PHYSICAL REVIEW A **82**, 042505 (2010)

Spin-polarized self-consistent-field equations for paired orbitals

Igor Zilberberg[*] and Sergey Ph. Ruzankin
Boreskov Institute of Catalysis and Novosibirsk State University, Novosibirsk 630090, Russian Federation

(Received 30 January 2010; published 13 October 2010)

Unrestricted Hartree-Fock-like equations are proposed to find multiple spin-symmetry-broken states of the molecular systems. Developed equations are pseudo-eigenvalue-type equations for the Fock-type operators constructed in such a way to include an effective field which makes different-spin orbitals biorthogonal. The eigenvectors of these operators are noncanonical Hartree-Fock orbitals becoming Löwdin-Amos-Hall paired (corresponding) orbitals after self-consistency is achieved. The eigenvalues of the modified Fock operators appear to be the energies of the paired orbitals. Because the paired orbitals do not follow the spatial symmetry of the molecular nuclear core, the equations allow one to obtain the broken symmetry states with relative ease as demonstrated for the model H_6 hexagon molecule. For this molecule, the Čížek-Paldus instability matrix analysis predicts the existence of three spin-symmetry-broken states. All these solutions are systematically achieved by the paired equations, unlike the standard unrestricted equations which basically converge to a single solution. The proposed approach is also valid for the density functional theory in which the spin-polarized Kohn-Sham equations might be transformed to paired equations.

DOI: 10.1103/PhysRevA.82.042505 PACS number(s): 31.10.+z, 31.15.xr

I. INTRODUCTION

The physical significance of spin-symmetry-broken (BS) solutions of the Hartree-Fock (HF) equations as the states revealing correlation effects beyond the HF approximation was recognized long ago by Löwdin, who translated into mathematical form Slater's idea of different orbitals for different spins (DODS) [1,2].

In the beginning, the DODS principle was applied by Löwdin to alternant hydrocarbons, resulting in the theory of alternant molecular orbitals (see the book by Paunz [3]). Alternant orbitals appear to be paired since they are combinations of the occupied and virtual orbitals of alternant systems for which molecular orbitals occur in pairs [2]. Later, Löwdin suggested that the molecular orbitals might be transformed to paired orbitals in the DODS approach for arbitrary molecular systems [4]. This suggestion was proved by Amos and Hall [5] for occupied orbitals and was extended for unoccupied orbitals by Karadakov [6] and Mayer [7]. Since then, paired orbitals have been widely used in numerous applications within the Hartree-Fock theory as well as the density functional theory (DFT), such as the spin-projection techniques [8,9], the calculation of the electron-transfer parameters [10], and the complete active space DFT scheme [11], among others.

In addition, in the basis of paired orbitals, an unrestricted determinant is conveniently transformed into a linear combination of restricted determinants, allowing one to assign a structure in question in terms of idealized covalent and charge-transfer configurations [12]. This approach has been used to investigate a few open-shell systems such as the Fe(II)–NO complex [13], the Fe(II)–nitrobenzene complex [14], ruthenium complexes with redox-active quinonoid ligands [15], and the Fe(II)–porphyrin nitroxyl complexes [16].

The BS solutions reveal themselves via nonzero spin contamination $\langle \hat{S}^2 - S_z(S_z+1)\rangle$, where $S_z = (N_\alpha - N_\beta)/2$ and N_α and N_β are the number of spin-up and spin-down electrons, respectively. In the basis of paired orbitals, spin contamination may be regarded as the effective number of pairs of spatially separated orbitals occupied by two electrons with antiparallel spins. Moreover, in this basis set the spin contamination may be expressed as a weighted sum of contributions from particular pairs [12]. This makes it possible to find out which orbital pair is responsible for the largest spin contamination. Therefore, paired orbitals might be considered orbital channels providing antiferromagnetic coupling within Noodleman's broken-symmetry approach developed to study antiferromagnetically coupled magnetic moments [17].

The conditions for the HF solutions to be unstable toward the spin or charge polarization were first formulated by Thouless [18]. Later these conditions were specialized to the restricted HF solutions for closed-shell systems and the concept of singlet and triplet instabilities were introduced by Čížek and Paldus [19]. Fukutome developed the classification of the BS solutions [20] (see also a review by Stuber and Paldus [21]).

It is nonlinearity of the HF and Kohn-Sham (KS) equations that may break the spin symmetry as well as the spatial symmetry (which the starting determinant possesses) to converge these equations to lower energy states. While the single BS state is relatively easy to find, locating additional (and ultimately all possible) BS solutions still remains a challenging computational problem. In the particular case of spin-preserving spatial symmetry-broken solutions, this problem was considered in Refs. [22,23]. The case of the spin-symmetry-broken solutions has not been addressed yet and current practice is still limited by obtaining a single spin-symmetry-broken solution revealing desired spin density.

Converging to the BS solution might be systematically achieved only if the starting symmetry-adapted (SA) solution is unstable with respect to the spin polarization [24]. The BS minimum might then be reached in the direction of the steepest descent on the energy hypersurface in the space of orbital variations within the analysis of the second energy variation (see Fig. 1(a) in Ref. [24]). If the SA state is unrestricted Hartree-Fock (UHF) stable being a local minimum

---

[*] I.L.Zilberberg@catalysis.ru

(see Fig. 1(b) in Ref. [24]), then the analysis of the second variation of energy is of no help in searching for the BS solution, which becomes unreachable in a systematic way even though it has lower energy than the SA solution.

Obtaining spin-symmetry-broken solutions usually relies on making a spin-polarized state from available SA solutions via some tricks and turns, which is especially required for the states with zero spin projection $S_z = 0$. The main idea of such recipes is to push the self-consistent field (SCF) converging toward a BS solution using a specifically prepared spin-polarized initial guess. Among such schemes the simplest one is the mixing of the highest occupied and lowest unoccupied molecular orbitals of the SA higher spin state to generate different α and β molecular orbitals as the initial guess for obtaining a low-spin BS state. Nowadays, the so-called constraint density functional theory (DFT) scheme [25] provides perhaps the most elaborate way to achieve BS solution. In this method the spin symmetry is made permanently broken by constraining the atomic-center localized spins to some intuitively defined values.

The idea of the present work is to develop the SCF equations for noncanonical orbitals which do not obey the symmetry of nuclear configuration. It is the paired-orbital basis set that is chosen as such noncanonical orbitals. Keeping untouched the total energy and the density matrix given by the canonical equations (i.e., those for canonical orbitals diagonalizing the Fock operators), these equations allow one to handle SA and BS states on equal terms.

II. PAIRED EQUATIONS

As was shown by Gilbert, the noncanonical restricted HF equations are transformed into the pseudo-eigenvalue-type equations by adding an operator $\rho\Lambda\rho$ (where ρ designates Dirac-Fock density and Λ is a Hermitian operator) to the Fock operator. This operator mixes canonical occupied HF orbitals between themselves to form localized orbitals [26].

A straightforward extension of Gilbert's technique for the spin-polarized case gives the following pseudo-eigenvalue equations:

$$\begin{aligned} R^\alpha|a_i\rangle &= \lambda_i^\alpha|a_i\rangle, \\ R^\beta|b_i\rangle &= \lambda_i^\beta|b_i\rangle, \end{aligned} \tag{1}$$

with modified Fock operators defined as

$$\begin{aligned} R^\sigma &= (1-\rho^\sigma)F^\sigma\rho^\sigma + \rho^\sigma F^\sigma(1-\rho^\sigma) \\ &\quad + \rho^\sigma\Lambda^\sigma\rho^\sigma + (1-\rho^\sigma)\Omega^\sigma(1-\rho^\sigma). \end{aligned} \tag{2}$$

Here F^σ are spin-polarized Fock (or Kohn-Sham) operators, and ρ^σ is the density for σ-spin electrons ($\sigma = \alpha,\beta$). The operators Λ^σ and Ω^σ are Hermitian operators mixing unrestricted Hartree-Fock occupied and unoccupied orbitals, respectively, between themselves within each σ-spin manifold.

The matrix of the modified Fock operator R^α for spin-up electrons in the basis of molecular orbitals reads as the following four-block matrix:

$$\begin{pmatrix} \langle a|\Lambda^\alpha|a\rangle & \langle a|F^\alpha|\bar{a}\rangle \\ \langle \bar{a}|F^\alpha|a\rangle & \langle \bar{a}|\Omega^\alpha|\bar{a}\rangle \end{pmatrix}, \tag{3}$$

where $|a\rangle$ and $|\bar{a}\rangle$ designate occupied and unoccupied α-spin orbitals, respectively. The matrix of the R^β operator in the basis of $|b\rangle$ and $|\bar{b}\rangle$ orbitals for β spin looks analogous. Upon achieving self-consistency, the off-diagonal blocks of matrix (3) become zero and the obtained occupied and unoccupied orbitals diagonalize the operators $\rho^\alpha\Lambda^\alpha\rho^\alpha$ and $(1-\rho^\alpha)\Omega^\alpha(1-\rho^\alpha)$. Therefore, the occupied and unoccupied orbitals satisfying Eqs. (1) and (2) are the Hartree-Fock noncanonical orbitals and simultaneous eigenvectors of the operators Λ^σ and Ω^σ. These noncanonical spin-polarized orbitals give the same total energy as that corresponding to the canonical HF orbitals, allowing one to fulfill any additional conditions on orbitals determined by the choice of the Λ^σ and Ω^σ operators.

Among noncanonical orbital sets, Löwdin-Amos-Hall paired orbitals [4,5] seem to be the best choice since they (i) are in general not symmetrical and (ii) allow one to directly assign antiferromagnetic coupling of the α and β spins to particular orbital pairs $|a_i\rangle$ and $|b_i\rangle$. The overlap between paired orbitals indicates the type of the unrestricted solution: if $\langle a_i|b_i\rangle = t_i = 1$ for all pairs in the determinant, then the solution is spin uncontaminated (i.e., symmetry adapted); for intermediate overlaps (when $0 \leqslant t_i < 1$), the solution is spin-symmetry broken. In the paired orbital basis set, the spin contamination is conveniently expressed as $\langle \hat{S}^2 - S_z(S_z+1)\rangle = \sum(1-t_i^2)$, where summation runs over all occupied pairs. Each orbital pair induces the spin contamination $\eta_i = 1 - t_i^2$, which might be considered the order parameters in the second-order phase transition between the symmetric SA phase and the spin-polarized BS phase. Any deviation of all η_i from zero splits the corresponding doubly occupied orbital into the pair of different orbitals. In turn, the initially symmetry-adapted determinant becomes spin-symmetry broken.

The paired orbitals for different spins (PODS) equations have been first derived by substituting the Fock operators for α and β spins by choosing $\Lambda^\alpha = \rho^\alpha + \rho^\beta$, $\Lambda^\beta = \rho^\alpha + \rho^\beta$, $\Omega^\alpha = \rho^\beta$, and $\Omega^\beta = \rho^\alpha$ [27]. The eigenvalues of these operators are in fact the squared overlap between the α and β orbitals, making them paired orbitals. Therefore, corresponding pseudo-eigenvalue-type equations for these operators (referred to below as PODS-I) appeared to have topological meaning in the sense that they determine pairwise connections of the α and β spins in the molecule.

In the present work, the PODS-I equations are rewritten in a more physical form using the Edmiston-Ruedenberg approach for localizing orbitals [28]. To obtain localized orbitals, these authors substituted only the off-diagonal elements of the Fock matrix by the matrix elements of some nonlocal operator. The diagonal of the Fock matrix was kept unchanged.

Adapting this idea to paired orbitals, one obtains the following pairing operators:

$$\begin{aligned} R^\alpha &= (1-\rho^\alpha)F^\alpha\rho^\alpha + \rho^\alpha F^\alpha(1-\rho^\alpha) \\ &\quad + \sum_{i=1}^{N_\alpha} |a_i\rangle\langle a_i|F^\alpha - \rho^\beta|a_i\rangle\langle a_i| + \rho^\alpha\rho^\beta\rho^\alpha \\ &\quad + \sum_{i=N_\alpha+1}^{N_{\text{basis}}} |\bar{a}_i\rangle\langle \bar{a}_i|F^\alpha - \rho^\beta|\bar{a}_i\rangle\langle \bar{a}_i| + (1-\rho^\alpha)\rho^\beta(1-\rho^\alpha), \end{aligned}$$

$$\begin{aligned} R^{\beta} &= (1-\rho^{\beta})F^{\beta}\rho^{\beta} + \rho^{\beta}F^{\beta}(1-\rho^{\beta}) \\ &\quad + \sum_{i=1}^{N_{\beta}} |b_i\rangle\langle b_i|F^{\beta}-\rho^{\alpha}|b_i\rangle\langle b_i| + \rho^{\beta}\rho^{\alpha}\rho^{\beta} \\ &\quad + \sum_{i=N_{\beta}+1}^{N_{\text{basis}}} |\bar{b}_i\rangle\langle \bar{b}_i|F^{\beta}-\rho^{\alpha}|\bar{b}_i\rangle\langle \bar{b}_i| + (1-\rho^{\beta})\rho^{\alpha}(1-\rho^{\beta}), \end{aligned} \tag{4}$$

where N_{α}, N_{β}, and N_{basis} are numbers of the α spins, β spins, and basis functions, respectively. In the basis of molecular orbitals, the matrices of the pairing operators (4) look schematically as follows:

$$\left(\begin{array}{cc|cc} \langle a_i|F^{\alpha}|a_i\rangle & \langle a_i|\rho^{\beta}|a_j\rangle & \multicolumn{2}{c}{\langle a|F^{\alpha}|\bar{a}\rangle} \\ \langle a_j|\rho^{\beta}|a_i\rangle & \langle a_j|F^{\alpha}|a_j\rangle & & \\ \hline \multicolumn{2}{c|}{\langle \bar{a}|F^{\alpha}|a\rangle} & \langle \bar{a}_k|F^{\alpha}|\bar{a}_k\rangle & \langle \bar{a}_k|\rho^{\beta}|\bar{a}_l\rangle \\ & & \langle \bar{a}_l|\rho^{\beta}|\bar{a}_k\rangle & \langle \bar{a}_l|F^{\alpha}|\bar{a}_l\rangle \end{array}\right). \tag{5}$$

The matrix of the R^{β} operator has an analogous form. As clearly seen from matrix (5) the pairing operators (4) are built from the Fock operators so that the eigenvalues of operators (4) can be considered the energies of the paired orbitals. To clarify the latter statement, let us suppose that for some system there are known canonical UHF (or unrestricted KS) orbitals ψ_i^{α} and ψ_i^{β}. Then diagonal matrix elements of the R^{α} and R^{β} operators in the basis of these canonical orbitals are the HF energies (i.e., $\epsilon_i^{\alpha} = \langle\psi_i^{\alpha}|F^{\alpha}|\psi_i^{\alpha}\rangle$ and $\epsilon_i^{\beta} = \langle\psi_i^{\beta}|F^{\beta}|\psi_i^{\beta}\rangle$). In accordance with a general property of square matrices, the trace of the matrix is the sum of its eigenvalues. Since the off-diagonal matrix elements $\langle\bar{a}|F^{\alpha}|a\rangle$ (and corresponding Hermitian conjugate integrals) coupling unoccupied and occupied Hartree-Fock orbitals are all equal to zero, these matrices are block diagonal. Therefore, for both blocks of the occupied and unoccupied orbitals, the diagonal sum rule holds:

$$\sum \epsilon_i^{\alpha} = \sum \lambda_i^{\alpha}.$$

The same rules hold for the β eigenvalues as well.

For both the occupied and unoccupied blocks, the off-diagonal elements

$$\langle\psi_i^{\alpha}|\rho^{\beta}|\psi_j^{\alpha}\rangle = \sum_{k}^{N_{\beta}} \langle\psi_i^{\alpha}|\psi_k^{\beta}\rangle\langle\psi_k^{\beta}|\psi_j^{\alpha}\rangle$$

are in general nonzero. These values are small compared with diagonal elements ϵ_i^{α} and ϵ_j^{α} except for the frontier orbital energies, which might be close to zero. Therefore, the eigenvalues of the modified pairing operators (4) may be interpreted as canonical Hartree-Fock orbital energies ϵ_i^{α} and ϵ_i^{β} each being split by a field (proportional to the density of the β and α electrons, respectively) such that the center of gravity of the one-electron levels is unchanged.

Obtained Eqs. (1) and (4), (called PODS-II), unlike PODS-I [27], do not in general guarantee self-consistent eigenvectors to be paired orbitals. That is because the diagonal blocks of the PODS-II matrices do not contain the entire matrix of the $\rho^{\alpha}\rho^{\beta}\rho^{\alpha}$. To ensure the biorthogonality of eigenvalues, the SCF convergence procedure is followed by a single singular-value decomposition (SVD) transformation of the overlap.

III. CYCLIC H$_6$: TEST CASE

Pseudo-eigenvalue PODS-II equations (1) and (4) have been programmed on the basis of the QMIC package written by Nichols and Simons [29]. Below, this modified program is referred to as the PODS program (and is available by request from authors of the present paper).

A model hexagonal H$_6$ molecular system with elongated H-H bonds was chosen as a test case, for which Bénard and Paldus showed that the nonsinglet stability matrix for this system has three negative roots when the H-H bond is longer than some critical value [30]. This implies the existence of three spin-symmetry-broken solutions.

This makes H$_6$ a very convenient test case for the PODS-II equations as it allows us to check whether they may converge to multiple spin-symmetry-broken solutions without the analysis of the stability matrix. The latter seems to be well defined only within the Hartree-Fock theory, where the two-electron integrals in the molecular-orbital basis of the general type $\langle\psi_i\psi_j|1/r_{12}|\psi_k\psi_l\rangle$ are available. Application of this analysis within DFT is conceptually questionable though practically possible via the construction of two-electron integrals for the Kohn-Sham orbitals.

The 3-21G basis set is employed to provide dimension of the PODS-II matrices large enough to include at least occupied and unoccupied paired orbitals. The PODS-II calculations have been compared with the standard UHF calculations using both the GAUSSIAN98 package [31] and the PODS program. The number of SCF iterations corresponds to the total energy convergence threshold of 10^{-8} a.u.. The initial guess is chosen to be that arising from the core Hamiltonian.

The closed-shell solution $^1A_{1g}$ (which is referred to as SA below) becomes UHF unstable for an H-H distance larger than 1.21 Å. The H-H distance has been chosen to be 2 Å to ensure the presence of low-lying broken-symmetry states. For this

TABLE I. PODS-II total energies E_{tot} (in a.u.) with respect to the SA energy of −2.775562 a.u., spin contamination $\eta_i = 1 - t_i^2$ for orbital pair (the sum of η_i is given in the parenthesis, i.e., $\langle \hat{S}^2 \rangle$), PODS-II orbital energies λ_i^α and λ_i^β (in a.u.), and the UHF orbital energies ϵ_i^α and ϵ_i^β (in a.u.) along the sum of energies for each set of energies (in parentheses).

State	E_{tot}	η_i	λ_i^α	λ_i^β	ϵ_i^α	ϵ_i^β
SA	0.0	0.0			−0.441	−0.441
					−0.350	−0.350
					−0.350	−0.350
BS-1	−0.228	0.69	−0.510	−0.510	−0.510	−0.510
		0.91	−0.485	−0.485	−0.485	−0.485
		0.91	−0.485	−0.485	−0.485	−0.485
		(2.51)	(−1.480)	(−1.480)	(−1.480)	(−1.480)
BS-2	−0.201	0.78	−0.556	−0.552	−0.551	−0.551
		0.96	−0.486	−0.538	−0.492	−0.492
		0.90	−0.440	−0.392	−0.439	−0.439
		(2.64)	(−1.482)	(−1.482)	(−1.482)	(−1.482)
BS-3	−0.173	1.00	−0.548	−0.526	−0.574	−0.574
		0.91	−0.495	−0.492	−0.495	−0.495
		0.89	−0.441	−0.467	−0.415	−0.415
		(2.80)	(−1.484)	(−1.485)	(−1.484)	(−1.484)

geometry the closed-shell singlet appears to be UHF unstable with three negative eigenvalues of the stability matrix (two of them being e_g degenerate). Two nondegenerate BS solutions and one doubly degenerate BS solution have been found for the PODS-II equations for $S_z = 0$ using the level shift. It is worthwhile to note that all solutions are obtained with the same initial guess by mixing of some pairs of the occupied and unoccupied molecular orbitals. Such mixing is a standard tool to obtain a BS UHF solution used, for instance, in GAUSSIAN98. Contrary to the PODS-II equations, the UHF equations allow one to find only the lowest energy solution (BS-1 state with $\langle \hat{S}^2 \rangle$=2.51 in Table I) being started from the same initial guess despite all attempts of the use of standard recipes including simple shifting of virtual orbital levels. "Additional" BS states with $\langle \hat{S}^2 \rangle$ equal to 2.64 and 2.80 appear to be local minima (designated BS-2 and BS-3, respectively, in Table I) as has been checked by running the UHF equations within the GAUSSIAN package starting with the BS-2 and BS-3 wave functions obtained by PODS. A schematic plot of the PODS-II total energy as a function of the spin contamination (which is equal to $\langle \hat{S}^2 \rangle$ in this particular case) is given in Fig. 1. Here the SA state represents a saddle point with zero spin density and three local BS minima having distinct spin polarizations.

The BS-1 state represents a spin-density wave with Mulliken atomic spin densities on hydrogens (shown as solid and open data point symbols in Fig. 1) being equal in absolute magnitude. Unlike the BS-1 solution, BS-2 and BS-3 reveal three different pairs of positive and negative Mulliken atomic spin densities. The latter pairing shown as linked symbols of different colors in Fig. 1 resembles the Rumer diagrams describing spin-singlet electron pairs to form the total singlet function [32].

In agreement with above-mentioned diagonal sum rule the calculated PODS-II eigenvalues obtained for all three BS solutions have center of gravity coinciding with that for the UHF orbital energies (see Table I, where values in parentheses are the sums of three eigenvalues). It is worthwhile to note that for the BS-1 solution the paired orbitals have energies coinciding with those for the UHF orbitals which appear biorthogonalized due to their spatial symmetry.

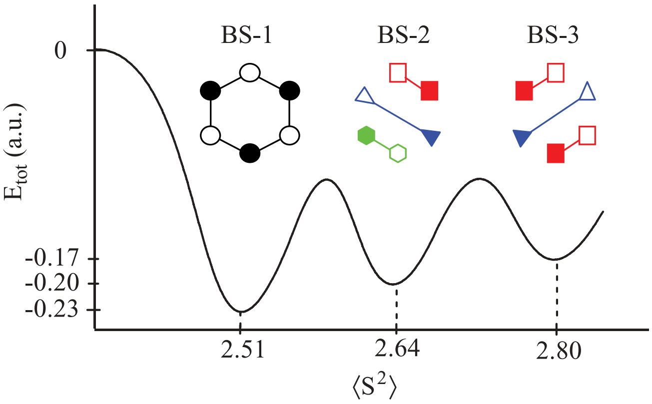

FIG. 1. (Color online) Schematic plot of the total energy E_{tot} of the H_6 hexagon $S_z = 0$ solutions as a function of the mean value of the spin operator $\hat{S}^2$ (dimensionless). Graphs above the plot show Mulliken atomic spin densities on hydrogen atoms for each broken-symmetry state; the open symbols denote positive density linking and the solid symbols denote negative density of the same absolute magnitude: (BS-1) circle = ±0.942, (BS-2) square = ±0.965, triangle = ±0.968, hexagon = ±0.939, (BS-3) square = ±0.965, triangle = ±0.998.

IV. CONCLUSION

In summary, we have developed modified (so-called PODS-II) unrestricted equations equally applicable for both Hartree-Fock and Kohn-Sham theories. The PODS-II equations are proved to allow metastable spin and charge polarized states to be reached (which might be achieved within the UHF equations just accidentally) via simple virtual level shifting. As compared with previously developed PODS-I equations which might be considered "orbital overlap" equations, the PODS-II equations are Hartree-Fock-like "orbital energy" equations. The PODS-II orbitals are noncanonical and in general unpaired, but they become biorthogonal via a single transformation. From the computational point of view, the PODS-II equations are less demanding than the PODS-I equations. The convergence of the PODS-II equations is much better than that of the PODS-I equations, as revealed for BS states of H_6. The PODS-II equations might be particularly useful in finding multiple BS solutions to estimate antiferromagnetic exchange parameters for molecular magnets containing a multiplicity of spin centers.

ACKNOWLEDGMENTS

The authors acknowledge support from the Siberian Supercomputer Center of SB RAS through Grant No. 26 and the Russian Foundation for Basic Research through Grant No. RFBR-10-03-00441a.

[1] J. C. Slater, Phys. Rev. **82**, 538 (1951).
[2] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).
[3] R. Paunz, *Alternant Molecular Orbital Method* (Saunders, Philadelphia, 1967).
[4] P.-O. Löwdin, J. Appl. Phys. Suppl. **33**, 251 (1962).
[5] A. T. Amos and G. G. Hall, Proc. R. Soc. London A **263**, 483 (1961).
[6] P. Karadakov, Int. J. Quantum Chem. **27**, 699 (1985).
[7] I. Mayer, Int. J. Quantum Chem. **29**, 31 (1986).
[8] F. Sasaki and K. Ohno, J. Math. Phys. **4**, 1140 (1963).
[9] M. G. Cory and M. Zerner, J. Phys. Chem. A **103**, 7287 (1999).
[10] A. A. Stuchebrukhov, Theor. Chem. Acc. **110**, 291 (2003).
[11] R. Takeda, S. Yamanaka, and K. Yamaguchi, Chem. Phys. Lett. **366**, 321 (2002).
[12] I. Zilberberg and S. P. Ruzankin, Chem. Phys. Lett. **394**, 165 (2004).
[13] I. Zilberberg, S. P. Ruzankin, S. Malykhin, and G. M. Zhidomirov, Chem. Phys. Lett. **394**, 392 (2004).
[14] I. Zilberberg, M. Ilchenko, O. Isayev, L. Gorb, and J. Leszczynski, J. Phys. Chem. A **108**, 4878 (2004).
[15] C. Remenyi and M. Kaupp, J. Am. Chem. Soc. **127**, 11399 (2005).
[16] N. Lehnert, V. K. K. Praneeth, and F. Paulat, J. Comput. Chem. **27**, 1338 (2006).
[17] L. Noodleman, J. Chem. Phys. **74**, 5737 (1981).
[18] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic, New York, 1961).
[19] J. Čížek and J. Paldus, J. Chem. Phys. **47**, 3976 (1967).
[20] H. Fukutome, Int. J. Quantum Chem. **20**, 955 (1981).
[21] J. L. Stuber and J. Paldus, in *Fundamental World of Quantum Chemistry: A Tribute Volume to the Memory of Per-Olov Löwdin*, edited by E. J. Brandas and E. S. Kryachko (Kluwer, Dordrecht, 2003), Vol. 1, Chap. 4, pp. 67–139.
[22] K. Kowalski and K. Jankowski, Phys. Rev. Lett. **81**, 1195 (1998).
[23] A. J. W. Thom and M. Head-Gordon, Phys. Rev. Lett. **101**, 193001 (2008).
[24] J. Paldus and J. Čížek, Can. J. Chem. **63**, 1803 (1985).
[25] I. Rudra, Q. Wu, and T. Van Voorhis, J. Chem. Phys. **124**, 024103 (2006).
[26] T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics and Biology*, edited by B. Pullman and P.-O. Löwdin (Academic, New York, 1964).
[27] I. Zilberberg and S. Ruzankin, J. Comput. Chem. **31**, 84 (2010).
[28] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).
[29] J. Nichols and J. Simons, *Quantum Mechanics in Chemistry* (Oxford University Press, 1997).
[30] M. Bénard and J. Paldus, J. Chem. Phys. **72**, 6546 (1980).
[31] M. J. Frisch *et al.*, computer code GAUSSIAN98, REV. A.11 (2001).
[32] R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, San Diego, 1992).