DEVELOPMENTS IN THE SEPARATED PAIR THEORY*

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In recent years, it has become possible to compute strongly orthogonal geminals for several smaller systems and to investigate the effectiveness of the conventional separated pair theory. The results are compared with those obtained by other many-electron theories and the sources of the main deficiencies are pointed out. Extensions of the separated pair theory using the optimized orbitals of the single antisymmetrized geminal product wave function are also discussed.

Introduction

It was FOCK who first proposed that two-electron functions should be used as building blocks in constructing the total wave function [1]. This method seemed to be the most natural extension of the Hartree—Fock scheme. It was expected that in this way the most important part of the correlation energy could be accounted for and the two-electron functions are transferable at least in certain "localized" systems. The calculation of the energy (and of other physical quantities) is, however, rather cumbersome unless special restrictions are imposed on the two-electron functions [2, 3]. To avoid this difficulty the concept of strong orthogonality was introduced [4]. Given an $2N$-electron system the total wave function Ψ_0 can be written as an antisymmetrized product of N geminals $\psi_K (1, 2)$, $K = 1, 2, \ldots N$. If the geminals are

a) normalized to unity:

$$\int \psi_K^* (1,2) \, \psi_K (1,2) \, d1 \, d2 = 1 \,, \tag{1}$$

b) antisymmetric in the (space-spin) variables of the electrons:

$$\psi_K (1,2) = - \psi_K (1,2) \,, \tag{2}$$

c) mutually orthogonal in the strong sense:

$$\int \psi_K^* (1, 2) \, \psi_L (1, 2') \, d1 = 0, \quad \text{if} \quad K \neq L \,, \tag{3}$$

the total wave function Ψ_0 normalized to unity has the following form:

$$\Psi_0 = \left[\frac{2^N}{(2N)!}\right]^{1/2} \sum_P (-1)^p P\psi_1(1,2)\psi_2(3,4)\ldots\psi_N(2N-1,2N). \qquad (4)$$

Here the summation should be extended over only those permutations which interchange the electrons between geminals.

By using (4) and taking into account restrictions (1), (2), (3), the energy expression can be easily calculated [4, 5, 6, 7, 8]

$$E_0 = H(0) + \sum_{K=1}^{N} \int \psi_K^*(1,2)\left[H(1) + H(2) + r_{12}^{-1}\right]\psi_K(1,2)\,d1\,d2 +$$

$$\qquad\qquad (5)$$

$$+ 2\sum_K \sum_{L(\neq K)} \int d1\,d2\,d3\,d4\,r_{13}^{-1}\left[1 - P_{13}\right]\psi_K^*(1',2)\psi_K(1,2)\psi_L^*(3',4)\psi_L(3,4).$$

The mean value of an operator O, being the symmetrical sum of one-electron operators

$$O = \sum_{i=1}^{2N} O(i),$$

has the following simple form

$$\bar{O} = 2\sum_{K=1}^{N} \int \psi_K^*(1,2)O(1)\psi_K(1,2)\,d1\,d2.$$

The above formalism has been generalized so that group functions of an arbitrary number of electrons were used as building blocks instead of geminals [7, 8, 9].

By using energy expression (5) and auxiliary conditions (1), (2), (3), a set of coupled integro-differential equations has been derived with the help of the variation theory for determining the best possible geminals [5, 8, 10]. The equations so obtained were inconvenient for practical use owing to the off-diagonal Lagrangian multipliers. To circumvent this difficulty PARKS and PARR suggested that the geminals should be constructed of given one-electron functions ϕ in the following way

$$\psi_K(1,2) = \sum_{\varkappa,\lambda} C_{\varkappa\lambda}^K \phi_\varkappa(1)\phi_\lambda(2). \qquad (6)$$

The strong orthogonality conditions (3) are satisfied when each of the one-electron functions $\phi_\varkappa$ enters the series (6) of only one geminal. PARKS and PARR also proposed that the coefficients $C_{\varkappa\lambda}^K$ should be calculated self-consistently by minimizing the energy expression of the individual geminals [5, 8]. The meaning of the strong orthogonality condition (SC) was later clarified by ARAI [11], and by LÖWDIN [12]. They proved the following theorem:

Given N strongly orthogonal geminals ψ_K, there always exists at least one complete set of orthonormal one-electron functions $\{\varphi\}$, which can be partitioned into N subsets having no common elements

$$\varphi_{11}, \varphi_{12}, \varphi_{13}, \ldots \varphi_{K1}, \varphi_{K2}, \varphi_{K3}, \ldots \varphi_{N1}, \varphi_{N2}, \varphi_{N3}, \ldots$$

such that each of the geminals can be expanded in terms of its own subset only:

$$\psi_K (1,2) = \sum_{\varkappa, \lambda} a_{\varkappa\lambda}^K \varphi_{K\varkappa} (1) \varphi_{K\lambda} (2) . \tag{7}$$

This means that the representation of the strongly orthogonal geminals by series (7) is completely general provided the coefficients $a_{\varkappa\lambda}^K$ and the one-electron functions $\varphi_{K\varkappa}$ are suitably determined.

This theorem made it possible to work out methods suitable for the practical determination of strongly orthogonal geminals. At the same time the separated pair theory became essentially a particular case of the method of "configuration interaction with optimalized basis functions".

The conventional separated pair theory

Geminals are uniquely defined by the coefficients $a_{\varkappa\lambda}^K$ and the one-electron functions $\varphi_{K\varkappa}$. (The converse is not necessarily true.) Using the variation theory we can derive equations for determining the coefficients $a_{\varkappa\lambda}^K$ and the one-electron functions $\varphi_{K\varkappa}$ [5, 7, 8, 13—15]. Substituting (7) into the energy expression (5) and varying the coefficients subject to the auxiliary conditions

$$\sum_{\varkappa, \lambda} |a_{\varkappa\lambda}^K|^2 = 1, \; K = 1, 2, \ldots N,$$

we obtain N sets of equations

$$\sum_{\mu, \nu} (H_{\varkappa\lambda, \mu\nu}^K - E^K \delta_{\varkappa\mu} \delta_{\lambda\nu}) a_{\mu\nu}^K = 0 , \tag{8}$$

for all $\varkappa$, λ, and K, where

$$H^K = H(1) + H(2) + r_{12}^{-1} +$$

$$+ 2 \sum_{L(\neq K)} \int d3 \, d4 \left[r_{13}^{-1} (1 - P_{13}) + r_{23}^{-1} (1 - P_{23}) \right] \psi_L^* (3', 4) \psi_L (3, 4).$$

Equs. (8) represent N pseudo-eigenvalue equations because the operators H^K depend on the coefficients $a_{\varkappa\lambda}^L$ of all the other geminals.

Varying the energy expression with respect to the one-electron functions $\varphi_{K\varkappa}$ taking into account the following auxiliary conditions

$$\int \varphi_{K\varkappa}^* (1) \varphi_{L\lambda} (1) \, d1 = \delta_{KL} \delta_{\varkappa\lambda} ,$$

we obtain a set of one-electron equations of the form

$$F_\varkappa^K \varphi_{K\varkappa} = \sum_L \sum_\lambda \varepsilon_{\varkappa\lambda}^{KL} \varphi_{L\lambda} \, . \tag{9}$$

Here the one-electron operators $F_\varkappa^K$ depend on all the coefficients $a_{\varkappa\lambda}^L$ and all the one-electron functions $\varphi_{L\lambda}$ except $\varphi_{K\varkappa}$.

Equs. (8) define the coefficients $a_{\varkappa\lambda}^K$ of the best possible geminals with fixed $\varphi_{K\varkappa}$'s, and Equs. (9) define the one-electron functions $\varphi_{K\varkappa}$ of the best possible geminals with fixed $a_{\varkappa\lambda}^K$'s. The $a_{\varkappa\lambda}^K$'s and the $\varphi_{K\varkappa}$'s are, however, not independent because any unitary transformation of the $\varphi_{K\varkappa}$'s (and the simultaneous transformation of the $a_{\varkappa\lambda}^K$'s with the corresponding adjoint) leaves ψ_K invariant. Instead of adding further auxiliary conditions it is more practical to use the natural spin-orbital expansion of the geminals. Assuming that the $\varphi_{K\varkappa}$ are the natural spin-orbitals of the corresponding geminal, for real ψ_K, only those coefficients $a_{\varkappa\lambda}^K$ differ from zero in the series (7) for which $\varphi_{K\lambda} = \varphi_{K\varkappa}^*$. As a consequence, Equs. (8) and (9) simplify to some extent [14, 15]. To obtain the best possible geminals these equations should be solved simultaneously [15]. The natural spin-orbitals of the geminals are automatically natural spin-orbitals of the total wave function.

All methods hitherto applied to obtain the best possible geminals are essentially equivalent to some approximate solution of Equs. (8) and (9) with a basis $\varphi_{K\varkappa}$ truncated to finite size.

A) If a set of orthonormal one-electron functions $\phi_{K\varkappa}$ is known which is presumably close to the optimal one, only the pseudo-eigenvalue equations (8) have to be solved. The solution can be carried out by iteration similarly to the Hartree—Fock—Roothaan equations [16, 17].

B) The above procedure can be combined with that of mixing the $\varphi_{K\varkappa}$'s by unitary transformation. The unitary transformation is determined by minimizing the total energy. The two procedures have to be continued alternately until self-consistency is achieved [18, 19].

C) An iterative procedure for solving Equs. (8) and (9) was proposed by KUTZELNIGG [15, 20]. As a first step he simplified Equs. (8) and (9) by decoupling those corresponding to coefficients $a_{\varkappa\lambda}^K$ and one-electron functions $\phi_{K\varkappa}$ of different geminals. The first natural orbital in each of the geminals was identified with a suitable "localized" unitary transform of the occupied Hartree—Fock orbitals. By using these decoupled equs. he determined the "excited" natural orbitals, which were required to be orthogonal to all occupied Hartree—Fock orbitals and to all "excited" natural orbitals of the same geminal but not to the "excited" natural orbitals of the other geminals. In the case of Be and LiH the correction owing to the nonorthogonality of the "excited"

natural orbitals was found to be small as the "excited" natural orbitals of different geminals are localized in different spatial regions. Nevertheless this method of approximation does not belong rigorously to the separated pair theory but is closely related to the independent pair model of SINANOĞLU [21, 22] and of NESBET [23].

Similar simplified equations were applied for determining the natural orbitals of geminals by EDMISTON and KRAUSS [24].

D) The method of "optimized valence configurations" is also a special case of the separated pair approximation [25]. Only the bonding pair was correlated but all the one-electron functions were optimized. The Equs. (9) were solved by expanding the $\varphi_{K\varkappa}$ in terms of a fixed set and the off-diagonal Lagrangian multipliers were absorbed in the operators $F_\varkappa^K$.

Method *B)* was applied to LiH [18] and to beryllium-like systems [26]. In the latter case 15 different Slater orbitals were used as basis functions and the exponents ζ were also varied. In the case of the Be atom 89.8% of the total correlation energy was recovered. Similar results were obtained for other systems.

Method *C)* was applied to Be, LiH [20] and to BeH_2, BH_3, CH_4 [26]. For Be and LiH the results are similar to those obtained by method *B)*. The correlation energy per equivalent geminal corresponding to the bond X—H was found to decrease continuously from LiH to CH_4. A comparison with the empirical correlation energies indicated that the sum of the intrageminal correlation energies comprises a continuously decreasing fraction of the total correlation energy. This means that the intergeminal correlation energies should also be taken into account and that the correlation energy of the X—H bonds is not transferable.

We can easily recognize the shortcomings of the conventional separated pair theory by comparing it with other theories of the correlation energy.

The most developed methods are the "many-electron theory" of SINA-NOĞLU [21, 22] and the "theory of *n*-th order Bethe—Goldstone equations" of NESBET [23]. They are closely related but the latter is more convenient for comparison because it applies one-electron function expansions. The exact wave function of a $2N$-electron system is determined by the successive variational solution of effective Schrödinger equations for clusters of one, two, three etc., electrons. Slater determinants Φ_k of $2N$-th order are used as basis functions, which are constructed out of a set of orthogonal one-electron functions $\{\underline{\phi}\}$:

$$\Phi_k = [(2N)!]^{-1\,2} \, \det \, |\phi_{\varkappa_1} \, \phi_{\varkappa_2} \ldots \phi_{\varkappa_{2N}}| \, .$$

The set $\{\phi\}$ is divided into two sets $\phi_\varkappa$, $\varkappa = 1, 2, \ldots 2N$, and ϕ_ϱ, $\varrho = 2N + 1$, $2N + 2, \ldots$, the first of which is usually identified with the occupied Hartree—Fock spin-orbitals. The Slater determinant containing only the functions of the

first set is denoted by Φ_0 and Slater determinants in which the occupied $\phi_\varkappa$, ϕ_λ, ϕ_μ, etc., are replaced by $\phi_\varrho, \phi_\sigma, \phi_\tau$, etc., are denoted by $\Phi_{\varkappa\lambda\mu}^{\varrho\sigma\tau}$.... The first order corrections $e_\varkappa$ to the Hartree—Fock energy E_{HF} are calculated by minimizing separately the expressions

$$e_\varkappa = \frac{\langle f_\varkappa | H | f_\varkappa \rangle}{\langle f_\varkappa | f_\varkappa \rangle} - E_{HF} \tag{10}$$

with respect to the coefficients of trial functions

$$f_\varkappa = \Phi_0 + \sum_\varrho b_\varkappa^\varrho \, \Phi_\varkappa^\varrho . \tag{11}$$

The second order corrections $e_{\varkappa\lambda}$ are calculated by minimizing separately the expressions

$$e_{\varkappa\lambda} = \frac{\langle f_{\varkappa\lambda} | H | f_{\varkappa\lambda} \rangle}{\langle f_{\varkappa\lambda} | f_{\varkappa\lambda} \rangle} - E_{HF} - e_\varkappa - e_\lambda \tag{12}$$

with respect to the coefficients of trial functions

$$f_{\varkappa\lambda} = \Phi_0 + \sum_\varrho b_\varkappa^\varrho \, \Phi_\varkappa^\varrho + \sum_\sigma b_\lambda^\sigma \, \Phi_\lambda^\sigma + \sum_{\varrho,\sigma} b_{\varkappa\lambda}^{\varrho\sigma} \, \Phi_{\varkappa\lambda}^{\varrho\sigma} . \tag{13}$$

The procedure can be continued by calculating higher order corrections.

The total correlation energy up to second order equals

$$E_C = \sum_{\varkappa=1}^{2N} e_\varkappa + \sum_{\varkappa > \lambda = 1}^{2N} e_{\varkappa\lambda} .$$

As the first sum in closed shell systems (Be, Ne) was found to be zero, the total correlation energy in this approximation consists of the sum of the independent pair correlation energies $e_{\varkappa\lambda}$. Calculations carried out on simpler systems indicated that in this approximation 97—98% of the total correlation energy could be recovered using a fairly large basis.

The lowering of the energy is brought about by terms

$$\int d1 \, d2 \, r_{12}^{-1} (1 - P_{12}) \, \phi_\varkappa^* (1') \, \phi_\lambda^* (2') \, \phi_\varrho (1) \, \phi_\sigma(2) \tag{14}$$

in the expression (12) of $e_{\varkappa\lambda}$ where they are multiplied by appropriate coefficients $b_{\varkappa\lambda}^{\varrho\sigma}$. As the matrix elements (14) represent exchange-like interactions their value is significant only when ϕ_ϱ and ϕ_σ are localized in the same regi-

ons of space where the corresponding $\phi_\varkappa$ and ϕ_λ are appreciably different from zero [28]. The electrons in $\phi_\varkappa$ and ϕ_λ can be excited to any ϕ_ϱ and ϕ_σ.

The correlation energy obtained by the separated pair theory can be written approximately in the following form [19, 20]

$$\sum_K \tilde{e}_K ,$$

where $\tilde{e}_K$ denotes that part of the correlation energy which comes from the geminal ψ_K.

This means that the separated pair theory has two main deficiencies:

a) It takes into account only N pair correlations (the so called intrageminal correlations) instead of $\binom{2N}{2}$.

b) Even the pair correlations included are restricted to some extent because the electrons in $\phi_\varkappa$ and ϕ_λ cannot be excited to any ϕ_ϱ and ϕ_σ but only to a subgroup of them as a consequence of the SC's.

These defects are not serious if the system consists of N completely isolated pairs because then

$$\psi_K (1, 2) \psi_L (1, 2') = 0, \quad \text{if} \quad K \neq L ,$$

automatically. This case is, however, an exceptional one. For strongly localized systems as e.g. for the Be atom, the error in the correlation energy caused by deficiency *b)* is not significant (2%). For weakly localized systems even this error may be more serious [29]. The neglect of intergeminal correlations (deficiency *a)*) is inadmissible, even for strongly localized systems. The importance of the interpair correlation energy was stressed by McKoy and Sinanoǧlu [30]. If accurate results are needed the conventional separated pair theory should be corrected.

Extension of the separated pair theory

Part of the intergeminal correlation energy within the framework of the separated pair theory can be taken into account as follows [7, 9, 31].

Each set of the equations (8) with fixed H^K has $\binom{n_K}{2}$ linearly independent solutions ψ_{Kk} one of which, ψ_{K1}, is identical with the best possible geminal; the others represent "excited" geminals. (n_K is the number of one-electron functions $\varphi_{K\varkappa}$ in the subspace K.) They obey the following orthogonality relations

$$\int \psi_{Kk}^* (1, 2) \psi_{Kl} (1,2) \, d1 \, d2 = \delta_{kl} ,$$

$$\int \psi_{Kk}^* (1, 2) \psi_{Ll} (1, 2') \, d1 = 0, \quad \text{if} \quad K \neq L .$$

The most general $2N$-electron function of the separated pair theory can be written in the form

$$\Psi_{SP} = \sum_{i,j,\ldots l} A^{ij\ldots l}\Psi^{ij\ldots l}, \qquad (15)$$

where the antisymmetrized products

$$\Psi^{ij\ldots l} = \left[\frac{2^N}{(2N)!}\right]^{1/2} \sum_P (-1)^p P\psi_{1i}(1,2)\,\psi_{2j}(3,4)\ldots\psi_{Nl}(2N-1,2N) \quad (16)$$

contain one geminal of each of the N subspaces. (The function $i = j = \ldots = l = 1$ corresponds to Ψ_0.)

Instead of solving the secular equation corresponding to (15) it is more practical to use the Rayleigh - Schrödinger perturbation theory based on partitioning techniques [7, 31, 32]. We have for the correction to the separated pair ground state energy (5) up to third order

$$\sum_{r>0} \frac{|H_{0r}|^2}{E_0 - H_{rr}} + \sum_{\substack{r>0 \\ s>0}} \frac{H_{0r}\,H_{rs}\,H_{s0}}{(E_0 - H_{rr})(E_0 - H_{ss})}\,, \qquad (17)$$

where

$$H_{rs} = \int \Psi_r^* H\Psi_s\,d\tau\,, \quad \int \Psi_r^*\Psi_s\,d\tau = \delta_{rs}\,.$$

The matrix element H_{0r} is different from zero only when the configuration Ψ_r contains two "excited" geminals.

It can easily be shown that the first sum of (16) includes the intergeminal correlations consistent with the SC's. If the Hartree−Fock approximation is a fairly good one the natural orbitals in the leading term of the best possible geminals are nearly identical with some unitary transforms of the doubly occupied Hartree−Fock orbitals. In this case we find among the "excited" geminals those the leading term of which is nearly identical with one of the possible singly-excited configurations within the corresponding subspace. These "singly-excited" geminals in the first sum of (17) account for all double excitations which conform to the SC's. Three- and four-particle excitations are also included.

It can be shown that configurations (16) above do not exhaust all the $2N$-electron states which can be constructed out of the known one-electron functions $\varphi_{K\varkappa}$. As a consequence of the SC's the number of electrons N_K in each of the subspaces are conserved and equal to 2 [31]. To get all linearly independent $2N$-electron functions $\Psi^{ij\ldots l}_{N_1 N_2 \ldots N_N}$ which can be derived from the $\varphi_{K\varkappa}$'s we have to construct also the functions corresponding to all possible partitions of the set $N_1, N_2, \ldots N_N$, $\Sigma N_K = 2N$, except for those where $N_1 = N_2 = \ldots = N_N = 2$.

The functions $\Psi^{ij...l}_{N_1 N_2...N_N}$ are expressed as antisymmetrized products containing one group function $\bar{\psi}_{N_K k}$ of each of the N subspaces [31]:

$$\Psi^{ij...l}_{N_1 N_2...N_N} = \left[\frac{N_1! N_2!...N_N!}{(2N)!}\right]^{1/2} \sum_P (-1)^p P \bar{\psi}_{N_1 i} \bar{\psi}_{N_2 j}...\bar{\psi}_{N_N l},$$

where

$$\bar{\psi}_{N_K k} \equiv 1, \quad \text{if} \quad N_K = 0,$$

$$\bar{\psi}_{N_K k} \equiv \varphi_{K\varkappa}, \quad \text{if} \quad N_K = 1,$$

$$\bar{\psi}_{N_K k} \equiv \psi_{Kk}, \quad \text{if} \quad N_K = 2,$$

and for $N_K > 2$

$$\bar{\psi}_{N_K k} \equiv (N_K!)^{-1/2} \det |\varphi_{K\varkappa}(1) \varphi_{K\lambda}(2)...\varphi_{K\nu}(N_K)|.$$

Every $\Psi^{ij...l}_{N_1 N_2...N_N}$ can be derived by "exciting" electrons out of the Ψ_0 by elementary excitations of two kinds

—simple excitation: replaces one group function by another belonging to the same subspace and occupation number

$$\bar{\psi}_{N_K k} \rightarrow \bar{\psi}_{N_K l}. \quad k \neq l,$$

—electron transfer excitation: transfer one electron from one subspace to another, altering two group functions simultaneously

$$\bar{\psi}_{N_K k} \bar{\psi}_{N_L l} \rightarrow \bar{\psi}_{N_K - 1 i} \bar{\psi}_{N_L + 1 j}.$$

The minimum number of simple excitations necessary to transfer a given state into another is always unique. This means that all states having nonzero matrix element with Ψ_0 can be derived from Ψ_0 by two elementary excitations. It is exactly these states which should be taken into account in calculating the correction up to third order (17). The corresponding functions $\Psi^{ij...l}_{N_1 N_2...N_N}$ can be grouped according to the minimum number of necessary elementary excitations to connect them with Ψ_0:

   I) two simple excitations. The corresponding configurations describe the correlations conforming to the SC's.

   II) one electron transfer excitations.

   III) one simple excitation + one electron transfer excitation,

   IV) two electron transfer excitations.

It can be shown that they include all possible two-electron excitations and in addition some of the many-electron excitations.

This procedure was applied to the π-electrons of trans-butadiene in the GOEPPERT—MAYER—SKLAR approximation [33, 34]. The separated pair ground state was calculated using equivalent orbitals constructed from the SCF orbitals of PARR and MULLIKEN [35], and all second order corrections were evaluat-

ed. It was found that the intrageminal correlation energy accounted for is 93% of the standard value which was identified with that obtained by the "full" CI. About 75% of the intergeminal correlation energy came from one electron transfer configurations of type II) and III). The contribution from configurations of type I) which conform to the SC's was less, 25%, and practically the whole came from configurations containing two "singly-excited" geminals. The contribution from two electron transfer configurations was found to be negligible. The result was superior to those obtained by other variants of the Rayleigh—Schrödinger perturbation theory.

The above procedure is convenient especially when perturbation theory is used.

MILLER and RUEDENBERG worked out a different method to obtain all $2N$-electron functions which can be constructed from the $\varphi_{K_\varkappa}$'s [26]. Using 28 configurations about 94% of the empirical correlation energy was recovered for beryllium-like systems. The natural orbitals obtained from the separated pair wave functions were very similar to those calculated from the 28 configuration wave function.

Conclusions

The conventional separated pair theory has not completely fulfilled all earlier expectations. The single antisymmetrized product of strongly orthogonal geminals accounts for only a fraction of the total correlation energy. Even for strongly localized systems (Be, CH_4) this fraction is about 90—50%. The transferability of the geminals seems to depend strongly on the environment of the corresponding pairs.

To achieve "chemical accuracy" it is necessary to go beyond the conventional separated pair theory. The extensions up to the present have used the one-electron functions optimized in the conventional theory and for small strongly localized systems have given promising results. The applicability depends mainly on the convergence of the expansion used in the extensions. If the natural orbitals of the separated pair wave function are very close to the natural orbitals of the exact wave function then the rate of convergence is nearly optimal and the second and third order correction of perturbation theory may be sufficient. The evaluation of the higher order corrections seems to be very clumsy. The practicability of the theory can be decided only when the results of further numerical calculations on various systems is available.

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РАЗВИТИЯ В РАЗДЕЛЕННОЙ ПАРНОЙ ТЕОРИИ

Э. КАПУИ

Резюме

В последние годы стало возможным определить строго ортогональные геминалы для некоторых малых систем и исследовать эффективность конвенциональной разделенной парной теории. Результаты сравниваются с полученными путем применения других многоэлектронных теорий. Обращается внимание на источники главных недостатков. Рассматривается дальнейшее расширение разделенной парной теории, применяющей оптимизированные орбитали волновой функции просто антисимметризированного геминального произведения.