfaces. The antisymmetry of the MWF with respect to particle permutations is inherent only in

many-electron systems. Many-electron wave functions differ appreciably from the single-electron functions familiar to chemists, namely AOs or MOs. (Note that the MWF is represented in the CI method as the sum of antisymmetrised derivatives of single-electron functions.[43]) For example, the spatial part of the MWF for the triplet state of a helium atom in the HF approximation has the form

$$^3\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=\frac{1}{\sqrt{2}}\left[\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)-\varphi_1(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_1)\right], \qquad (25)$$

where φ_1 and φ_2 are the Hartree-Fock AOs. Even if the coordinates of, for example, electron 1 are such that they correspond to the node of the φ_1-AO, *i.e.*, $\varphi(\boldsymbol{r}_1)=0$, the function $^3\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ still does not necessarily become zero, because the term $[-\varphi_1(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_1)]$ can be non-zero. The condition $^3\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=0$ is attained only when both constituents in the right-hand part of Eqn (25) coincide. Similarly, it can be considered that (except for the ground states of two-electron systems, for which spatial antisymmetry is completely ruled out) an antisymmetrised MWF has nodes even when it is constructed from nodeless AOs or MOs.

In the case of the ^{3}S state of helium, the MWF can be expressed exactly through the electron–nuclear (r_1,r_2) and electron–electron (r_{12}) distances.[58] The MWF should be antisymmetric with respect to the permutation of electrons 1 and 2, *i.e.*,

$$\Psi(r_1,r_2,r_{12})=-\Psi(r_2,r_1,r_{21}); \qquad (26)$$

hence, taking into account that $r_{12}=r_{21}$, we get the condition $r_1=r_2$, at which the MWF vanishes.

Unfortunately, the cases in which the exact form of the $(3N-1)$-dimensional MWF nodal surface can be established *a priori* from symmetry considerations alone are very scarce. As a rule, this task cannot be solved, first of all due to the large number of variables.

In view of the special significance of the MWF nodes, it appears expedient to introduce a special factor into the expression for the trial wave function, which could specify explicitly the form of its nodal surface. One more factor should be defined only in one of the constant-sign MWF regions (see above). According to a hypothesis,[8,47] the eigen functions of the N-electron Schrödinger operator have nodal surfaces defined by the equation with the potential functions of form

$$U_{ij}=\sum_{k\neq i,j}^{N}\left(\frac{e^2}{r_{ki}}-\frac{e^2}{r_{kj}}\right)-\sum_{A=1}^{M}\left(\frac{Z_Ae}{r_{Ai}}-\frac{Z_Ae}{r_{Aj}}\right)\equiv 0. \qquad (27)$$

It is assumed that electrons (i,j) have the same spin orientation. This means that any two electrons with parallel spins are prohibited from occurring on the same equipotential surface (the equipotential surface prohibition principle).

In the general case, one should expect that for isoelectronic compounds of different types, the forms of the equipotential surfaces would be different, first of all, due to differences between their nuclear configurations. According to the equipotential surface prohibition principle, the function $\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ must have the same nodes as found for the set of potential functions U_{ij} of the electron–nuclear system. This requirement specifies the form and the minimum number of nodal surfaces related to the coordinate permutations for any electron pair. This eliminates the necessity of solution antisymmetry, because, as noted above, it is ensured automatically by the procedure of further construction of the full MWF.

The sought-after function $\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ can, of course, have additional nodal surfaces, which are missing from the set of potential functions U_{ij}. Moreover, it cannot be ruled out that the proposed hypothesis would not find a reasonable substantiation; however, it appears expedient to verify this hypothesis by means of high-precision *ab initio* calculations for simple test objects.

IV. Testing of many-electron wave functions

The statements outlined above form the basis of the MWF method. They can be validated using a simple example — the calculation of the ground triplet state of helium (^{3}S). Experimental chemists usually treat the 'quantum chemistry of helium' as useless and dull. However, the unique opportunity to obtain results of exceptionally high accuracy has become the reason why the helium atom is most often chosen as the test system to verify many-electron theories.

In 1959, Pekeris[59] used a 1078-term trial function and obtained the best, at that time, value for the total energy of the $1s^2$ (^{1}S) state of helium

$$E_0 = -2.903724375 \text{ a.u.}$$

Later,[60] using the approach proposed by Fok,[61] the basis set was reduced to 246 functions and the accuracy of calculations was increased, giving the value

$$E_0 = -2.9037243770326 \text{ a.u.}$$

The same procedure, together with additional analysis[62] using only a 230-term function of the same form, gave the value

$$E_0 = -2.90372437703407 \text{ a.u.}$$

Note that according to some estimates,[63] attaining a comparable accuracy in the CI method would require $\sim 10^4$ terms in the Legendre expansion and $\sim 10^{12}$ electron configurations.

Calculations for the 1s2s (^{3}S) state should be better performed by a different technique.[64] Formally, the permutation of particles in the configuration space $\{r_1,r_2,r_{12}\}$ implies the interchange of r_1 and r_2 for $r_{12}=r_{21}$. Thus, the $r_1=r_2$ surface divides the configuration space into two regions, and in one of them ($r_1\geqslant r_2$ or $r_2\geqslant r_1$), one has to find the solution of the Schrödinger equation that takes into account the boundary condition imposed on the wave function

$$\Psi(r_1,r_2,r_{12})|_{r_1=r_2}=0.$$

With this approach, it is possible to use trial wave functions of two types

$$\Psi(r_1,r_2,r_{12})=(e^{-\alpha r_1}-e^{-\alpha r_2})e^{-\beta(r_1+r_2)}\Psi_n^{s}(r_1,r_2,r_{12}), \qquad (28)$$

$$\Psi(r_1,r_2,r_{12})=(e^{-\alpha r_1}-e^{-\alpha r_2})e^{-\beta(r_1+r_2)}\Psi_n^{u}(r_1,r_2,r_{12}), \qquad (29)$$

where Ψ_n^{s} is symmetric and Ψ_n^{u} is an arbitrary polynomial containing n terms. The first exponential factor in these functions corresponds to the antisymmetry condition, while the second one corresponds to the requirement of fast vanishing at large distances between the nucleus and the electrons. Function (28) is antisymmetric, unlike function (29); however, it can be reflected on the other half of the configuration space antisymmetrically, relative to the $r_1=r_2$ surface.

A practical advantage of expression (29) is that the class of functions used to approximate the solution of the Schrödinger equation is much broader, as the set of symmetric polynomials $\{\Psi_n^{s}\}$ is a subset of the arbitrary polynomials $\{\Psi_n^{u}\}$; therefore, the polynomial expansion (29) converges much faster than the expansion of (28). Rejection of the symmetry restrictions allows one to construct a broader class of trial functions using arbitrary polynomials. For example, in the case of a second-order polynomial, expressions (28) and (29) acquire the form

$$\Psi_7^{s}=a_0+a_1(r_1+r_2)+a_2r_{12}+a_3(r_1^2+r_2^2)+ \qquad (30)$$
$$+a_4r_1r_2+a_5(r_1+r_2)r_{12}+a_6r_{12}^2 \quad (n=7),$$

$$\Psi_{10}^{u}=b_0+b_1r_1+b_2r_2+b_3r_{12}+b_4r_1^2+b_5r_2^2+ \qquad (31)$$
$$+b_6r_1r_2+b_7r_1r_{12}+b_8r_2r_{12}+b_9r_{12}^2 \quad (n=10).$$

For the ^{3}S state of the helium atom and with an arbitrary five-order $\{\Psi_{47}^{u}\}$ polynomial (47 variable linear coefficients [64]), the energy value $^3E = -2.1752288$ a.u. was obtained; this is 5×10^{-7} a.u lower than the value calculated by Pekeris [59] using a function containing 715 parameters (the experimental ^3E value is -2.175230 a.u.). This example is indicative of the advantage of the MWF method in applied quantum-chemical calculations.

This is exemplified in Fig. 1, which shows the nodal surface of the triplet helium atom, complying with the equipotential surface prohibition principle, in Cartesian coordinates. The Figure clearly illustrates the fact that in this state, irrespective of the distance between the electrons, their location in one sphere, centred in the atom nucleus, should be prohibited.

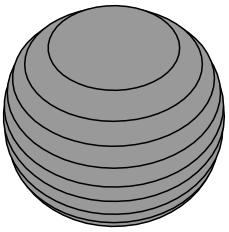


Figure 1. Spherical shape of the nodal surface for the triplet state of a helium atom.

Apart from helium, lithium is often used as the test system. The lithium atom has three electrons and can serve as the simplest model species for which the electron correlation effects are, firstly, rather substantial (due to the incomplete electron shell) and, secondly, include contributions from both the core and valence electrons. Therefore, it is not by chance that in recent years, a number of high-precision quantum-mechanical calculations for the ^{2}S ground state of this atom have been carried out.

It is noteworthy in this context that in the case of three-electron systems with one unpaired electron, the structure of the three 9-dimensional subspaces and the action of P_{ij} transpositions (pair permutations belonging to the spin-invariant S_3 group) on them can be depicted,[47] as shown in Fig. 2. It can be seen that each of the three 9-dimensional subspaces is divided into two regions of constant MWF sign (wavy line). Any point of the configuration space ($\boldsymbol{r}_1\boldsymbol{s}_1; \boldsymbol{r}_2\boldsymbol{s}_2; \boldsymbol{r}_3\boldsymbol{s}_3$) with specified coordinates ($\boldsymbol{r}$) and spins ($\boldsymbol{s}$) of the three electrons is allocated one of these subspaces. Obviously, the three spatial functions corresponding to the scheme shown in Fig. 2 are interrelated, and it is sufficient to find the solution of the stationary Schrödinger equation for only one of the subspaces.[7]

Among the most accurate is the detailed variational calculation [65] of the lithium atom carried out using the trial wave function

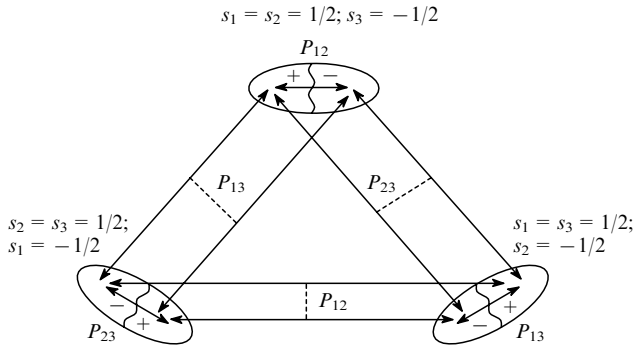


Figure 2. Scheme of the configuration space for the ground state of a three-electron system (see text).

$$\Psi_t = A \sum_{\mu=1}^{M} C_\mu \varphi_\mu \chi_\mu , \tag{32}$$

where A is the antisymmetriser, M is the number of basis functions, C_μ are the expansion coefficients determined by the variational method

$$\varphi_\mu = R_\varphi(r_1, r_2, r_3, r_{12}, r_{13}, r_{23}) \exp(-\alpha_\mu r_1 - \beta_\mu r_2 - \gamma_\mu r_3), \tag{33}$$

[$R_\varphi(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$ is the product of the distances r raised to relatively small powers, $\alpha_\mu, \beta_\mu, \gamma_\mu$ are the varied parameters], χ_μ are the eigen doublet spin functions (all identical)

$$\chi_\mu = \chi = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3), \tag{34}$$

and α and β are functions dependent on the spin coordinates of the electron.

In the case of polynomial trial function (32), the number of variable power exponents is excessively high. Therefore, this function was constructed term-by-term, only the exponents of newly added terms being optimised. Without this restriction, the calculation on a CRAY-1M type computer proved impossible. However, it should be emphasised that for a 296-term function, a new attempt at optimising the power exponents for the first five basis functions ($\varphi_1, ..., \varphi_5$) resulted in a negligibly minor correction to the total energy; therefore, the researchers [65] no longer performed the new optimisation procedure.

Analysis of the 296-term function [65] for the lithium atom, taking into account its component distribution among the three subspaces (see Fig. 2), has shown [66] that a substantial part of these components have $r_i = r_j$ nodal surfaces corresponding to the hypothesis stated in a publication.[8] The other components possess nodal surfaces whose differences from the $r_i = r_j$ surfaces are insignificant. The results of this analysis can also been interpreted as an argument supporting the equipotential surface prohibition principle.

In addition, special comparative calculations on the lithium ground state (^{2}S) have been carried out [67] in identical basis sets [function of type (33)], but using either a standard antisymmetrisation procedure (E_1) [65] or boundary conditions corresponding to the equipotential surface prohibition principle (E_2). The values for the total energy obtained by IBM PC-486 (in a.u.) are as follows:

n	m	E_1	E_2
1	5	7.421257	7.444296
2	17	7.465906	7.470490

[n is the maximum order of the type (33) function in the basis set, m is the number of functions in the basis set]. Comparison of the energies presented above with the experimental value $E = -7.478069$ a.u.[65] has shown that on application of the boundary conditions corresponding to the above-mentioned principle, one can obtain better agreement with the experimental value by using small and moderately-sized basis sets. For the lithium atom, as for the helium atom, convergence has been substantially improved.[67]

For the ground state of the lithium atom, the equipotential surfaces and their cross-sections have more complex shapes than those of the excited triplet state of the helium atom. Nevertheless, a clear idea of the nodal surfaces for electrons 1 and 2, with parallel spins, can be gained by fixing the position of electron 3, with the opposite spin at some distance r_3 from the lithium nucleus. According to the equipotential surface prohibition principle [see Eqn (27)], one should analyse the expression

$$\frac{3}{r_1} - \frac{1}{r_{13}} = C, \tag{35}$$

in which C can be represented by any real number. For example, a set of equipotential lines is formed in the (x,y) plane when the Cartesian coordinates of the lithium nucleus are (0,0) and those of the third electron are (2,0). One of these lines, corresponding to

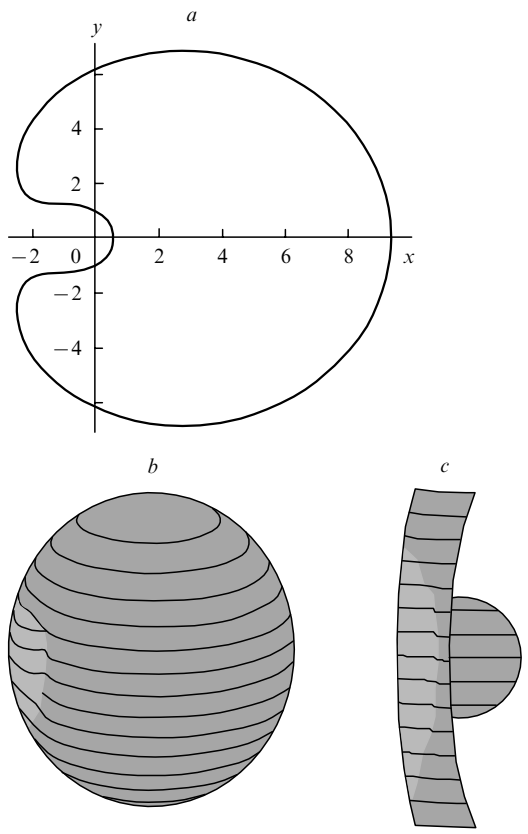


Figure 3. Equipotential surface ($C = 0.3$) for the ground state of a lithium atom.
(*a*) Vertical cross-section, (*b*) three-dimensional image, (*c*) enlarged concave part of the nodal surface.

$C = 0.3$, is shown in Fig. 3 *a*. Its rotation around the x axis yields a slightly distorted spherical surface with a rather small cavity (Fig. 3 *b*,*c*). For $C \sim 0.25$, the cavity becomes closed and is located inside the closed, somewhat distorted spherical surface.

The role of pre-determination of the nodal surfaces in the quantum-chemical calculations of molecular systems should be even more weighty, because for these, almost every basis function has its own nodal surface, often markedly different from the surfaces of other functions.

Thus a calculation of the $^3\sum_u^+$ triplet state of the hydrogen molecule by the DQMC method for a nuclear – nuclear distance of 1.4 a.u. had been carried out [31] assuming that the trial wave function Ψ_t should be symmetric with respect to rotation around the internuclear axis z and antisymmetric with respect to the inversion centre on axis z. The following trial wave function, satisfying these conditions, was used:[31]

$$\Psi_t = \{\exp[-a(r_{1A} + r_{2B})] - \exp[-a(r_{2A} + r_{1B})]\} \exp\left[\frac{br_{12}}{(1 + cr_{12})}\right], \quad (36)$$

where $a = 1.0$, $b = 0.25$ and $c = 0.25$ (a.u.)$^{-1}$. It can be seen that $\Psi_t = 0$ for $r_{1A} - r_{1B} = r_{2A} - r_{2B}$. The use of function (36) gave $E = -0.7838 \pm 0.0007$ a.u., which is in good agreement with a value of -0.7830 a.u. found [68] by the variational method.

For the triplet state of the hydrogen molecule, with allowance for the equipotential surface prohibition principle [see Eqn (27)], the following expression should be analysed

$$\frac{1}{r_{1A}} + \frac{1}{r_{1B}} = C; \quad (37)$$

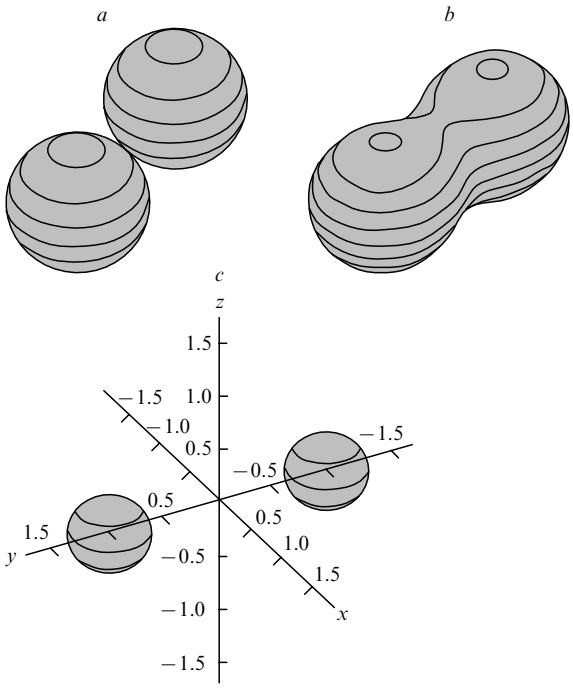


Figure 4. Form of the equipotential surfaces for the triplet state of a hydrogen molecule for $C = 2$ (*a*), $C < 2$ (*b*) and $C > 2$ (*c*).

here C is any positive number, and r_{1A} and r_{1B} are the distances from electron 1 to each of the two protons located at distances R from each other. The nodal surfaces for the triplet state of the hydrogen molecule are shown in Fig. 4. When $C = 2$ (see Fig. 4 *a*), the equipotential surface has a dumbbell shape.

When $C < 2$, the point of contact between the two distorted spheres disappears and, as C successively approaches zero, every outer equipotential surface in the set under consideration becomes more and more like a sphere flattened from above and below (see Fig. 4 *b*). This was to be expected, bearing in mind the 'limiting transition' of the helium atom into the triplet state with an increase in r_{1A} and r_{1B} to such an extent that the distance R between the protons can be neglected.

When $C > 0$, the dumbbell becomes broken into two closed topologically separate parts of the equipotential surface, the centre of each being occupied by its own proton (see Fig. 4 *c*). When the first electron is located on one fragment of this separated surface, *e.g.*, that concentrated around nucleus A, the positions of the second electron, not only on the same surface, but also on the other part of this surface, *i.e.,* that centred at nucleus B, are forbidden.

V. Conclusion

The subject matter of today's conferences on quantum chemistry and its computational applications include theoretical sections devoted to molecular spectroscopy, intermolecular interactions, quantum molecular dynamics, the modern theory of valence bonding, methods for taking into account electron correlation, achievements of density functional theory, computational quantum-chemical prediction of the properties of new materials for emerging technologies, the biological activity of compounds, the results of the analysis of elementary processes in condensed media, calculation of potential energy surfaces, elucidation of the mechanisms of chemical reactions, and the development of new quantum chemical methods for studying the electronic structures of molecular systems in their ground and excited states. The method of many-electron wave functions belongs to the last of these lines of research.

The current state of high-precision *ab initio* calculations cannot be considered satisfactory, despite the progress achieved. The problems of taking account of electron correlation in molecular systems with partially filled electron shells and quasi-degenerate states still have not been solved. Problems related to the mathematics also exist. If they are solved, the development of the MWF method will be substantially accelerated.

In recent years, interest in the Valence Bond (VB) method has been revived, and has been clearly depicted in a small review.[69] The inevitability of the revival of the VB method, which had once lost its primary position in theoretical chemistry, is a result of the fact that it is based on the chemical bond concept.

The VB theory became widespread in the 1930s owing to L Pauling's work. However, by the 1950s, MO theory, which has developed successfully since, became more popular. Among other reasons, the loss in popularity of the VB method was due to the fact that it predicts a diamagnetic ground state with a Lewis pairing of electrons for the oxygen molecule rather than the paramagnetic state (established experimentally and reproduced by the MO method). The results of this and some other applications of the VB method were responsible for it being regarded as a failure.

The reason for the lack of success was the imperfection of an early variant of this method: at that time, the method was actually reduced to a simplified resonance variant with a non-productive counting of resonance structures. Compared with the resonance theory, even the simple MO method looked much more fruitful. Firstly, it has attracted the attention of spectroscopists (owing to a unified interpretation of optical, IR and UV spectra), radiospectroscopists (who started interpreting their EPR spectra using the new notion of 'spin density') and finally organic chemists (who recognised the reliability of the proposed qualitative explanation of the stability of diverse systems and, hence, the possibility of deliberate planning of new purpose-directed experiments).

Analysis of the reactivity of organic compounds at the time of rapid development of MO theory was carried out almost exclusively within the framework of this theory, as indicated by the exceptional popularity of the Woodward – Hoffmann rules. The MO schemes were universally preferred in the interpretation of spectroscopic data.

Undoubtedly, the skew towards MO theory has been due, among other reasons, to advances in computing machinery. In particular, the versatile quantum-chemical software package GAUSSIAN, with exceptionally high computation potential, has become universally available. Therefore, experimental chemists started to resort, more and more often, to specialists who were able to perform at least semi-quantitative quantum-chemical calculations for the systems they were interested in.

However, it has become clear with time that the MO method with full allowance for the configuration interaction is equivalent to the VB method taking into account all ionic structures. The relationship between the MO and VB methods is reflected in the growing trend to localise the calculated MO, although consideration of localised orbitals implies the VB theory.

The use of the MO method is more expedient in cases where electron delocalisation is essential. In calculations on large molecules, the MO method is preferred, as the obtained wave functions are less cumbersome than those of the VB method.

However, using the VB theory, one can more easily represent the electron redistribution during chemical transformations or mechanisms of forming of activation barriers in diverse chemical processes by means of correlation diagrams of valence bonds. These diagrams allow one to predict the activation barriers proceeding from the structural parameters, ionisation potentials and electron affinities of the reactants, the singlet – triplet splitting energies of the chemical bond being cleaved, the substituent and solvation effects, *etc*. Resorting to VB models resulted in the discovery of a new type of bonding in metal clusters (ferromagnetic bonding), determination of the structures of unusual transition metal complexes, and so on. The above is indicative of the significant role played by the VB method in theoretical chemistry.[69]

Experimental chemists are unlikely to do away with using vivid resonance structures. However, it should be borne in mind that two approaches to the description of the electronic structure and physicochemical properties of molecules exist that fruitfully supplement rather than exclude each other.

In order to increase the reliability of the results of any quantum-chemical method, a more adequate description of the electron motion is required. From general considerations, taking account of the correlation in motion of 'separate' electron pairs is expected to be most important. This assumption is based on the fact that the Pauli principle generally forbids three or more electrons from being at the same point in the configuration space, thus decreasing the correlation error for such electron groups (conglomerates). Therefore, many modern techniques for investigation correlation effects imply the 'intuitive concept' of electron pairs in some form.

The exclusion by the Pauli principle of ternary electron collisions clearly demonstrates that this principle has something in common with nodal surfaces. We attempted to reflect the correspondence between the Pauli exclusion principle and nodal surfaces, which can hardly provoke serious objections, by means of a simple physical hypothesis, according to which two electrons with parallel spins cannot occur on the same equipotential surface.

Undoubtedly, this hypothesis requires comprehensive verification and further development. It might prove untenable for complex molecular systems, or perhaps, it will have to be corrected or modified. In any case, the problem definition will remain topical. Successful solution of this problem will open up new prospects for the elaboration of high-precision quantum-chemical methods. Indeed, of the multitude of sets of antisymmetrical MWFs that can serve as the basis for finding approximate solutions to the Schrödinger equation, this method allows one to choose reliably the optimal solution for each particular system.

Some MWF nodal surfaces (including those for the degenerate states) can be established *a priori* by a generalised graph-theoretical method, according to which the MWF nodes are classified to an accuracy of equivalence and the configuration space is split into the smallest number of regions of constant sign.[70] The Fermi correlation of electrons with parallel spins, caused by the Pauli principle and related to the geometry of the MWF nodal surfaces, has a special significance.[71, 72] Of interest are a new type of correlation effect, called geometrical,[71] which are closely related to electron density minima in the excited states of a two-electron atom. These effects result in the prohibition of seemingly quite plausible electronic configurations, as one of the electrons is 'ejected' from the inner three-dimensional region of the coordinate space when another electron is located at a definite distance from the atomic nucleus.

Detailed analysis of the wave functions of the beryllium atom in a Hartree – Fock approximation has shown[73] that particular quantum-chemical calculations may give rise to false nodes for the functions obtained due to the incompleteness and specificity of the basis set, limited convergence of the iteration procedure, and so on. It should also be borne in mind that even if the search for fundamentally new avenues in modern quantum chemistry does not always prove successful, this field of science would still gain new valuable experience.

The Pauli exclusion principle seems to be common knowledge, so no comments on this point are needed. However, in actual fact, it turns out that even the question 'what does the Pauli principle exclude in a particular many-electron system?' has not been answered as yet. The difficulty of understanding the Pauli principle was noted a long time back by L de Broglie: '... currently, it is almost impossible to understand how two identical particles forbid each other to occupy the same state'.[74] R Feynman expressed an even more categorical opinion concerning this principle: 'Probably, this is one of the few items in physics where

the rule formulation is very simple, but no equally simple explanation has been found. Apparently, this means that we do not fully understand the principle that underlies it. Let us consider it, as yet, to be a Law of the Universe'.[75]

References

1. N D Chuvylkin *Zh. Vsesoyuz. Khim. O-va im. D I Mendeleeva* **35** 660 (1990) [a]
2. P v R Schleyer, N L Allinger, T Clark, J Gasteiger, P A Kollman, H F Schlaefer III, P R Schreiner (Eds) *Encyclopedia of Computational Chemistry* Vols 1 – 5 (Chichester: Wiley, 1998)
3. R Carbo (Ed.) *Quantum Chemistry: Basic Aspects, Actual Trends* (Amsterdam, Oxford, New York, Tokyo: Elsevier, 1989)
4. V I Minkin, B Ya Simkin, M N Glukhovtsev *Usp. Khim.* **58** 1067 (1989) [*Russ. Chem. Rev.* **58** 622 (1989)]
5. N P Gambaryan, I V Stankevich *Usp. Khim.* **58** 1945 (1989) [*Russ. Chem. Rev.* **58** 1103 (1989)]
6. E A Smolenskii, N D Chuvylkin, in *Tezisy Dokladov X Vsesoyuznogo Soveshchaniya po Kvantovoi Khimii, Kazan', 1991* (Abstracts of Reports of the Xth All-Union Meeting on Quantum Chemistry, Kazan', 1991) p. 293
7. E A Smolenskii, I V Stankevich *Teor. Mat. Fiz.* **88** 46 (1991)
8. E A Smolenskii *Dokl. Akad. Nauk SSSR* **304** 595 (1989) [b]
9. M Krauss, W J Stevens *Annu. Rev. Phys. Chem.* **35** 357 (1984)
10. P Hohenberg, W Kohn *Phys. Rev. B* **136** 86 (1964)
11. W Kohn, L J Sham *Phys. Rev. A* **140** 1133 (1965)
12. J P Dahl, J Avery (Eds) *Local Density Approximation in Quantum Chemistry and Solid State Physics* (New York, London: Plenum, 1984)
13. R O Johes, in *Ab initio Method in Quantum Chemistry* Pt. I (Ed. K P Lawley) (New York: Wiley-Interscience, 1987)
14. R G Parr, W Yang *Density Functional Theory of Atoms and Molecules* (New York, Oxford: Oxford University Press, 1989)
15. T Ziegler *Chem. Rev.* **91** 651 (1991)
16. J Andzelm, E Wimmer *J. Chem. Phys.* **96** 1280 (1992)
17. A D Becke *J. Chem. Phys.* **96** 2155 (1992)
18. B G Johnson, P M W Gill, J A Pople *J. Chem. Phys.* **98** 5612 (1993)
19. A D Becke *J. Chem. Phys.* **98** 5648 (1993)
20. G J Laming, V Termath, N C Handy *J. Chem. Phys.* **99** 8765 (1993)
21. E Fermi *Z. Phys.* **48** 73 (1928)
22. L H Thomas *Proc. Cambridge Philos. Soc.* **23** 542 (1927)
23. M Karelson, V Lobanov, A R Katrizky *Chem. Rev.* **96** 1027 (1996)
24. R O Jones, O Gunnarsson *Phys. Rev. Lett.* **55** 107 (1985)
25. O Gunnarsson, R O Jones *Phys. Rev. B* **31** 7588 (1985)
26. B H Wells, in *Methods in Computational Chemistry* Vol. 1 (Ed. S Wilson) (New York, London: Plenum, 1987) p. 311
27. D M Ceperley, L Mitas *Adv. Chem. Phys.* **93** 1 (1996)
28. J B Anderson, in *Reviews in Computational Chemistry* Vol. 13 (Eds K B Lipkowitz, D B Boyd) (New York: Wiley-VCH, 1999) p. 133
29. R C Grimm, R G Storer *J. Comput. Phys.* **7** 134 (1971)
30. D R Garmer, J B Anderson *J. Chem. Phys.* **86** 4025 (1987)
31. J B Anderson, C A Traynor, B M Boghosian *J. Chem. Phys.* **95** 7418 (1991)
32. D M Ceperley, B Bernu *J. Chem. Phys.* **93** 552 (1990)
33. J Carlson, M H Kalos *Phys. Rev. C* **32** 1735 (1985)
34. K Jankowski, in *Methods in Computational Chemistry* Vol. 1 (Ed. S Wilson) (New York, London: Plenum, 1987) p. 1
35. T Koga *J. Chem. Phys.* **96** 1276 (1992)
36. W Pauli *Z. Phys.* **31** 765 (1925)
37. P A M Dirac *Proc. R. Soc. London, Ser. A* **112** 661 (1926)
38. W Heisenberg *Z. Phys.* **38** 411 (1926)
39. E Wigner *Z. Phys.* **40** 492 883 (1927)
40. F Hund *Z. Phys.* **43** 788 (1927)
41. W Heitler *Z. Phys.* **46** 47 (1928)
42. J C Slater *Phys. Rev.* **34** 1293 (1929)
43. P-O Löwdin *Adv. Chem. Phys.* **2** 207 (1959)
44. B Anderson *Phys. Rev. A* **35** 3550 (1987)
45. R N Barnett, P J Reynolds, W A Lester *J. Chem. Phys.* **82** 2700 (1985)
46. V A Fok *Zh. Eksp. Teor. Fiz.* **10** 961 (1940) [c]
47. E A Smolenskii *Izv. Akad. Nauk, Ser. Khim.* 1666 (1995) [d]
48. I V Stankevich, E A Smolenskii, N S Zefirov *Dokl. Akad. Nauk SSSR* **314** 213 (1991) [b]
49. E A Smolenskii, M S Molchanova, M Kh Klin, N D Chuvylkin, in *Tezisy Dokladov I Vsesoyuznoi Konferentsii po Teoreticheskoi Organicheskoi Khimii* (Abstracts of Reports of the First All-Union Conference on Theoretical Organic Chemistry) (Volgograd: VATOKh, 1991) p. 103
50. E A Smolenskii, I V Stankevich, N S Zefirov *Dokl Akad. Nauk SSSR* **317** 413 (1991) [b]
51. E A Smolenskii *Dokl. Akad. Nauk SSSR* **266** 160 (1982) [b]
52. E A Smolenskii *Dokl. Akad. Nauk SSSR* **289** 664 (1986) [b]
53. E A Smolenskii *Zh. Fiz. Khim.* **62** 3273 (1988) [e]
54. E A Smolenskii, N S Zefirov *Dokl. Akad. Nauk* **329** 40 (1993) [b]
55. E A Smolenskii, S A Shpilkin, N S Zefirov *J. Chem. Inf. Comp. Sci.* **36** 409 (1996)
56. R Kurant, D Gil'bert *Metody Matematicheskoi Fiziki* (The Methods of Mathematical Physics) (Moscow, Leningrad: Gostekhizdat, 1951) Vol. 1
57. G M Zhislin *Usp. Matem. Nauk* **16** (1) 149 (1961) [*Russ. Math. Surv.* **16** (1) (1961)]
58. D M Ceperley *J. Stat. Phys.* **63** 1237 (1991)
59. C L Pekeris *Phys. Rev.* **115** 1216 (1959)
60. K Frankowski, C L Pekeris *Phys. Rev.* **146** 46 (1966)
61. V A Fok *Izv. Akad. Nauk SSSR, Ser. Fiz.* **18** 161 (1954)
62. D E Freund, B D Huxtable, J D Morgan *Phys. Rev. A* **29** 980 (1984)
63. D P Carroll, H J Silverstone, R M Metzger *J. Chem. Phys.* **71** 4142 (1979)
64. E A Smolenskii *Teor. Eksp. Khim.* **19** 523 (1983) [f]
65. F W King, M P Bergsbaken *J. Chem. Phys.* **93** 2570 (1990)
66. E A Smolenskii, T S Pivina, S A Shpilkin, L K Maslova, N D Chuvylkin, in *Euro Pyro 95, Tours, France 1995* p. 503
67. E A Smolenskii, P P Aristov, S Ya Itshenko, S A Shpilkin *J. Chem. Inf. Comp. Sci.* **36** 402 (1996)
68. W Kolos, C C J Roothaan *Rev. Mod. Phys.* **32** 219 (1960)
69. R Hoffmann, S Shaik, P C Hiberty *Acc. Chem. Rec.* **36** 750 (2003)
70. S N Maximoff, S A Shpilkin, E A Smolenskii *Phys. Rev. A* **61** 2250 (2000)
71. E A Smolenskii, S N Maksimov, S A Shpil'kin *Dokl. Akad. Nauk* **394** 65 (2004) [b]
72. E A Smolenskii, S N Maksimov, S A Shpil'kin *Dokl. Akad. Nauk* **362** 187 (1998) [b]
73. J Hachmann, P T A Galek, T Yanai, G K-L Chan, N C Handy *Chem. Phys. Lett.* **392** 55 (2004)
74. L de Broglie *La Physique Nouvelle et les Quanta* (Paris: Flammarion, 1937)
75. R P Feynman, R B Leighton, M Sands *The Feynman Lectures on Physics* Vol. 3 (Reading, MA: Addison-Wesley, London: Palo Alto, 1965)

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Dokl. Phys. (Engl. Transl.)*
[c] — *J. Exp. Theor. Phys. (Engl. Transl.)*
[d] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Theor. Exp. Chem. (Engl. Transl.)*