Brief Communications

Nodal surfaces of the wave functions of the hydrogen molecule in the triplet state $^3\Sigma_u^+$

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For molecular hydrogen in the triplet state $^3\Sigma_u^+$, the nodal surfaces of the wave function corresponding to the minimum basis set of Slater orbitals in the Hartree—Fock approximation and those of the wave function used in calculations by the diffusion quantum Monte Carlo method were plotted and analyzed. Taking account of the condition for antisymmetrical wave function of the triplet state ^3S of He atom, the Hartree—Fock approximation in the minimum basis set of one-electron orbitals is inappropriate for *a priori* determination of the nodal surfaces of many-electron wave functions (MWF). An MWF quantum chemical method developed by the authors is outlined. The alternative nodal surfaces for H_2 ($^3\Sigma_u^+$) *a priori* specified in this method are presented.

Key words: many-electron wave functions (MWF), MWF nodal surfaces, hydrogen molecule, Hartree—Fock approximation, diffusion quantum Monte Carlo method, MWF quantum chemical method.

In 1926, Schrödinger reported[1] his famous equation and in 1927 the hydrogen molecule was treated within the framework of the new quantum theory.[2] The earlier results obtained for this molecule using quantum mechanical methods were of qualitative or, at best, semiquantitative character. With the development of quantum chemistry (a new branch of chemical science based on the quantum mechanical formalism) the calculable properties of molecular hydrogen were revised and an increasingly improved agreement with the experimental data was achieved. The two-electron molecule, H_2, always played the role of a model system for testing various concepts and quantum chemical methods, among which the Hartree—Fock approximation (a self-consistent field method with quantum exchange)[3] occupies a special position.

When working in the Hartree—Fock approximation within the framework of the MO LCAO method and using two Slater-type 1*s*-orbitals (1*s*-STO) as the basis functions (1*s*-STO is the exact solution to the Schrödinger equation for H atom), the unnormalized wave function of the triplet state $^3\Sigma_u^+$ of H_2 molecule after opening of the Slater determinant[3] and straightforward transformations has the form

$$^3\Psi(r_1,r_2) = \exp[-(r_{1A} + r_{2B})] - \exp[-(r_{2A} + r_{1B})], \qquad (1)$$

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where the subscripts A and B refer to protons while the subscripts "1" and "2" refer to electrons in this molecule. Equation (1) shows that in the minimum basis set of STO the variety of nodal surfaces (${}^3\Psi(r_1,r_2) = 0$) of the Hartree—Fock wave function is given by the condition

$$r_{1A} - r_{1B} = r_{2A} - r_{2B} = C, \tag{2}$$

where C is a real number.

The condition (2) is met for the trial wave function

$$\Psi_t = \{\exp[-a(r_{1A} + r_{2B})] - \\ - \exp[-a(r_{2A} + r_{1B})]\}\exp[br_{12}/(1 + cr_{12})], \tag{3}$$

which was used in quantum chemical calculations[4] of the triplet state ${}^3\Sigma_u{}^+$ of H_2 molecule by the diffusion quantum Monte Carlo (DQMC) method at a proton-proton distance of 1.4 a.u. Calculations with the function (3) for which the nodal surface is specified by the Hartree—Fock condition (2) for the minimum basis set of STO using $a = 1.0$ a.u.$^{-1}$, $b = 0.25$ a.u.$^{-1}$, and $c = 0.25$ a.u.$^{-1}$ gave the energy $E = -0.7838 \pm 0.0007$ a.u., which is in good agreement with the value -0.783150 a.u. determined[5] by the variational method using a 34-termed wave function.

As an example, Fig. 1 presents the (x,y)-sections for the Cartesian coordinates $(-1,0,0)$ and $(1,0,0)$ of the protons A and B, respectively, at $|C| = 0.5$, 1, 1.5, 1.75, and 1.99 (see expression (2)). For $|C|$ in the range from about 2 to 0, the sections of the nodal surfaces represent two parabolas that continuously approach each other and become wider until becoming a straight line (y axis) at $C = 0$. Rotation of the corresponding lines about the x axis gives a set of approaching pairs of elliptical paraboloids which become the (y,z) plane at $|C| \to 0$. Interestingly, the same shape of the nodal surfaces was found in our Hartree—Fock calculations in the extended basis set 6-31G* by varying the internuclear distance from 1 to 3 a.u.

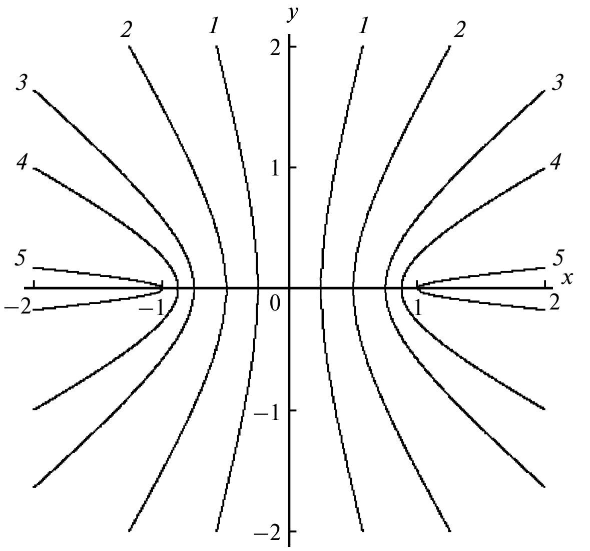

Fig. 1. (x,y)-Sections of the nodal surfaces for the triplet state of H_2 molecule; $|C|$ in Eq. (2): 0.5 (*1*), 1 (*2*), 1.5 (*3*), 1.75 (*4*), and 1.99 (*5*).

The Hartree—Fock nodal surfaces were successfully used in high-precision quantum Monte Carlo (QMC) calculations of some simple atoms, hydrogen molecule, and other simple compounds, as well as model fermion systems.[4,6—9] Nevertheless, the problem of approximate and exact nodes of many-fermion wave functions still remains one of the most intriguing when using stochastic methods, such as DQMC. In such approaches, this problem is eliminated by assuming the existence of some fixed unsurmountable boundaries for fictitious, positively and negatively charged species (so-called "walkers") confined within different spatial regions (see Refs 4, 6—9 and references cited therein).

When using the Hartree—Fock fixed-node surfaces in the QMC methods, the degree of inclusion of the electron correlation energy for molecules, clusters, and model solids is often about 90% (see Refs 6—9). However, one should keep in mind that such nodal surfaces may strongly differ from the Schrödinger nodal surfaces (which correspond to the exact solutions to the Schrödinger equation). This is, in particular, indicated by slow convergence of the configuration interaction (CI) procedure which requires calculations of a large number of Slater determinants (their nodal surfaces are almost always different from one another) to approach the Schrödinger nodal surface.

Incorrectness of the Hartree—Fock nodal surfaces calculated in the minimum basis set can be illustrated taking the triplet state ${}^3S$ of He atom as an example. The exact nodal surfaces of this system are known *a priori* (according to the Pauli exclusion principle, these are spheres centred at the atomic nucleus[10,11]). Indeed, if one uses the 1*s* and 2*s* STO for the He atom as the minimum basis set by analogy with H_2 (see above), the unnormalized spatial wave function of the triplet state ${}^3S$ of the He atom in the Hartree—Fock approximation is given by (a.u.):

$${}^3\Psi(r_1,r_2) = r_1 \exp[-(\xi_1 r_2 + \xi_2 r_1)] - \\ - r_2 \exp[-(\xi_1 r_1 + \xi_2 r_2)], \tag{4}$$

where ξ_1 and ξ_2 are the constants in the expressions for the orbital exponents.[12] For spheres ($r_1 = r_2$) to be the nodes (${}^3\Psi(r_1,r_2) = 0$) of the function (4), the condition $\xi_1 = \xi_2$ should be met; however, this is inadmissible because the diffusivities of the 1*s* and 2*s* STO can not be the same. In addition, incorrectness of the Hartree—Fock nodal surfaces becomes even more pronounced owing to very strongly increasing complexity of their use in high-precision Monte Carlo quantum chemical calculations of atoms and molecules with increasingly more complex structures.[4,6—9]

The aforesaid gives an impetus to the search for basically different (non-Hartree—Fock) methods of construction of many-electron wave functions. Our studies are aimed at developing a novel quantum chemical approach (see below) called the method of many-electron wave functions (MWF),[13] which would give an answer to the question: "What does the Pauli exclusion principle prohibit for each particular electron-nuclear configuration?".

The MWF method is based on two fundamental statements: 1) generalization[14] of the Courant—Gilbert theorem to the case of exact nonrelativistic MWF Ψ for an electron state with a specified spin and 2) an original hypothesis of prohibition of equipotential surfaces (HPES), according to which the Pauli exclusion principle should be interpreted as the prohibition for two electrons with the same spin to be on the same equipotential surface due to the presence of a certain spatial electron configuration (the spin is taken into account using "spin-invariant subgroups"[10,11]). Taking into account a particular significance of the MWF nodes, it seems appropriate to augment the expression for the trial wave function by a factor which explicitly specifies the shape of the nodal surface determined in accordance to the HPES.

Considering the triplet state of H_2 molecule within the framework of the MWF method and following the HPES, for any trial wave function one should geometrically analyze the expression[10,11]

$$1/r_{1A} + 1/r_{1B} = C, \qquad (5)$$

where C is a positive number and r_{1A} and r_{1B} are the corresponding distances from the electron denoted by "1" to the protons A and B separated by the distance R_{AB}. Assuming that the Cartesian coordinates of the protons A and B are (−1,0,0) and (1,0,0), respectively, and taking into account the symmetry of the H_2 molecule, the following three cases deserve attention.

1. $C = 2$. According to Eq. (5), the nodal surface represents two slightly distorted spheres which are tangent each other at the point (0,0,0); this is quite clear assuming that the radius of each sphere around the protons A and B is unity ($r_{1A} = r_{1B} = 1$). The section of this surface in the (x,y) plane is shown in Fig. 2, *a*.

2. $C > 2$. This condition is, in particular, met at $r_{1A} = r_{1B} < 1$, which follows from Eq. (5). This means that the spheres that were tangent each other ($C = 2$) are now separated by some distance (the closer the radii r_{1A} and r_{1B} to zero the smaller the spheres). According to the HPES, if the first electron is on one of two topologically unconnected areas of the equipotential surface surrounding the proton A, the second electron is prohibited to be not only on that area of the equipotential surface, but also on the other area of this equipotential surface, localized around the proton B.

3. $0 < C < 2$. In this case, as C decreases, the spheres increasingly interpenetrate, as indicated by Eq. (5) at $r_{1A} = r_{1B} > 1$. Because of this, the nodal surface initially (at C ~2) has the shape of a dumb-bell (see the section in Fig. 2, *b* and Fig. 3), which gradually transforms to an ellipsoid at $C \to 1$ (see the section in Fig. 2, *c*) and then to a sphere of radius $r = \infty$ at $C \to 0$ (*i.e.*, at ave $r_{1A} + r_{1B} \to \infty$). Taking into account the fact that at $C \cong 0$ the proton-

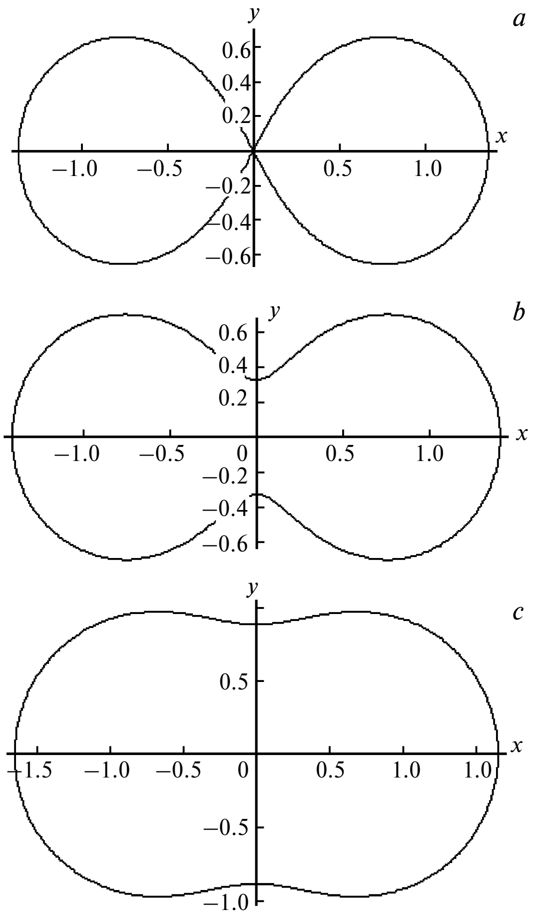

Fig. 2. (x,y)-Sections of the nodal surfaces for the triplet state of H_2 molecule; C in Eq. (5): 2 (*a*), 1.9 (*b*), and 1.5 (*c*).

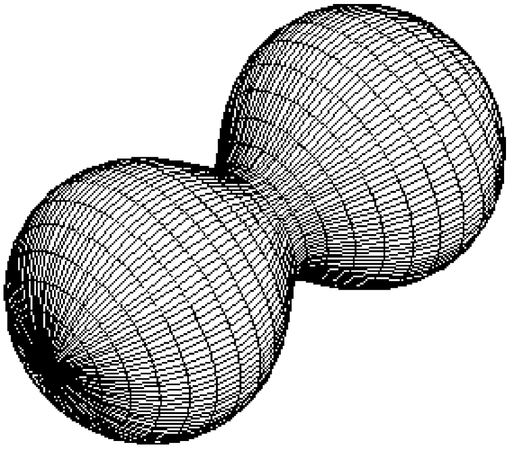

Fig. 3. The nodal surface for the triplet state of H_2 molecule at $C = 1.9$ (see Eq. (5)).

proton distance R_{AB} is negligible ($r = \infty$) compared to r_{1A} and/or r_{1B}, this transformation seems to be quite expectable based on the idea of the "limiting transition" H_2 ($^3\Sigma_u{}^+$) → He (^3S), because for the triplet state of He atom (^3S) the exact nodal surface is a sphere.[10,11]

Of course, the HPES should be comprehensively tested and developed; probably, it should be revised or modified in some way. However, in any case the formulation of the HPES itself is topical and its consideration will enrich the experience of quantum chemists in search for fundamentally new non-Hartree—Fock approaches.

References

1. E. Shrödinger, *Ann. Physik*, 1926, **79**, 361.
2. W. Heitler, E. London, *Z. Physik*, 1927, **44**, 455.
3. I. Mayer, *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*, Kluwer Academic—Plenum Publishers, New York—Boston—Dordrecht—London—Moscow, 2003, 352 pp.
4. J. B. Anderson, C. A. Traynor, B. M. Boghosian, *J. Chem. Phys.*, 1991, **95**, 7418.
5. W. Kolos, C. C. J. Roothaan, *Rev. Mod. Phys.*, 1960, **32**, 219.
6. J. B. Anderson, *Phys. Rev. A: At. Mol. Opt. Phys.*, 1987, **35**, 3550.
7. D. M. Ceperley, *J. Stat. Phys.*, 1991, **63**, 1237.
8. M. W. C. Foulkes, L. Mitas, R. J. Needs, G. Rajagopal, *Rev. Mod. Phys.*, 2001, **73**, 33.
9. M. Bajdich, L. Mitas, G. Drobny, L. K. Wagner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 075131.
10. N. D. Chuvylkin, E. A. Smolenskii, N. S. Zefirov, *Usp. Khim.*, 2005, **74**, 1118 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2005, **74**, 1027].
11. N. D. Chuvylkin, E. A. Smolenskii, M. S. Molchanova, N. S. Zefirov, *Int. J. Quant. Chem.*, 2010, **110**, 1809.
12. V. I. Minkin, B. Ya. Simkin, R. M. Minyaev, *Teoriya stroeniya molekul* [*Theory of Molecular Structure*], Feniks, Rostov-na-Donu, 1997, p. 68 (in Russian).
13. E. A. Smolenskii, N. D. Chuvylkin, *Tez. dokl. X Vsesoyuz. soveshch. po kvantovoi khimii* [*Abstrs Xth All-Union Meeting on Quantum Chemistry*], Kazan, 1991, p. 293 (in Russian).
14. E. A. Smolenskii, I. V. Stankevich, *Teoret. Mat. Fiz.*, 1991, **88**, 46 [*Theor. Math. Phys.* (*Engl. Transl.*), 1991, **88**, 706].

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