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First-order correlation orbitals for the spin-unrestricted Hartree–Fock zero-order wave function. Electron affinities of C_4 clusters

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The second-order Hylleraas functional and the Newton–Raphson optimization technique have been used to generate first-order correlation orbitals (FOCOs) for the spin-unrestricted Hartree–Fock (UHF) zero-order wave function. The correlation orbitals are linear combinations of the UHF virtual orbitals and are different for electrons with α and β spins. We show that even the number of FOCOs is significantly reduced with respect to the number of all UHF virtual orbitals, the decrease of the second-order correlation energy is rather small. The primary application of the FOCO UHF method is to study larger open-shell molecular systems at higher correlated levels of the theory. The coupled-cluster calculations with FOCOs on the electron affinities of the linear and rhombic carbon C_4 clusters, presented here, illustrate the capabilities of the proposed methodology.

I. INTRODUCTION

The application of the *ab initio* quantum chemistry methods for calculating electronic structures, which include higher-order correlation effects, are usually limited to rather small molecular systems due to the limitations of what can be accomplished by even the fastest computers. In spite of that, a lot of the theoretical effort has been devoted to the development and implementation of very sophisticated correlated approaches such as higher-order perturbation theory (beyond the fourth order),[1] the full configuration integration method,[2] the coupled cluster techniques which include triple and quadruple amplitudes,[3] the multireference configuration interaction method,[4] etc. For most of those methods, the applications are limited to rather small "benchmark" examples and more complex, chemically interesting problems have to wait for a significant increase of the power of future computers.

A critical factor, which makes the application of the high-level *ab initio* methodology so limited, is the slow convergence of both the configuration expansion of the wave function and the AO representation of the occupied and correlation molecular orbitals. Ideally, in a high-level correlated calculation on a molecular system one usually wants to utilize a good, well-saturated basis set which produces the SCF energy in close proximity to the Hartree–Fock limit and, in addition, adequately represents the correlation component of the wave function. A very good SCF energy is relatively easy to accomplish for even more extended systems; however, to achieve a similar quality of the correlation corrections is much more difficult due to a much stronger dependency of the computer time on the number of orbitals. For example, the MBPT(4) (many-body perturbation theory fourth-order level) has an asymptotic dependency on the number of orbitals, of $n_{occ}^3 n_{corr}^4$ (n_{occ} and n_{corr} are the number of occupied SCF orbitals and the number of correlation orbitals, respectively), while each iteration of the CCSDT (coupled-cluster with single, double, and triple excitations) method the proportionality factor is equal to $n_{occ}^3 n_{corr}^5$.

In a series of our recent papers,[5] we demonstrated that our method for generating first-order correlation orbitals (FOCOs), which is based on the second-order Hylleraas functional and the Newton–Raphson optimization approach, enables high-level correlation calculations for larger closed-shell molecular systems. This is accomplished by replacing the SCF virtual orbital set in the post-SCF calculation by a much smaller set of first-order correlation orbitals which are linear combinations of the virtual orbitals with the linear coefficients generated by the minimization of the Hylleraas functional. The FOCO method in conjunction with the coupled-cluster method was used for example to determine the tautomerization energy of several nucleic acid bases and their derivatives.[6] Recently, we also presented the results for the dipole-bound state of the nitromethane molecule.[7] All applications of the FOCO method revealed good convergence of the Newton–Raphson orbital optimization process, which obviously is a very desirable feature. Worth mentioning is that a similar technique applied in the MCSCF orbital optimizations sometimes fails to converge.

There have been several previous proposed procedures to obtain shorter sets of improved correlation orbitals from the SCF orbitals. One needs to mention early the V^{n-1} approach of Kelly[8] and similar approaches proposed by Silver and Bartlett,[9] Silverstone and Yin,[10] and Huzinaga and Arnau.[11] Another group of methods is based on pseudonatural orbitals.[12] An array of very interesting approaches have been proposed by Davidson *et al.*[13] The difference in the previous proposals and the presently proposed method is the utilization of the Hylleraas functional in combination with the Newton–Raphson orbital optimization technique.

The previously reported FOCO method was developed based on the close-shell restricted SCF zero-order wave function. Obviously, numerous chemical transformations require that the molecular system under consideration assumes an open-shell electronic state. An electron attachment process exemplifies one category of such transformations. The simplest possible representation of the open-shell wave function is the spin-unrestricted Hartree–Fock determinant, in which electrons of the opposite spins are attributed different sets of orbitals. Although the UHF wave func-

tion remains an eigenfunction of the S_z operator, it is not an eigenfunction of the S^2 operator, and therefore any calculation performed based on this function has to be carefully monitored for a possible spin contamination. The convenience of using the UHF wave function in the MBPT expansion for the energy and the wave function rests on the fact that like for the closed-shell restricted Hartree–Fock (RHF) wave function the zero-order Hamiltonian can be expressed as a simple sum of the Fock operators. Consequently, the correlation corrections are expressed through products of two-electron integrals and the SCF orbital energies. This also makes it possible to develop a first-order correlation orbital method based on the UHF wave function in an analogical way as it was accomplished for the RHF case. Obviously, since there are two different sets of occupied orbitals for α and β electrons, the correlation orbitals will also form two distinct sets. The present paper presents how the generation of these orbital sets can be accomplished based on the minimization of the second-order Hylleraas functional. In the first section of this paper we present the theoretical details and the implementation scheme. This is followed by some numerical examples in the second section.

A particularly exciting application of the FOCO UHF method is to study electron attachment processes to molecular clusters. It has been well documented in various investigations on anions that higher-order correlation effects cannot be neglected in the evaluation of the most basis characteristic of the attachment process, the electron affinity.[14] A flexible basis set including diffused functions is also an essential component of a successful calculation. The use of FOCOs enables a better fulfillment of both requirements. In the second section of this paper we present the evaluation of the electron affinities of the C_4 molecule using the coupled-cluster method with single, double, and noniteratively determined triple excitations, CCSD + T(CCSD).[15] The CCSD + T(CCSD) model exploits the fact that a final single iteration for the triple excitations using the T_2 amplitudes from a converged CCSD calculation is usually a quite accurate approximation to the iterative CCSDT-1 model that allows T_3 amplitudes to affect the value of the T_1 and T_2 amplitudes. Since the evaluation of the triple excitation contribution is the rate determining step in most CC/MBPT calculations, the T(CCSD) model is a much more expeditious model computationally.

II. METHODOLOGY

A. General formulation

In the present implementation of the FOCO method we consider an open-shell system with N_α electron of the α spin and N_β electrons of the β spin ($N = N_\alpha + N_\beta$). The zero-order wave function is a UHF Slater determinant:

$$\Phi_0^{UHF} = \frac{1}{\sqrt{N!}} |\phi_1^\alpha(1)\bar{\phi}_1^\beta(2)\phi_2^\alpha(3)\bar{\phi}_2^\beta(4)\cdots|, \qquad (1)$$

where the two sets of orbitals, $\{\phi_i^\alpha\}$ and $\{\phi_i^\beta\}$, are obtained by solving the UHF problem. The total Hamiltonian is partitioned into the zero-order Hamiltonian H_0 and the perturbation V. H_0 is the usual sum of the α and β Hartree–Fock operators:

$$H_0 = \sum_{i=1}^{N_\alpha} f^\alpha(i) + \sum_{i=1}^{N_\beta} f^\beta(i), \qquad (2)$$

where

$$f^\alpha(1) - \frac{\Delta(1)}{2} + v(1) + \sum_{i=1}^{N_\alpha} [J_i(1) - K_i(1)]$$
$$+ \sum_{i=1}^{N_\beta} J_i(1), \qquad (3)$$

$$f^\beta(1) - \frac{\Delta(1)}{2} + v(1) + \sum_{i=1}^{N_\beta} [J_i(1) - K_i(1)]$$
$$+ \sum_{i=1}^{N_\alpha} J_i(1), \qquad (4)$$

where $v(1)$ represents the interaction with the nuclei and the Coulomb and exchange operators are defined in convectional way as

$$J_i(1) = \int d2 \frac{\phi_i(2)\phi_i(2)}{r_{12}}, \qquad (5)$$

$$K_i(1)\phi(1) = \int d2 \frac{\phi_i(2)\phi_i(2)}{r_{12}} \phi_i(1),$$
$$\phi_i \epsilon \{\phi_i^\alpha\} \text{ or } \{\phi_i^\beta\}. \qquad (6)$$

Assuming the correlation perturbation operator as $V = H - H_0$, one gets the Hartree–Fock energy as the sum of the zero-order and the first-order correlation corrections, $E_{HF} = E_0 + E_1$, where the E_0 is simply the sum of the orbital energies corresponding to the occupied α and β spin orbitals:

$$E_0 = \sum_{i_\alpha} \epsilon_i^\alpha + \sum_{i_\beta} \epsilon_i^\beta. \qquad (7)$$

The lowest-order correlation correction energy is the second-order correction, E_2. Assuming the intermediate normalization for the wave function, which corresponds to the orthogonality of the UHF wave function to the first-order correlation correction Φ_1, one can construct a functional which constitutes an upper bound to E_2 for a trial wave function:

$$E_2 \leqslant \langle \Phi_1 | H_0 - E_0 | \Phi_1 \rangle$$
$$+ 2\langle \Phi_1 | V - E_1 | \Phi_0 \rangle \equiv J_2, \quad \langle \Phi_1 | \Phi_0 \rangle = 0. \qquad (8)$$

The functional (8) is called the second-order Hylleraas functional and its formal variation with respect to Φ_1 leads to the first-order perturbation equation

$$\frac{\delta}{\delta\Phi_1} J_2 \rightarrow (H_0 - E_0)|\Phi_1\rangle + (V - E_1)|\Phi_0\rangle = 0. \qquad (9)$$

If one employs the UHF canonical virtual orbitals to construct the first-order correlation wave function, then it can be simply expressed through the two-electron exchange molecular integrals, the orbital energies, and the doubly excited Slater determinants in the following fashion:

$$\Phi_1 = \Phi_1^{\alpha\alpha} + \Phi_1^{\beta\beta} + \Phi_1^{\alpha\beta}, \qquad (10a)$$

$$\Phi_1^{\alpha\alpha} = \sum_{\substack{i_\alpha > j_\alpha \\ a_\alpha > b_\alpha}} \frac{\langle a_\alpha b_\alpha \| i_\alpha j_\alpha \rangle}{\epsilon_{a_\alpha} + \epsilon_{b_\alpha} - \epsilon_{i_\alpha} - \epsilon_{j_\alpha}} \left| \begin{matrix} a_\alpha b_\alpha \\ i_\alpha j_\alpha \end{matrix} \right\rangle, \qquad (10b)$$

$$\Phi_1^{\alpha\beta} = \sum_{i_\alpha a_\alpha} \sum_{i_\beta a_\beta} \frac{\langle a_\alpha a_\beta | i_\alpha i_\beta \rangle}{\epsilon_{a_\alpha} + \epsilon_{a_\beta} - \epsilon_{i_\alpha} - \epsilon_{i_\beta}} \left| \begin{matrix} a_\alpha a_\beta \\ i_\alpha i_\beta \end{matrix} \right\rangle, \qquad (10c)$$

and similarly for $\Phi_1^{\beta\beta}$.

Notice the separation of Φ_1 into three distinct components. In the above equations we identify the occupied orbitals by letters $i,j,...$ and unoccupied orbitals by letters $a,b,...$.

In the next step we partition the manifold of the virtual orbitals for α and β sets into active and nonactive subsets of orbitals. In general, this partitioning can be different for α and β blocks, considering that the system under consideration may have considerably different numbers of α and β electrons. To distinguish between active and nonactive correlation subspecies, letters $a,b,...$ and $e,f,...$ will be used to denote active and nonactive orbitals, respectively. The way the virtual orbital manifold is partitioned depends on the individual case. Usually, for more extended basis sets, the active set will be relatively shorter in comparison with the full virtual space than for less extended basis sets. A limiting factor is also how many correlation orbitals one can afford to use in the post-SCF calculations considering the available computational resources. If the generation of the active correlation orbitals is performed assuming a particular spatial symmetry of the system, then one needs to select an orbital symmetry distribution. A possible scheme for making this selection can be based on determining the approximate natural orbitals and their occupancies through the diagonalization of the second-order density matrix. A particular selection of the cutoff threshold for the occupation numbers leads to a particular symmetry distribution for the active subspecies. Another possibility is to determine the approximate contribution of a particular virtual orbital to the total second-order energy according to the following formula:

$$\epsilon_{a,2}^\alpha = \frac{1}{2}\left(\sum_{i_\alpha > j_\alpha} \frac{\langle a_\alpha b_\alpha \| i_\alpha j_\alpha \rangle^2}{\epsilon_a^\alpha + \epsilon_a^\alpha - \epsilon_i^\alpha - \epsilon_i^\alpha} \right.$$
$$\left. + \sum_{i_\alpha} \sum_{i_\beta a_\beta} \frac{\langle a_\alpha a_\beta | i_\alpha i_\beta \rangle^2}{\epsilon_a^\alpha + \epsilon_a^\beta - \epsilon_i^\alpha - \epsilon_i^\beta} \right) \qquad (11)$$

and similarly for the β orbitals. The orbitals with the most negative contributions are accepted into the initial active sets.

The strategy for the optimization of the active correlation orbitals rests on the minimization of the second-order Hylleraas functional determined with the active orbital of the α and β subspecies with respect to all possible unitary rotations of active orbitals with nonactive orbitals. The new active correlation orbital after rotations are linear combinations of all old active and nonactive orbitals:

$$\phi_a^{\alpha\prime} = \sum_b U_{ba}^\alpha \phi_b^\alpha + \sum_e U_{ea}^\alpha \phi_e^\alpha, \qquad (12a)$$

$$\phi_a^{\beta\prime} = \sum_b U_{ba}^\beta \phi_b^\beta + \sum_e U_{ea}^\beta \phi_e^\beta. \qquad (12b)$$

The orbital rotations are accomplished by two unitary matrices, U^α and U^β, which are represented in exponential forms with antisymmetric matrices, R^α and R^β. This approach is similar to the one effectively used for MCSCF problems:[16-19]

$$U^{\alpha\dagger}U^\alpha = 1, \quad U^{\beta\dagger}U^\beta = 1,$$
$$U^\alpha(R^\alpha) = \exp(R^\alpha),$$
$$U^\beta(R^\beta) = \exp(R^\beta), \qquad (13)$$
$$(R^\alpha)^T = -R^\alpha$$
$$(R^\beta)^T = -R^\beta.$$

Next, a power expansion of the exponential operators is used:

$$\exp(R) = 1 + R + \tfrac{1}{2} R\cdot R + \cdots . \qquad (14)$$

The value of the second-order functional does not depend on the particular choice of the orbital basis in the active correlation space; however, it is usually convenient to use the HF canonical orbitals. For this reason, any transformation within the active space cannot change the value of J_2, and, consequently, the R^α and R^β matrices can be assumed in the following block forms:

$$R^\alpha = \begin{bmatrix} O & -R_{ea}^\alpha \\ R_{ae}^\alpha & O \end{bmatrix} \qquad (15)$$

and similarly for R^β.

Using expansion (14), the new active correlation orbitals for α and β electrons can be expressed as follows:

$$\phi_a^{\alpha\prime} = \phi_a^\alpha + \sum_e R_{ea}^\alpha \phi_e^\alpha$$
$$- \frac{1}{2} \sum_b \sum_e R_{ea}^\alpha R_{eb}^\alpha \phi_b^\alpha + \cdots, \qquad (16a)$$

$$\phi_a^{\beta\prime} = \phi_a^\beta + \sum_e R_{ea}^\beta R_{eb}^\beta \phi_b^\beta$$
$$- \frac{1}{2} \sum_b \sum_e R_{ea}^\beta R_{eb}^\beta \phi_b^\beta + \cdots . \qquad (16b)$$

In the following development of the theory, only terms up to second order in R will be retained in the expansions (16). Now, we determine the second-order functional for the active α and β correlation subspecies. It conveniently separates into $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$ pair contributions:

$$J_2 = J_2^\alpha + J_2^\beta + J_2^{\alpha\beta} = \sum_{i_\alpha > j_\alpha} J_{2,i_\alpha j_\alpha}^\alpha + \sum_{i_\beta > j_\beta} J_{2,i_\beta j_\beta}^\beta$$
$$+ \sum_{i_\alpha} \sum_{j_\beta} J_{2,i_\alpha j_\beta}^{\alpha\beta}, \qquad (17)$$

where

$$J_{2,i_\alpha j_\alpha}^\alpha = \sum_{\substack{a_\alpha > b_\alpha \\ c_\alpha > d_\alpha}} t_{ij}^{ab,\alpha} t_{ij}^{cd,\alpha}$$
$$\times [(f_{ac}^\alpha \delta_{bd} + f_{bd}^\alpha \delta_{ac} - f_{ad}^\alpha \delta_{bc} - f_{bc}^\alpha \delta_{ad})$$
$$- (\epsilon_i^\alpha + \epsilon_j^\alpha)(\delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc})]$$
$$+ 2 \sum_{a_\alpha > b_\alpha} t_{ij}^{ab,\alpha} \langle a_\alpha b_\alpha \| i_\alpha j_\alpha \rangle \qquad (18a)$$

and similar expression for $J_{2,i_\beta j_\beta}^\beta$ and

$$J^{\alpha\beta}_{2,i_\alpha j_\beta} = \sum_{a_\alpha c_\alpha} \sum_{b_\beta d_\beta} t^{ab,\alpha\beta}_{ij} t^{cd,\alpha\beta}_{ij}$$

$$\times [(f^\alpha_{ac}\delta_{bd} + f^\beta_{bd}\delta_{ac}) - (\epsilon^\alpha_i + \epsilon^\beta_j)\delta_{ac}\delta_{bd}]$$

$$+ 2\sum_{a_\alpha}\sum_{b_\beta} t^{ab,\alpha\beta}_{ij}\langle a_\alpha b_\alpha | i_\alpha j_\beta\rangle. \tag{18b}$$

The coefficients t in Eqs. (18) are first-order configuration amplitudes determined as

$$t^{ab,\alpha}_{ij} = \frac{\langle a_\alpha b_\alpha \| i_\alpha j_\alpha\rangle}{\epsilon_{a_\alpha} + \epsilon_{b_\alpha} - \epsilon_{i_\alpha} - \epsilon_{j_\alpha}} \tag{19a}$$

and similarly for $t^{ab,\beta}_{ij}$ and

$$t^{ab,\alpha\beta}_{ij} = \frac{\langle a_\alpha b_\beta | i_\alpha j_\beta\rangle}{\epsilon_{a_\alpha} + \epsilon_{b_\beta} - \epsilon_{i_\alpha} - \epsilon_{j_\beta}}. \tag{19b}$$

The matrix elements f^α_{ac} and f^β_{bd} indicate Fock matrix elements for the α and β orbitals, respectively. Next, in the expression for J_2, all active orbitals are replaced by their rotated counterparts using Eqs. (12). This results in an expression for J_2 as a function of the rotation parameters $J_2(\mathbf{R}^\alpha,\mathbf{R}^\beta)$. Now, in order to determine the most optimal orbital rotations, we determine the first and second derivatives of J_2 with respect to the rotation parameters. This is accomplished independently for the α and β active–nonactive orbital rotations:

$$G^\alpha_{ea} = \frac{\delta J_2}{\delta R^\alpha_{ea}}\bigg|_{\mathbf{R}^\alpha = 0, \mathbf{R}^\beta = 0}$$

$$= \frac{\delta (J^\alpha_2 + J^{\alpha\beta}_2)}{\delta R^\alpha_{ea}}\bigg|_{\mathbf{R}^\alpha = 0, \mathbf{R}^\beta = 0} \quad \text{(gradient),} \tag{20a}$$

$$H^{\alpha\alpha}_{ea,fb} = \frac{\delta^2 (J^\alpha_2 + J^{\alpha\beta}_2)}{\delta R^\alpha_{ea}\delta R^\alpha_{fb}}\bigg|_{\mathbf{R}^\alpha = 0, \mathbf{R}^\beta = 0} \quad \text{(Hessian),} \tag{20b}$$

and similar expressions for $\mathbf{G}^\beta$ and $\mathbf{H}^{\beta\beta}$. In the present procedure we do not determine $\mathbf{H}^{\alpha\beta}$. The gradient and Hessian matrices for α orbital rotations can be expressed as follows:

$$\mathbf{G}^\alpha_{ea} = 2\sum_{i_\alpha > j_\alpha}\sum_{b_\alpha} t^{ab,\alpha}_{ij}\langle e_\alpha b_\alpha \| i_\alpha j_\alpha\rangle + 2\sum_{b_\alpha} D^\alpha_{ab} f^\alpha_{eb}$$

$$+ 2\sum_{i_\alpha}\sum_{j_\beta}\sum_{b_\beta} t^{ab,\alpha\beta}_{ij}\langle e_\alpha b_\beta | i_\alpha j_\beta\rangle \tag{21a}$$

and

$$H^{\alpha\alpha}_{ea,fb} = 2\sum_{i_\alpha > j_\alpha} t^{ab,\alpha}_{ij}\langle e_\alpha f_\alpha \| i_\alpha j_\alpha\rangle - \sum_{i_\alpha > j_\alpha}\sum_{c_\alpha}[t^{ab,\alpha}_{ij}$$

$$\times\langle b_\alpha c_\alpha \| i_\alpha j_\alpha\rangle + t^{cb,\alpha}_{ij}\langle c_\alpha a_\alpha \| i_\alpha j_\alpha\rangle]\delta_{ef}$$

$$+ 2D^\alpha_{ab} f^\alpha_{ef} - D^\alpha_{ab} (f^\alpha_{aa} + f^\alpha_{bb}) - \sum_{i_\alpha}\sum_{j_\beta}\sum_{c_\beta}[t^{ac,\alpha\beta}_{ij}$$

$$\times\langle b_\alpha c_\beta | i_\alpha j_\beta\rangle + t^{bc,\alpha\beta}_{ij}\langle a_\alpha c_\beta | i_\alpha j_\beta\rangle]\delta_{ef}, \tag{21b}$$

where the active α block of the second-order density matrix is defined as

$$D^\alpha_{ab} = \sum_{i_\alpha > j_\alpha}\sum_{c_\alpha} t^{ac,\alpha}_{ij} t^{bc,\alpha}_{ij}$$

$$+ \sum_{i_\alpha}\sum_{j_\beta}\sum_{c_\beta} t^{ac,\alpha\beta}_{ij} t^{bc,\alpha\beta}_{ij}. \tag{22}$$

One derives similar expressions for G^β_{ea} and $H^{\beta\beta}_{ea,fb}$. The above equations have been derived with the assumption that the active correlation orbitals for α and β electrons diagonalize the respective α and β Fock operators. This can be easily accomplished by constructing the Fock matrices within the α and β active spaces and subsequent diagonalizations.

An important feature of Eqs. (21) is that they exhibit a similar pair separability as the second-order functional. This makes the computational algorithm for calculating the gradient and Hessian matrices very similar to calculating the second-order correlation energy. The computational implementation of the present methodology will be discussed in the next section.

The optimal rotation matrices R^α and R^β are determined using the Newton–Raphson equations:

$$\mathbf{R}^\alpha = -(\mathbf{H}^{\alpha\alpha})^{-1}\mathbf{G}^\alpha,$$

$$\mathbf{R}^\beta = -(\mathbf{H}^{\beta\beta})^{-1}\mathbf{G}^\beta. \tag{23}$$

Once R^α and R^β are determined, the unitary matrices U^α and U^β are calculated using the formula[16]

$$\mathbf{U} = \exp(\mathbf{R}) = \mathbf{X}\cosh(\mathbf{d})\mathbf{X}^\dagger + \mathbf{R}\mathbf{X}\sinh(\mathbf{d})\mathbf{d}^{-1}\mathbf{X}^\dagger, \tag{24}$$

where $\mathbf{d}$ is the square root of a diagonal matrix, which results from the diagonalization of R^2,

$$\mathbf{d}^2 = \mathbf{X}^\dagger\mathbf{R}^2\mathbf{X}. \tag{25}$$

B. Computational implementation

Computational implementation of the generation procedure of the first-order correlation orbitals for the UHF zero-order wave function involved the following steps:

(i) The solution of the UHF problem.

(ii) The transformation of atomic integrals to molecular integrals. Three sets of molecular integrals are generated by a direct transformation of atomic integrals and include the following sets:

$$\langle i_\alpha j_\alpha | a_\alpha b_\alpha\rangle,$$

$$\langle i_\beta j_\beta | a_\beta b_\beta\rangle,$$

$$\langle i_\alpha j_\beta | a_\alpha b_\beta\rangle. \tag{26}$$

Each set of integrals is sorted so that for a given i,j indices, integrals corresponding to all distinct virtual a and b indices reside in one record. The integral transformation routine effectively employs the supermatrix symmetry of the integral matrix and is readily vectorizable.

(iii) The initial active correlation orbitals are selected. This selection in the calculation presented in the third section of this paper was done based on the second-order orbital contributions calculated according to the scheme mentioned before.

(iv) Optimization of the active correlation orbitals is accomplished in an iterative procedure. The procedure involves the following steps:

· Calculation of gradient and Hessian matrices for α and β orbital rotation parameters ($\mathbf{G}^\alpha$, $\mathbf{G}^\beta$, $\mathbf{H}^{\alpha\alpha}$, and $\mathbf{H}^{\beta\beta}$). The Hessian matrices are stored on the disk.

· Solution of the Newton–Raphson equations [Eqs.

(23)] to determine orbital rotation parameters R^α and R^β. The solution is accomplished using an out-of-core iterative procedure. The convergence of this procedure is accelerated by calculating a partial inverse of the Hessian matrices. This is based on an observation that the Hessian matrices are usually dominated by diagonally located blocks, each corresponding to the rotation parameters of all active orbitals with a single nonactive orbital. All such inverses are kept in the core memory and reused in the iterative procedure. The partial inverse approach allows us to solve the Newton–Raphson equations in a few iterations, what is much faster than the conventional approach which utilizes only the inverses of the diagonal elements of the Hessian.

· Determination of the unitary orbital transformation matrices U^α and U^β and generating new sets of active α and β correlation orbitals.

· Construction and diagonalization of the Fock matrices (f^α and f^β) for the new active correlation orbitals. The results of this step are two sets of canonical Hartree–Fock orbitals.

· Calculation of the value of the second-order functional J_2 for the new active α and β correlation orbitals. This value, which is equivalent to the second-order correlation energy, is compared to the result of the previous iteration and the iteration process is continued if the energy lowering is still significant. If the convergence criterion is accomplished, the active correlation orbitals are transformed to the atomic basis to be used in the subsequent coupled-cluster calculation.

Our numerical experience indicates that the most time-consuming step of the above procedure is the generation of the Hessian matrices. Typically, the time needed to generate FOCOs is only slightly longer than the time to perform the SCF calculation. The convergence of the iterative optimization procedure in all calculations done so far has been quite satisfactory. It usually takes about 10 to 20 iterations to accomplish the convergence. The stability of the procedure is a result of keeping the occupied Hartree–Fock orbitals frozen and varying only the correlation orbitals. In this aspect, the present method differs from the MCSCF optimization in which all orbitals are optimized, which sometimes leads to instabilities and divergence symptoms.

Also worth mentioning is that in the present method we generate and store the full orbital Hessian matrices. The generation of these matrices are significantly easier than in the MCSCF procedure due to the fact that only exchange integrals involving two occupied and two virtual indices are needed. Furthermore, the pair separability of the Hessian matrices, which we mentioned above, enables a sequential access to the integral file and keeping in the operational memory at one time only integrals with the same two occupied orbital indices and all possible virtual indices.

III. APPLICATIONS

A. Electron affinities of linear and rhombus C_4 clusters

Many reports have recently appeared concerning the formation and spectroscopical properties of pure carbon clusters.[20–24] It has been well documented that carbon clusters of different sizes and shapes exhibit considerable electron affinities,[25,26] which enable studies on these systems by various spectroscopical methods. The electron affinities of the carbon clusters have been estimated by Smalley et al.[25] by means of the ultraviolet photoelectron spectroscopy (UPS). The UPS data indicated that carbon clusters in the 2–9 range take the form of linear chains; the even-numbered chains having open shell electronic structures with high electron affinity, the odd chains having closed shell singlet ground states and substantially lower electron affinity. Recently, a number of high-level ab initio calculations have indicated that the smaller carbon clusters can also appear in a monocyclic structure and this can extend as low as to C_4.[26–29] As pointed out by Bartlett et al.,[30] the linear and rhombus structures can be differentiated based on the measurement of the electron affinities, which are significantly different for two isomers.

The ab initio quantum mechanical calculations of electron affinities (EAs) for larger molecular systems is a difficult task for several reasons. The basis set problem is more critical than for the processes involving neutral systems due to the greater spatial extensity of the anionic wave function. The inclusion of the lower and higher correlation effects are usually essential to obtain not only the correct EA value but also the right sign. Finally, the electron attachment process, which changes the number of electrons in the system, mandates a size-extensive theoretical treatment such as guaranteed by the many-body perturbation theory (MBPT) approach or the coupled cluster (CC) method.

For the above reasons the present UHF FOCO methodology has been first applied to determine the vertical electron affinities on two theoretically possible structures of the C_4 cluster, the linear form and the rhombus.[29]

B. Basis set and structures

In the present calculations we used $4s2p$ Dunning's basis set[31] augmented by the polarization function (d exponent = 0.654) of Redmon, Purvis, and Bartlett[32] and additional two s (exponents 0.06 and 0.02) and one p (exponent 0.0438) diffused functions. This gave a basis of 140 uncontracted Gaussians and 84 contracted basis functions.

The molecular structures used in the calculations resulted from a MBPT(2)/6-31G** geometry optimizations accomplished with the GAUSSIAN86 computer program.[33] Since we have been concerned with the vertical electron affinities, we used the geometries of the neutral systems in calculations for anions. The coordinates of the linear and rhombus structures are presented in Table I.

C. FOCO generation

All calculations reported here have been accomplished on the VAX 3100 workstation. More extended studies on the electron affinities of longer carbon chains, which are currently in progress on the CONVEX 210 minisupercomputer, will be reported latter. The UHF FOCO generation has been accomplished with our program, which enables an extensive vectorization. The subsequent MBPT/CC calculations with FOCOs have been done using the PROPAGATOR program

TABLE I. MBPT(2)/6-31G** optional geometries for the linear and rhombus structure of the C_4 cluster used in the present calculations.

	Cartesian coordinates in angstroms		
	x	y	z
Linear structure			
C_1	0	0	1.960 678
C_2	0	0	0.647 963
C_3	0	0	− 0.647 963
C_4	0	0	− 1.960 678
Rhombus structure			
C_1	0	0	1.235 163
C_2	0	0	− 1.235 163
C_3	0	0.761 235	0
C_4	0	− 0.761 235	0

written by Bartlett et al.[34]

In Table II we present results of several FOCO calculations for the linear C_4, which differ in the number of the active correlation orbitals and in their symmetry distributions. One notices, that the number of FOCOs oscillates around 50% of the number of all virtual orbitals, which for the size of the basis set used is an acceptable amount in most cases. The number of FOCOs for α electrons for both the neutral and the anionic systems is smaller than for β electrons. However, the sum of the number of occupied UHF orbitals and the number of correlation orbitals for both spin

symmetries in each symmetry block remains the same. One may question the validity of this restriction, but it results from the limitations in the PROPAGATOR program, which requires the same number of orbitals in the α and β blocks. The total number of orbitals (occupied plus correlation) for the neutral system was assumed the same as for the anion. In effect, the number of correlation orbitals generated for the anion was always by one smaller than for the neutral. This caused the values of the FOCO second-order functional for the anion to constitute a slightly higher percentage of the second-order energy determined with all virtual orbitals than for the neutral system. The percentage difference does not exceed 1%, which does not noticeably affect the accuracy of the calculations. As a remedy to this problem, one should probably include more active correlation orbitals for the anion than for the neutral. However, this may easily lead to an even greater imbalance.

Upon examining the results in Table II, one notices that if we restrict the active space to less than 50% of the virtual space (30/32 and 30/31 sets) we get nearly 90% of the full second-order energy. A small increase in the active spaces (34/36 and 34/35 sets) raises the percentile to 93, and with the 38/40 and 38/39 sets one gets already over 95% of the second-order energy. Worth noticing is that for the 30/32 and 30/31 active orbital sets the percentages of the full second-order energy for the neutral and for the anion agree the best, and for this reason we used these sets for the subsequent

TABLE II. Linear C_4/C_4^-. The optimal values of the second-order Hylleraas functional for various numbers of active correlation orbitals. In atomic units.

Symmetries		Occupied orbitals							
		σ_g	π_{ux}	π_{uy}	δ_g	σ_u	π_{gx}	π_{gy}	δ_u
C_4	α:	5	1	1	0	4	1	1	0
	β:	5	1	1	0	4	0	0	0
C_4^-	α:	5	1	1	0	4	1	1	0
	β:	5	1	1	0	4	1	0	0

		Number of FOCOs (orbital symmetry distribution[a])	Second-order functional (percentage with respect to the result for the full space)
1.			
C_4	α:	71 (19 7 7 2 20 7 7 2)	full space − 0.465 414 (100%)
	β:	73 (19 7 7 2 20 8 8 2)	
C_4^-	α:	71 (19 7 7 2 20 7 7 2)	full space − 0.522 467 (100%)
	β:	72 (19 7 7 2 20 7 8 2)	
2.			
C_4	α:	30 (8 3 3 1 8 3 3 1)	− 0.415 027 (89.17%)
	β:	32 (8 3 3 1 8 4 4 1)	
C_4^-	α:	30 (8 3 3 1 8 3 3 1)	
	β:	31 (8 3 3 1 8 3 4 1)	− 0.464 165 (88.84%)
3.			
C_4	α:	34 (9 4 4 1 9 3 3 1)	− 0.435 951 (93.67%)
	β:	36 (9 4 4 1 9 4 4 1)	
C_4^-	α:	34 (9 4 4 1 9 3 3 1)	
	β:	35 (9 4 4 1 9 3 4 1)	− 0.484 970 (92.82%)
4.			
C_4	α:	38 (10 4 4 1 10 4 4 1)	− 0.447 693 (96.19%)
	β:	40 (10 4 4 1 10 5 5 1)	
C_4^-	α:	38 (10 4 4 1 10 4 4 1)	
	β:	40 (10 4 4 1 10 4 5 1)	− 0.498 373 (95.39%)

[a] The order of the symmetry representations are the same as for occupied orbitals.

TABLE III. Linear C_4/C_4^-. Convergence of the Newton–Raphson procedure for the optimization of the first-order correlation orbitals.

Iter.	FOCOs C_4 (α: 8 3 3 1 8 3 3 1) (β: 8 3 3 1 8 4 4 1) Second-order functional	FOCOs C_4^- (α: 8 3 3 1 8 3 3 1) (β: 8 3 3 1 8 3 4 1) Second-order functional
1	− 0.262 679	− 0.269 585
2	− 0.373 340	− 0.388 293
3	− 0.407 662	− 0.447 932
4	− 0.413 873	− 0.461 125
5	− 0.414 361	− 0.462 408
6	− 0.414 584	− 0.462 679
7	− 0.414 718	− 0.462 991
8	− 0.414 809	− 0.463 342
9	− 0.414 875	− 0.463 635
10	− 0.414 952	− 0.463 826
11	− 0.414 957	− 0.463 939
12	− 0.414 981	− 0.464 006
13	− 0.414 997	− 0.464 049
14	− 0.415 008	− 0.464 077
15	− 0.415 015	− 0.464 097
20	− 0.415 027	
29		− 0.464 165

high-order calculations. Slightly larger sets of 34/34 and 33/45 orbitals were also used for the calculations on the rhombic structure of C_4 and C_4^-.

Another aspect of the FOCO generation, which may be of interest, is the convergence of the Newton–Raphson optimization procedure. In Table III we present the values of the second-order functional from the consecutive iterations in the optimization of the 30/32 FOCO set for the neutral linear cluster and 30/31 FOCO set for the corresponding anion. We see that the convergence for the neutral is somewhat better than for the anion. In both cases, a satisfactory convergence is achieved in less than 30 iterations. This required about 11 cpu h for the neutral and 15 h for the anion on the VAX 3100. In general, the FOCO procedure seems to converge quite well. The presented example represents a rather typical performance of the method.

D. MBPT/CC calculations with UHF FOCOs

In Tables IV and V we present the MBPT/CC results which have been obtained with the 30/32 correlation orbital set for both the linear and rhombic neutral C_4 clusters and

TABLE IV. MPBT/CC calculations of C_4 and C_4^- for linear and rhombic geometry done with FOCOs. In atomic units.

	Linear structure	
	C_4	C_4^-
SCF	− 151.203 385	− 151.287 139
MBPT(2)	− 0.465 414	− 0.522 467
Calculations with FOCOs:		
FOCO symmetry distribution	α: 8 3 3 1 8 3 3 1 β: 8 3 3 1 8 4 4 1	α: 8 3 3 1 8 4 4 1 β: 8 3 3 1 8 3 4 1
MBPT(2)	− 0.415 028	− 0.464 166
MBPT(3)	− 0.444 405	− 0.479 899
CCSD	− 0.454 994	− 0.488 674
CCSD + T(CCSD)	− 0.473 438	− 0.508 679
	Rhombus structure	
	C_4	C_4^-
SCF	− 151.168 932	− 151.234 853
MBPT(2)	− 0.529 873	− 0.541 648
Calculations with FOCOs:		
FOCO symmetry distribution	α: 8 4 6 2 6 4 3 1 β: 8 4 6 2 6 4 3 1	α: 8 4 6 2 6 3 3 1 β: 8 4 6 2 6 4 3 1
MBPT(2)	− 0.491 675	− 0.464 166
MBPT(3)	− 0.502 057	− 0.505 760
CCSD	− 0.510 265	− 0.514 299
CCSD + T(CCSD)	− 0.534 927	− 0.537 718

Symmetry distribution of the occupied orbitals of the rhombic C_4 and C_4^-

Symmetry representations

Symmetry planes:		1	2	3	4	5	6	7	8
yz		+	−	+	−	+	−	+	−
xz		+	+	−	−	+	+	−	−
xy		+	+	+	+	−	−	−	−
C_4	α:	5	1	2	0	3	0	1	0
	β:	5	1	2	0	3	0	1	0
C_4^-	α:	5	1	2	0	3	1	1	0
	β:	5	1	2	0	3	0	1	0

Same order of the symmetry representations is used for FOCOs

TABLE V. MBPT/CC vertical electron affinities of the linear and rhombic C_4 molecule in eV.

	Linear structure	Rhombic structure
SCF	2.28	1.79
Correlation contributions		
MBPT(2)	1.55	0.32
E_3/FOCO	− 0.37	− 0.05
CCSD/FOCO	− 0.42	− 0.05
CCSD + T(CCSD)/FOCO	− 0.38	− 0.08
Total		
SCF + MBPT(2) + Δ[CCSD + T(CCSD)]/FOCO	3.45	2.03
Other theoretical results		
MBPT SDQ(4)	3.29	2.02
Ref. 30[a]		
Experiment		
Ref. 25[b]	3.70	---

[a] MBPT SDQ(4) result obtained with $5s3p1d$ basis set.
[b] Estimated by the observed photodetachment onsets, approximately corrected for thermal effects and instrument resolution.

respective anions. The final value of the electron affinity was calculated as the sum of the SCF value, the second-order correlation correction calculated with all virtual orbitals and the higher-order correlation contribution calculated as the difference between the CCSD + T(CCSD) and the MBPT(2)/FOCO results. For the linear chain, our EA result of 3.45 eV obtained in this manner is slightly smaller than the experimental estimation of Smalley et al.[35] of 3.70 eV, but closer to this estimation than the previous theoretical MBPT SDQ(4) result of Bartlett et al.[40] For the rhombic structure, where the higher-order correlation contributions to the electron affinity are significantly smaller, our result agrees with that of Bartlett et al.

IV. CONCLUSIONS

This paper presents an extension of the FOCO method to the UHF zero-order wave function. This development enables high-level correlation calculations for larger open-shell systems such as neutral and charged carbon clusters. The active correlation orbitals result from a minimization of the second-order Hylleraas functional which represents the second-order correlation energy of the system. The size extensivity and the perturbation character of the Hylleraas functional agrees with the purpose of generating the FOCOs which is their subsequent utilization in higher-order MBPT and CC calculations. Obviously, since the first-order wave function, which appears in the second-order functional, comprises only doubly excited determinants, the FOCOs will serve better the pair correlation effects rather than effects described by single and triple excitations. For these latest effects one would need to generate the second-order correlation orbitals (SOCOs) by the minimization of the fourth-order Hylleraas functional, which we intend to accomplish in the future. SOCOs will probably be more important in evaluating properties other than the total energy of the system.

The best way to use the UHF FOCO procedure would be for correlated calculations which require extended basis sets with numerous polarization functions such as calculations on larger molecular anions and radicals. These kinds of calculations with all virtual orbitals are still excessively expensive even for supercomputers. The present method offers an alternative, which makes such predictive calculations possible.

Another possible application of the UHF FOCO method could be in preoptimization of the active correlation orbitals for a subsequent use in an MCSCF calculation. There is also a possibility of developing an atomic orbital contraction scheme based on the FOCOs in a similar way as this is accomplished with the atomic natural orbitals.

It is worth mentioning that the computational implementation of the UHF FOCO method is fully automatic and can be used as a "black box" unit for generating correlation orbitals. It reads the SCF orbitals and atomic integrals and replaces the SCF virtual orbitals by the active and nonactive first-order correlation orbitals.

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