Theor Chem Acc (2010) 127:311–325
DOI 10.1007/s00214-009-0719-5

REGULAR ARTICLE

The role of orbital transformations in coupled-pair functionals

Christian Kollmar · Andreas Heßelmann

Received: 18 September 2009 / Accepted: 9 December 2009 / Published online: 27 December 2009

Abstract The replacement of single excitations by orbital transformations in coupled-pair functionals derived from a single double configuration interaction approach is discussed. It is demonstrated that this modification leads to considerably improved density matrices and better agreement with results from coupled cluster singles doubles calculations taken as a reference. A comparison between the variationally optimized orbitals and the Brueckner orbitals shows that these two sets of orbitals are different.

Keywords Configuration interaction · Coupled-pair functional · Orbital optimization · Brueckner orbitals · Size extensivity

1 Introduction

The method of configuration interaction (CI) is one of the standard approaches for the treatment of electron correlation in molecules. However, a serious problem exhibited by any limited CI expansion of an electronic wave function is its lack of size extensivity. Size extensivity is here defined as the additivity of electronic energies for an ensemble of molecules separated by an infinite distance from each other. There are several approaches compensating for the lack of size extensivity, such as correction terms added a posteriori to the energy of a limited CI wave function [1–6], many-body perturbation theory as formulated by Møller and Plesset (MP) [7], various coupled electron pair approximations (CEPA) [8–11], the coupled cluster (CC) method [12–14], and the quadratic CI (QCI) method [15]. None of these methods is variational in the sense that the electronic energy is obtained by variational optimization of an energy functional.

Instead, they might be denoted as projective methods because the equations for the amplitudes of the excited states are obtained by projecting with determinants on the Schrödinger equation as in the case of the MP, CEPA, CC, and QCI methods. In general, these methods employ Hartree–Fock (HF) orbitals. Alternatively, one can use Brueckner orbitals [16] which are obtained from a projective elimination of the amplitudes of the single excitations as for example in the Brueckner CCD (BCCD) [17] method.

There are also methods where the excitation amplitudes are obtained from a variational condition for an energy functional. These are in general derived from the CI singles doubles (CISD) energy expression which is modified such that the energy becomes at least approximately size extensive. The first of these functionals developed by Pulay [18] has been followed by the coupled-pair functional (CPF) [19], the averaged coupled-pair functional (ACPF) [20], and the averaged quadratic CC (AQCC) functional [21]. None of these methods corresponds to a wave function approach but the variables to be optimized are still CI-like singles and doubles excitation amplitudes. HF orbitals are used in general so that the functionals are not optimized with respect to the orbitals. Thus, fully relaxed density matrices can only be obtained by solving coupled-perturbed HF equations. Nonetheless, the variational optimization with respect to the amplitudes leads to a

C. Kollmar (✉)
Lehrstuhl für Theoretische Chemie, Universität Bonn,
Wegelerstr. 12, 53115 Bonn, Germany
e-mail: kollmar@thch.uni-bonn.de

A. Heßelmann
Lehrstuhl für Theoretische Chemie, Universität Erlangen,
Egerlandstraße 3, 91058 Erlangen, Germany
e-mail: andreas.hesselmann@chemie.uni-erlangen.de

considerable simplification in the evaluation of response properties, e.g., energy gradients [18].

Most of the approaches just mentioned seem to have been forgotten to a large extent after CCSD has evolved as a kind of standard method for correlation calculations of small molecules. This is a consequence of the fact that CCSD is generally accepted as the most rigorous method among those limited to the amplitudes of double excitations. However, the evaluation of response properties in CCSD requires the solution of *Z*-vector equations [22] which is as expensive as the solution of the CCSD equations thus doubling the computational cost as compared to CISD-based methods allowing direct variational optimization of an energy functional. Hence, the interest in coupled-pair methods and related approaches has been revived just recently [23–25]. The present contribution has to be situated in this context.

Apart from simplified gradients, there is yet another reason for the renewed interest in coupled-pair methods. It is generally recognized that CCSD(T), i.e, CCSD with perturbative inclusion of triple excitations sets the standard for the calculation of ground state properties in the single reference case yielding atomization energies and reaction energies within chemical accuracy [26]. However, CCSD(T) calculations are expensive due to the unfavorable scaling behavior of this method (N^7 if N is a measure for the size of the molecule). Thus, there is clearly a need for cheaper methods restricted to the amplitudes of single and double excitations which scale as N^6 (CCSD) or N^5 (MP2). It has been found that atomization and reaction energies obtained from CCSD calculations are only slightly superior to the corresponding MP2 results [26]. On the other hand, it has been demonstrated that coupled-pair and CEPA methods (also scaling as N^6) outperform CCSD with respect to reaction energies and other energetic properties [25, 27]. This is surprising given the fact that CCSD is in principle the more rigorous method. It has been speculated that CEPA and coupled-pair functionals simulate the effect of connected triples to some extent [8, 10, 28] but the phenomenon is perhaps not well-understood. Nonetheless, these encouraging results stimulate the further development of coupled-pair methods thus strengthening their position in a hierarchy between the less rigorous but cheap density functional approaches and the accurate but expensive CCSD(T) method.

There is, however, one aspect where CCSD is clearly superior to the coupled-pair methods. The exponential treatment of the single excitations ($e^{\hat{T}_1}$ with $\hat{T}_1$ being the single excitation operator) in the wave function makes CCSD relatively insensitive to the underlying orbital basis and thus capable to deal with cases where orbital relaxation effects are important. It has been shown that QCISD [15] which employs a linear instead of an exponential ansatz for the singles fails in such cases whereas CCSD is well-behaved [29]. The coupled-pair methods suffer from the same drawback. This difficulty has led to modified versions of the averaged coupled-pair functional (ACPF) [20] which have been denoted as ACPF-2 [30] and NACPF [25] and differ just by a different treatment of the singles from the original ACPF approach. Although it would in principle be possible to employ the exponential $e^{\hat{T}_1}$ ansatz in conjunction with CEPA, there are alternatives which avoid the appearance of single excitations at the outset. First, there is the concept of Brueckner orbitals [16] which is based on a projective condition for the elimination of the singles. Second, if the energy is given in the form of a functional, it can also be variationally optimized with respect to the orbitals which necessitates the elimination of the single excitations to avoid a redundant parametrization. As far as we know, this possibility has not yet been explored for the coupled-pair and related functionals. The present contribution is intended to fill this gap. An analogous procedure has already been applied in a recently proposed energy functional based on a CID approach [23]. Since orbital optimized versions of coupled-pair methods dispense with the single excitations altogether the abovementioned ambiguity with respect to the treatment of the singles in the ACPF method is avoided. Another important advantage of the replacement of single excitations by orbital optimization is the fully variational nature of the resulting energy functional in the sense that the electronic energy is optimized with respect to *all* variables, i.e., both the orbital coefficients and the amplitudes of the excited states. Thus, fully relaxed density matrices are obtained directly without solving any type of coupled-perturbed equations.

In the present contribution the replacement of the single excitations by orbital transformations will be discussed focussing on the ACPF method and a variational analogue to the CEPA(1) approach. The variationally optimized orbitals will also be compared to Brueckner orbitals.

2 CISD-based energy functionals

Formal aspects concerning CISD-based energy functionals will be discussed in this section. The general form of the functional, its variational optimization with respect to the excitation amplitudes and orbitals, and the corresponding density matrices will be presented. A comparison with the coupled-pair functional of Ahlrichs et al. [19] and the CEPA approach points to the close relationship with these methods. The main aspect of this contribution, i.e., the replacement of single excitations by orbital optimization will be elucidated. Finally, a comparison of the orbital gradient with the Brueckner condition shows that the optimized orbitals differ from the Brueckner orbitals.

2.1 The form of the functional

The following considerations will be restricted to the single reference closed-shell case. A spin-adapted notation first suggested by Pulay et al. [31] is used in a slightly modified version of Hampel et al. [32]. The spin-adapted CISD wave function on which the functionals considered in the following are based reads

$$\begin{aligned}|\Psi\rangle &= b_0|\Phi_0\rangle + \sum_{\substack{i\\a}} B^i_a|\Phi^a_i\rangle + \frac{1}{2}\sum_{\substack{ij\\ab}} B^{ij}_{ab}|\Phi^{ab}_{ij}\rangle \\ &= b_0|\Phi_0\rangle + \sum_{\substack{i\\a}} \tilde{B}^i_a|\tilde{\Phi}^a_i\rangle + \sum_{\substack{ij\\ab}} \tilde{B}^{ij}_{ab}|\tilde{\Phi}^{ab}_{ij}\rangle \end{aligned} \tag{1}$$

where the spin-adapted singly and doubly excited configurations

$$\begin{aligned}|\Phi^a_i\rangle &= E^a_i|\Phi_0\rangle = \Psi^a_i + \Psi^{\bar{a}}_{\bar{i}} \\ |\Phi^{ab}_{ij}\rangle &= E^b_j E^a_i|\Phi_0\rangle = \Psi^{ab}_{ij} + |\Psi^{\bar{a}\bar{b}}_{\bar{i}\bar{j}}\rangle + |\Psi^{a\bar{b}}_{i\bar{j}}\rangle + |\Psi^{\bar{a}b}_{\bar{i}j}\rangle \end{aligned} \tag{2}$$

and their contravariant counterparts

$$\begin{aligned}|\tilde{\Phi}^a_i\rangle &= \frac{1}{2}|\Phi^a_i\rangle \\ |\tilde{\Phi}^{ab}_{ij}\rangle &= \left(\frac{1}{3}E^b_j E^a_i + \frac{1}{6}E^a_j E^b_i\right)|\Phi_0\rangle = \frac{1}{6}\left(2|\Phi^{ab}_{ij}\rangle + |\Phi^{ba}_{ij}\rangle\right)\end{aligned} \tag{3}$$

are obtained by application of the excitation operators

$$E^a_i = \hat{a}^\dagger_a \hat{a}^\dagger_i + \hat{a}^\dagger_{\bar{a}} \hat{a}^\dagger_{\bar{i}}. \tag{4}$$

As can be seen from Eq. (1), the contravariant amplitudes are given by

$$\begin{aligned}\tilde{B}^i_a &= 2B^i_a \\ \tilde{B}^{ij}_{ab} &= 2B^{ij}_{ab} - B^{ij}_{ba}.\end{aligned} \tag{5}$$

The introduction of contravariant configurations leads to the orthogonality relations

$$\begin{aligned}\langle\tilde{\Phi}^a_i|\Phi^c_k\rangle &= \delta_{ik}\delta_{ac} \\ \langle\tilde{\Phi}^{ab}_{ij}|\Phi^{cd}_{kl}\rangle &= \delta_{ik}\delta_{jl}\delta_{ac}\delta_{bd} + \delta_{il}\delta_{jk}\delta_{ad}\delta_{bc}\end{aligned} \tag{6}$$

and thus to a simplification of the wave function algebra [31].

The wave function equation (1) is assumed to be conventionally normalized, i.e., $\langle\Psi|\Psi\rangle = 1$. This distinguishes the present approach from the coupled-pair functional of Ahlrichs et al. [19] which is based on an intermediately normalized wave function, i.e., $\langle\Phi_0|\Psi\rangle = 1$ with $|\Phi_0\rangle$ being the reference determinant. b_0 is the corresponding CI coefficient. The symbol B refers to excitation amplitudes in conventional normalization whereas C is reserved for the corresponding amplitudes in intermediate normalization. The two possible spin orientations are distinguished by attaching a bar for β spins ($m_s = -\frac{1}{2}$) to the corresponding orbital index. If the bar is missing the corresponding spin function refers to spin α ($m_s = \frac{1}{2}$). In the doubly excited determinant $|\Psi^{ab}_{ij}\rangle$ the orbitals ψ_i and ψ_j of the reference determinant $|\Phi_0\rangle$ are replaced by the unoccupied orbitals ψ_a and ψ_b. Subscripts $i, j, \ldots$ and $a, b, \ldots$ refer to the occupied and virtual orbitals, respectively, and subscripts $p, q, r, s, \ldots$ denote general indices. The symmetry relation $B^{ij}_{ab} = B^{ji}_{ba}$ has been used in Eq. (1).

The modified energy functional suggested for CID [23] and supplemented with single excitations by DePrince and Mazziotti [33] reads in a simplified version adapted to the coupled-pair functionals:

$$\begin{aligned}E = E_0 &+ \langle\Phi_0|\hat{H}|\sum_{\substack{i\\a}} b_{0,ii}B^i_a\Phi^a_i + \sum_{\substack{ij\\ab}} b_{0,ij}\frac{1}{2}B^{ij}_{ab}\Phi^{ab}_{ij}\rangle \\ &+ \sum_{\substack{k\\c}} \tilde{B}^k_c\langle\tilde{\Phi}^c_k|\hat{H} - E_0|b_{0,kk}\Phi_0 + \sum_{\substack{i\\a}} B^i_a\Phi^a_i + \sum_{\substack{ij\\ab}}\frac{1}{2}B^{ij}_{ab}\Phi^{ab}_{ij}\rangle \\ &+ \sum_{\substack{kl\\cd}} \tilde{B}^{kl}_{cd}\langle\tilde{\Phi}^{cd}_{kl}|\hat{H} - E_0|b_{0,kl}\Phi_0 + \sum_{\substack{i\\a}} B^i_a\Phi^a_i + \sum_{\substack{ij\\ab}}\frac{1}{2}B^{ij}_{ab}\Phi^{ab}_{ij}\rangle\end{aligned} \tag{7}$$

with

$$E_0 = \langle\Phi_0|\hat{H}|\Phi_0\rangle. \tag{8}$$

The crucial modification of the energy functional arises from the introduction of the factor f_{ijkl} in the modified normalization condition

$$b^2_{0,ij} + \sum_{\substack{k\\c}} B^k_c\tilde{B}^k_c f_{ijkk} + \sum_{\substack{kl\\cd}} B^{kl}_{cd}\tilde{B}^{kl}_{cd} f_{ijkl} = 1 \tag{9}$$

with $b_{0,ij} > 0$. The various methods considered in this contribution differ by the choice of the factor f_{ijkl}. If this factor were chosen equal to one, the energy functional equation (7) would simply correspond to the energy of the CISD wave function equation (1) and Eq. (9) would just represent the normalization condition for this wave function. In this case the energy obtained from Eq. (7) would not be size extensive. Thus, one wishes the factor f_{ijkl} to be chosen in accordance with the requirement of size extensivity. This corresponds to the condition that this factor must vanish whenever the index sets $\{ij\}$ and $\{kl\}$ are completely disjoint [23] which leads to the appearance of Kronecker deltas such as $\delta_{ik}, \delta_{il}, \delta_{jk}, \delta_{jl}$. Thus, f_{ijkl} has the form of a contraction factor reducing the sum on the left-hand side of Eq. (9) from four to three or less indices. It has also been denoted as a topological factor by Ahlrichs et al. [19]. There have been efforts to derive contraction factors f^{abcd}_{ijkl} including indices of virtual orbitals in accordance with N representability conditions [23, 34, 35]. Similar factors without indices of virtual orbitals are known from the CEPA methods [8–11]. They lead to size extensivity if the orbitals are localized on the individual subsystems. The most popular of these methods is CEPA(1) for which the contraction factor reads

$$f_{ijkl} = \frac{1}{4}\left(\delta_{ik} + \delta_{il} + \delta_{jk} + \delta_{jl}\right). \tag{10}$$

Employing this factor in Eq. (9) leads to a kind of variational CEPA method (a comparison with the original CEPA method and the coupled-pair functional [19] will be given in Sect. 2.4). Note that the functional arising from Eq. (10) is not invariant with respect to unitary transformations within the subset of the occupied orbitals. This invariance can be restored by employing a simplified factor corresponding to the averaged coupled-pair functional (ACPF) [20]. In this case the factor does not depend on any orbital index. One has:

$$f = \frac{2}{N} \tag{11}$$

where N is the number of correlated electrons. The functional resulting from Eq. (11) is only size extensive for a system of identical molecules. It has the advantage of being invariant with respect to orbital rotations within the subsets of both the occupied and the virtual orbitals.

2.2 Variational optimization with respect to the excitation amplitudes

The variational problem posed by Eqs. (7) and (9) can be solved by forming the Lagrangian

$$\mathcal{L} \equiv E - \sum_{ij} \epsilon_{ij} g_{ij} \tag{12}$$

with Lagrangian multipliers ϵ_{ij} and the constraints

$$g_{ij} = b_{0,ij}^2 + \sum_{\substack{k\\c}} B_c^k \tilde{B}_c^k f_{ijkk} + \sum_{\substack{kl\\cd}} B_{cd}^{kl} \tilde{B}_{cd}^{kl} f_{ijkl} - 1. \tag{13}$$

The gradient components required for the minimization of the energy are obtained as

$$\begin{aligned}
\frac{\partial\mathcal{L}}{\partial\tilde{B}_c^k} &= \langle\tilde{\Phi}_k^c|\hat{H} - E_0 - \Delta_{kk}|b_{0,kk}\Phi_0 \\
&\quad + \sum_{\substack{i\\a}} B_a^i \Phi_i^a + \frac{1}{2}\sum_{\substack{ij\\ab}} B_{ab}^{ij}\Phi_{ij}^{ab}\rangle \\
\frac{1}{\tau_{cd}^{kl}}\frac{\partial\mathcal{L}}{\partial\tilde{B}_{cd}^{kl}} &= \langle\tilde{\Phi}_{kl}^{cd}|\hat{H} - E_0 - \Delta_{kl}|b_{0,kl}\Phi_0 \\
&\quad + \sum_{\substack{i\\a}} B_a^i \Phi_i^a + \frac{1}{2}\sum_{\substack{ij\\ab}} B_{ab}^{ij}\Phi_{ij}^{ab}\rangle \\
\frac{1}{2}\frac{1}{\tilde{\tau}_{kl}}\frac{\partial\mathcal{L}}{\partial b_{0,kl}} &= \delta_{kl}\sum_{c}\langle\Phi_0|\hat{H}|B_c^k\Phi_k^c\rangle \\
&\quad + \sum_{cd}\langle\Phi_0|\hat{H}|\frac{1}{2}B_{cd}^{kl}\Phi_{kl}^{cd}\rangle - \epsilon_{kl}b_{0,kl}
\end{aligned} \tag{14}$$

with

$$\Delta_{kl} = \sum_{ij}\epsilon_{ij}f_{ijkl} \tag{15}$$

$$\tau_{cd}^{kl} = 2 - \delta_{kl}\delta_{cd} \tag{16}$$

$$\tilde{\tau}_{kl} = \frac{2}{1 + \delta_{kl}}. \tag{17}$$

The factor τ_{cd}^{kl} accounts for the twofold appearance of each coefficient except for $k = l$ and $c = d$ as a consequence of the symmetry relation $B_{cd}^{kl} = B_{dc}^{lk}$. Equation (17) arises from the symmetry relation $b_{0,kl} = b_{0,lk}$.

Defining a kind of intermediately normalized coefficients as

$$C_{ab}^{ij} \equiv \frac{B_{ab}^{ij}}{b_{0,ij}} \qquad C_a^i \equiv \frac{B_a^i}{b_{0,ii}}, \tag{18}$$

the variational condition

$$\frac{\partial\mathcal{L}}{\partial\tilde{B}_c^k} = 0 \qquad \frac{\partial\mathcal{L}}{\partial\tilde{B}_{cd}^{kl}} = 0 \qquad \frac{\partial\mathcal{L}}{\partial b_{0,kl}} = 0 \tag{19}$$

leads to

$$\begin{aligned}
&\langle\tilde{\Phi}_k^c|\hat{H} - E_0|\Phi_0 + \sum_{\substack{i\\a}} C_a^i \frac{b_{0,ii}}{b_{0,kk}}\Phi_i^a + \frac{1}{2}\sum_{\substack{ij\\ab}} C_{ab}^{ij}\frac{b_{0,ij}}{b_{0,kk}}\Phi_{ij}^{ab}\rangle = C_c^k\Delta_{kk} \\
&\langle\tilde{\Phi}_{kl}^{cd}|\hat{H} - E_0|\Phi_0 + \sum_{\substack{i\\a}} C_a^i \frac{b_{0,ii}}{b_{0,kl}}\Phi_i^a + \frac{1}{2}\sum_{\substack{ij\\ab}} C_{ab}^{ij}\frac{b_{0,ij}}{b_{0,kl}}\Phi_{ij}^{ab}\rangle = C_{cd}^{kl}\Delta_{kl}
\end{aligned} \tag{20}$$

and

$$\epsilon_{kl} = \delta_{kl}\sum_{c}\langle\Phi_0|\hat{H}|C_c^k\Phi_k^c\rangle + \sum_{cd}\langle\Phi_0|\hat{H}|\frac{1}{2}C_{cd}^{kl}\Phi_{kl}^{cd}\rangle. \tag{21}$$

It can be shown that the sum of the Lagrangian multipliers ϵ_{ij} gives the correlation energy $E - E_0$ for the variationally optimized coefficients. Using Eqs. (7) and (14), we have:

$$\begin{aligned}
&\sum_{\substack{k\\c}} \tilde{B}_c^k \frac{\partial\mathcal{L}}{\partial\tilde{B}_c^k} + \sum_{\substack{kl\\cd}} \tilde{B}_{cd}^{kl}\frac{1}{\tau_{cd}^{kl}}\frac{\partial\mathcal{L}}{\partial\tilde{B}_{cd}^{kl}} + \frac{1}{2}\sum_{kl} b_{0,kl}\frac{1}{\tilde{\tau}_{kl}}\frac{\partial\mathcal{L}}{\partial b_{0,kl}} \\
&\quad = E - E_0 - \sum_{\substack{k\\c}} \tilde{B}_c^k B_c^k \Delta_{kk} - \sum_{\substack{kl\\cd}} \tilde{B}_{cd}^{kl} B_{cd}^{kl}\Delta_{kl} - \sum_{kl}\epsilon_{kl} b_{0,kl}^2.
\end{aligned} \tag{22}$$

From Eq. (19) it can be seen that the left-hand side of Eq. (22) has to vanish. Using Eq. (15), rearranging some terms and partially renaming the indices, we then obtain from Eq. (22):

$$E - E_0 = \sum_{ij} \epsilon_{ij} \left(b_{0,ij}^2 + \sum_{\substack{k \\ c}} B_c^k \tilde{B}_c^k f_{ijkk} + \sum_{\substack{kl \\ cd}} B_{cd}^{kl} \tilde{B}_{cd}^{kl} f_{ijkl} \right). \tag{23}$$

Using Eq. (9), we finally arrive at:

$$E - E_0 = \sum_{ij} \epsilon_{ij}. \tag{24}$$

Inserting Eq. (21) into Eq. (24) leads to:

$$E - E_0 = \sum_{\substack{k \\ c}} \langle \Phi_0 | \hat{H} | \Phi_k^c \rangle C_c^k + \frac{1}{2} \sum_{\substack{kl \\ cd}} \langle \Phi_0 | \hat{H} | \Phi_{kl}^{cd} \rangle C_{cd}^{kl}. \tag{25}$$

Equation (25) has the same form as the energy obtained by projection of the reference function $|\Phi_0\rangle$ on the Schrödinger equation if the wave function is given in intermediate normalization.

2.3 Density matrices

The functional form of the energy has the big advantage that first-order and second-order density matrices can be directly extracted from the energy equation (7). Evaluating the matrix elements in Eq. (7) in terms of the integrals

$$\begin{aligned} h_{pq} &= \langle \psi_p | -\frac{1}{2}\Delta + V(\mathbf{r}) | \psi_q \rangle \\ \langle \psi_p \psi_q | \psi_r \psi_s \rangle &= \int \psi_p(\mathbf{r}_1) \psi_q(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times \psi_r(\mathbf{r}_1) \psi_s(\mathbf{r}_2)\, \mathrm{d}^3\mathbf{r}_1\, \mathrm{d}^3\mathbf{r}_2, \end{aligned} \tag{26}$$

the energy can also be expressed as

$$E = \sum_{pq} {}^1\Gamma_{pq} h_{qp} + \sum_{pqrs} {}^2\Gamma_{pqrs} \langle \psi_r \psi_s | \psi_p \psi_q \rangle \tag{27}$$

where $V(\mathbf{r})$ is the external potential and ${}^1\Gamma_{pq}$ and ${}^2\Gamma_{pqrs}$ are the first-order and second-order reduced density matrices (1-RDM and 2-RDM), respectively. Their elements are determined by the coefficients $b_{0,ij}$, B_a^i, and B_{ab}^{ij}. The elements of the 1-RDM are given by:

$$\begin{aligned} {}^1\Gamma_{ij} &= 2(\delta_{ij} - B^{ij}) \\ {}^1\Gamma_{ab} &= 2B_{ab} \\ {}^1\Gamma_{ia} &= 2b_{0,ii} B_a^i + 2 \sum_{\substack{k \\ c}} B_c^k \tilde{B}_{ac}^{ik} \end{aligned} \tag{28}$$

with

$$\begin{aligned} B^{ij} &= \sum_{\substack{k \\ ab}} \tilde{B}_{ab}^{ik} B_{ab}^{jk} + \sum_a B_a^i B_a^j \\ B_{ab} &= \sum_{\substack{ij \\ c}} \tilde{B}_{ac}^{ij} B_{bc}^{ij} + \sum_i B_a^i B_b^i. \end{aligned} \tag{29}$$

The elements of the 2-RDM read

$$\begin{aligned} {}^2\Gamma_{ijkl} &= 2\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - 2B^{ik}\delta_{jl} - 2B^{jl}\delta_{ik} + B^{il}\delta_{jk} \\ &\quad + B^{jk}\delta_{il} + \sum_{ab} B_{ab}^{ij} \tilde{B}_{ab}^{kl} \\ {}^2\Gamma_{iajb} &= 2B_{ab}\delta_{ij} - \frac{1}{2} \sum_{kc} \left(\tilde{B}_{bc}^{ik} \tilde{B}_{ac}^{jk} + 3B_{bc}^{ki} B_{ac}^{kj} \right) - B_b^i B_a^j \\ {}^2\Gamma_{iabj} &= -B_{ab}\delta_{ij} + \sum_{kc} \tilde{B}_{bc}^{ik} \tilde{B}_{ac}^{jk} + 2B_b^i B_a^j \\ {}^2\Gamma_{abcd} &= \sum_{ij} B_{ab}^{ij} \tilde{B}_{cd}^{ij} \\ {}^2\Gamma_{ijab} &= b_{0,ij} \tilde{B}_{ab}^{ij} \\ {}^2\Gamma_{alij} &= 2 \left(b_{0,ii}^{aa} B_a^i + \sum_{\substack{k \\ c}} B_c^k \tilde{B}_{ac}^{ik} \right) \delta_{jl} \\ &\quad - \left(b_{0,jj}^{aa} B_a^j + \sum_{\substack{k \\ c}} B_c^k \tilde{B}_{ac}^{jk} \right) \delta_{il} + \sum_c B_c^l \tilde{B}_{ca}^{ij} \\ {}^2\Gamma_{abdi} &= \sum_k B_d^k \tilde{B}_{ab}^{ki} \end{aligned} \tag{30}$$

Thus, the functional form of the energy leads to a direct availability of the density matrices. Equations (28)–(30) hold for all CISD-based functionals considered in the following and will be used for the evaluation of expectation values. The amplitudes of the singles must be set to zero in the case of orbital optimized functionals (see below). It is only in this latter case that the density matrices given by Eqs. (28) and (30) are fully relaxed. Employing HF orbitals instead of optimized orbitals, one has to solve coupled-perturbed HF equations to obtain fully relaxed density matrices.

2.4 Comparison with CEPA and the coupled-pair functional of Ahlrichs et al.

In contrast to the approach described in Sect. 2.1, the CEPA methods are not based on the variational optimization of an energy functional. Assuming a full CI wave function in intermediate normalization ($\langle \Phi_0 | \Psi \rangle = 1$), i.e.,

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{\substack{i \\ a}} C_a^i |\Phi_i^a\rangle + \frac{1}{2} \sum_{\substack{ij \\ ab}} C_{ab}^{ij} |\Phi_{ij}^{ab}\rangle + \cdots, \tag{31}$$

the equations to be solved for the excitation amplitudes are obtained by projecting with the ground and excited state configurations $|\Phi_0\rangle$, $|\tilde{\Phi}_k^c\rangle$, and $|\tilde{\Phi}_{kl}^{cd}\rangle$ on the Schrödinger equation $(\hat{H} - E)|\Psi\rangle = 0$. In the case of the ground state $|\Phi_0\rangle$, this results in the energy given by Eq. (25). Projection with $|\tilde{\Phi}_k^c\rangle$ and $|\tilde{\Phi}_{kl}^{cd}\rangle$ leads to the residuals σ_k^c and σ_{kl}^{cd}, respectively, which are approximated as

$$\sigma_k^c = \langle \tilde{\Phi}_k^c | \hat{H} - E_0 - \Delta_{kk} | \Phi_0 + \sum_{\substack{i\\a}} C_a^i \Phi_i^a + \frac{1}{2} \sum_{\substack{ij\\ab}} C_{ab}^{ij} \Phi_{ij}^{ab} \rangle$$

$$\sigma_{kl}^{cd} = \langle \tilde{\Phi}_{kl}^{cd} | \hat{H} - E_0 - \Delta_{kl} | \Phi_0 + \sum_{\substack{i\\a}} C_a^i \Phi_i^a + \frac{1}{2} \sum_{\substack{ij\\ab}} C_{ab}^{ij} \Phi_{ij}^{ab} \rangle \tag{32}$$

in the case of the CEPA methods. The energy shifts Δ_{kl} have to be defined such that they take into account the effects of higher excitation levels, i.e., triples and quadruples in an approximate fashion so that size extensivity is guaranteed. They are given by Eq. (15) where the contraction factor f_{ijkl} has to be chosen accordingly. The excitation amplitudes have to be determined such that the residuals vanish. The similarity between the conditions $\sigma_k^c = 0, \sigma_{kl}^{cd} = 0$ according to Eq. (32) and the variational condition equation (20) is obvious. The only difference is the appearance of the ratio $\frac{b_{0,ij}}{b_{0,kl}}$ in the latter which can be expected to be close to one. In the case of ACPF, where the factors b_0 do not depend on any orbital index (see Eqs. 9 and 11) it is even exactly equal to one. Note that the CEPA equations $\sigma_k^c = 0$ and $\sigma_{kl}^{cd} = 0$, in contrast to Eq. (20), do not correspond to a variational condition for an energy functional except for ACPF. The functional form of the energy is a prerequisite for the replacement of single excitations by orbital optimization.

The advantage of a functional form for the electronic energy missing in the CEPA methods is retained in the coupled-pair functional of Ahlrichs et al. [19]. In contrast to the previous approach defined by Eqs. (7) and (9) which is based on a conventionally normalized wave function, Ahlrichs et al. start from a wave function in intermediate normalization. The coupled-pair functional is based on the energy expression $E = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$ with the modification affecting the squared norm $\langle \Psi | \Psi \rangle \equiv c_0^2$ of the wave function. The modified energy reads

$$\begin{aligned} E = {} & E_0 + \langle \Phi_0 | \hat{H} | \sum_{\substack{i\\a}} \frac{1}{|c_{0,ii}|^2} C_a^i \Phi_i^a + \sum_{\substack{ij\\ab}} \frac{1}{|c_{0,ij}|^2} \frac{1}{2} C_{ab}^{ij} \Phi_{ij}^{ab} \rangle \\ & + \sum_{\substack{k\\c}} \frac{\tilde{C}_c^k}{c_{0,kk}} \langle \tilde{\Phi}_k^c | \hat{H} - E_0 | \frac{1}{c_{0,kk}} \Phi_0 + \sum_{\substack{i\\a}} \frac{C_a^i}{c_{0,ii}} \Phi_i^a + \sum_{\substack{ij\\ab}} \frac{1}{2} \frac{C_{ab}^{ij}}{c_{0,ij}} \Phi_{ij}^{ab} \rangle \\ & + \sum_{\substack{kl\\cd}} \frac{\tilde{C}_{cd}^{kl}}{c_{0,kl}} \langle \tilde{\Phi}_{kl}^{cd} | \hat{H} - E_0 | \frac{1}{c_{0,kl}} \Phi_0 + \sum_{\substack{i\\a}} \frac{C_a^i}{c_{0,ii}} \Phi_i^a + \sum_{\substack{ij\\ab}} \frac{1}{2} \frac{C_{ab}^{ij}}{c_{0,ij}} \Phi_{ij}^{ab} \rangle \end{aligned} \tag{33}$$

with

$$c_{0,ij}^2 = 1 + \sum_{\substack{k\\c}} C_c^k \tilde{C}_c^k f_{ijkk} + \sum_{\substack{kl\\cd}} C_{cd}^{kl} \tilde{C}_{cd}^{kl} f_{ijkl}. \tag{34}$$

Equations (33) and (34) should be compared to Eqs. (7) and (9). Whereas the contraction factor leading to size extensivity modifies the coefficient b_0 of the reference determinant in the latter case, it is now introduced to modify the squared norm $\langle \Psi | \Psi \rangle$ which is recovered by setting $f_{ijkl} = 1$ in Eq. (34). In this particular case, the energy equation (33) has the standard form $E = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$ with Ψ being the CISD wave function in intermediate normalization. Size extensivity can be obtained in complete analogy to the procedure described in Sect. 2.1 by adopting the contraction factor from the CEPA methods. Ahlrichs et al. [19] have chosen the factor corresponding to CEPA(1) as given by Eq. (10) in their coupled-pair functional. Defining

$$\begin{aligned} B_c^k & \equiv \frac{C_c^k}{c_{0,kk}} \\ B_{cd}^{kl} & \equiv \frac{C_{cd}^{kl}}{c_{0,kl}} \end{aligned} \tag{35}$$

with analogous definitions for the contravariant coefficients, a comparison of Eqs. (7) and (33) shows that these are strictly equivalent if $b_{0,kl} = \frac{1}{c_{0,kl}}$. Such an equivalence is only obtained if the contraction factor is constant as, e.g., in the ACPF case, Eq. (11), and for CISD ($f = 1$), but not for the CEPA contraction factor equation (10). This can be seen by inserting Eq. (35) into Eq. (34) leading to

$$c_{0,ij}^2 \bar{b}_{0,ij}^2 = 1 \tag{36}$$

with

$$\bar{b}_{0,ij}^2 = 1 - \sum_{\substack{k\\c}} B_c^k \tilde{B}_c^k f_{ijkk} \frac{c_{0,kk}^2}{c_{0,ij}^2} - \sum_{\substack{kl\\cd}} B_{cd}^{kl} \tilde{B}_{cd}^{kl} f_{ijkl} \frac{c_{0,kl}^2}{c_{0,ij}^2}. \tag{37}$$

A comparison of Eqs. (37) and (9) shows that in general $\bar{b}_{0,ij} \neq b_{0,ij}$ so that Eq. (36) is not compatible with the requirement $b_{0,ij} = \frac{1}{c_{0,ij}}$ except for a constant factor f.

The variational problem for the coupled-pair functional is again solved by forming a Lagrangian including the constraints equation (34) in complete analogy to Eq. (12). The equations for the components of the gradient are a bit more involved than Eqs. (14) and will not be presented here. Moreover, the variational energy obtained by inserting the optimized coefficients in Eq. (33) is in general not exactly equal to the energy obtained with the same coefficients from the projective energy equation (25).

2.5 The replacement of single excitations by orbital rotations and the orbital gradient

The essential new feature of the methods discussed in this contribution is the orbital optimization of the energy. This necessitates the elimination of the single excitations from the energy equation (7) to avoid a redundant parametrization as has already been observed for the orbital optimized CCD method [36]. Thus, the orbital optimized ACPF approach dispenses with the aforementioned ambiguity with respect to the treatment of single excitations [25, 30].

The redundancy of single excitations in orbital optimized treatments of the correlation problem is due to a close relationship between single excitations and orbital transformations. It can be shown [37] that application of the operator $e^{\hat{Q}}$ with

$$\begin{aligned}\hat{Q} &= \sum_{p>q} Q_{pq}\left(\hat{a}_p^\dagger \hat{a}_q + \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{q}} - \hat{a}_q^\dagger \hat{a}_p - \hat{a}_{\bar{q}}^\dagger \hat{a}_{\bar{p}}\right) \\ &= \sum_{pq} Q_{pq}\left(\hat{a}_p^\dagger \hat{a}_q + \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{q}}\right)\end{aligned} \tag{38}$$

to any Slater determinant built with orbitals ψ_q is equivalent to forming the same Slater determinant with the orbitals ψ_q being replaced by the transformed orbitals

$$\tilde{\psi}_q = \sum_p \psi_p (e^{\mathbf{Q}})_{pq} \tag{39}$$

where $\mathbf{Q}$ is an anti-Hermitean matrix so that $e^{\mathbf{Q}}$ is unitary. Assuming $|Q_{pq}| \ll 1$ the expansion of the exponential $e^{\hat{Q}}$ can be terminated after the linear term so that the resulting operator just adds singly excited states to the reference determinant. This linear approximation therefore provides some justification for the replacement of the singly excited states by a unitary transformation of the orbitals as shown in Eq. (39). In contrast to the single excitation operator $\hat{T}_1 = \sum_{ia} T_a^i (\hat{a}_a^\dagger \hat{a}_i + \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{i}})$, however, the anti-Hermiticity of the operator $\hat{Q}$ leads to the appearance of the corresponding deexcitation operators $-T_a^i (\hat{a}_i^\dagger \hat{a}_a + \hat{a}_{\bar{i}}^\dagger \hat{a}_{\bar{a}})$. Thus, the application of the operator $e^{\hat{T}_1}$ in the CC method is not completely equivalent to an orbital transformation employing the amplitudes of the singles in the transformation matrix $e^{\mathbf{Q}}$.

The orbital gradient needed for the update of the orbitals in each iteration cycle can be evaluated by employing the exponential ansatz equation (39) for a unitary transformation as suggested a long time ago for orbital optimization in the multiconfiguration self-consistent field (MCSCF) method [38]. The variational condition for the optimized orbitals can be obtained by expanding the exponential in Eq. (39) in a power series. The first order variation of the orbital ψ_q is then given by

$$\delta\psi_q = \sum_p \psi_p Q_{pq}. \tag{40}$$

Inserting Eq. (40) into Eq. (27), the corresponding first order variation of the electronic energy reads

$$\delta E = 2 \sum_{pq} Q_{pq} (g_{qp} - g_{pq}) \tag{41}$$

with

$$g_{pq} = \frac{1}{2} \sum_r {}^1\Gamma_{pr} h_{rq} + \sum_{rst} {}^2\Gamma_{ps,rt} \langle \psi_r \psi_t | \psi_q \psi_s \rangle. \tag{42}$$

Defining

$$f_{pq} \equiv g_{pq} - g_{qp}, \tag{43}$$

the variational condition for the orbitals is simply given by $f_{pq} = 0$. The ACPF energy is invariant with respect to unitary transformations within the subsets of occupied and virtual orbitals so that the equations $f_{ij} = 0$ and $f_{ab} = 0$ are fulfilled identically. Thus, only the matrix elements f_{ia} of the occupied-virtual subblock are of interest. These can be obtained by inserting Eqs. (28) and (30) with vanishing amplitudes of the singles in Eq. (42) and using Eq. (43) as

$$\begin{aligned}f_{ia} = F_{ia} &- \sum_j B^{ij} F_{ja} - \sum_b B_{ab} F_{bi} \\ &- \sum_{kl} B^{kl} (2\langle \psi_i \psi_l | \psi_a \psi_k \rangle - \langle \psi_l \psi_i | \psi_a \psi_k \rangle) \\ &+ \sum_{cd} B_{cd} (2\langle \psi_i \psi_d | \psi_a \psi_c \rangle - \langle \psi_d \psi_i | \psi_a \psi_c \rangle) \\ &+ \sum_{jkl} \sum_{cd} B_{cd}^{ik} \tilde{B}_{cd}^{jl} \langle \psi_j \psi_l | \psi_a \psi_k \rangle \\ &- \sum_{bcd} \sum_{kl} \tilde{B}_{ac}^{kl} B_{bd}^{kl} \langle \psi_b \psi_d | \psi_i \psi_c \rangle \\ &- \sum_{\substack{j \\ cb}} \sum_{\substack{k \\ d}} \left(\frac{1}{2} (\tilde{B}_{bd}^{ik} \tilde{B}_{cd}^{jk} + 3 B_{bd}^{ki} B_{cd}^{kj}) \langle \psi_j \psi_b | \psi_a \psi_c \rangle \right. \\ &\qquad\qquad \left. - \tilde{B}_{bd}^{ik} \tilde{B}_{cd}^{jk} \langle \psi_b \psi_j | \psi_a \psi_c \rangle \right) \\ &+ \sum_{\substack{kj \\ b}} \sum_{\substack{l \\ c}} \left(\frac{1}{2} (\tilde{B}_{ac}^{jl} \tilde{B}_{bc}^{kl} + 3 B_{ac}^{lj} B_{bc}^{lk}) \langle \psi_b \psi_j | \psi_i \psi_k \rangle \right. \\ &\qquad\qquad \left. - \tilde{B}_{ac}^{jl} \tilde{B}_{bc}^{kl} \langle \psi_j \psi_b | \psi_i \psi_k \rangle \right) \\ &+ \sum_{\substack{j \\ bc}} b_{0,ij} \tilde{B}_{bc}^{ij} \langle \psi_b \psi_c | \psi_a \psi_j \rangle - \sum_{\substack{jk \\ b}} b_{0,jk} \tilde{B}_{ab}^{jk} \langle \psi_j \psi_k | \psi_i \psi_b \rangle\end{aligned} \tag{44}$$

with

$$\begin{aligned}F_{pq} &= \langle \psi_p | \hat{h} | \psi_q \rangle + \sum_i (2\langle \psi_p \psi_i | \psi_q \psi_i \rangle - \langle \psi_p \psi_i | \psi_i \psi_q \rangle) \\ &= \langle \chi_p | \hat{F} | \chi_q \rangle.\end{aligned} \tag{45}$$

$\hat{F}$ is the HF operator.

Orbital invariance within the subspace of occupied orbitals is no longer guaranteed if the contraction factor equation (10) corresponding to CEPA(1) is employed so that $f_{ij} \neq 0$ (note, however, that orbital invariance within the subspace of virtual orbitals is still preserved in this case ($f_{ab} = 0$)). To avoid convergence problems the orbital optimization must still be restricted to orbital rotations between occupied and virtual orbitals. A unique set of orbitals can then be obtained by diagonalizing the occupied–occupied subblock of the Fock matrix defined in Eq. (45) such that $F_{ij} = F_{ii}\delta_{ij}$.

2.6 Brueckner orbitals

Singly excited states can be removed from a correlated wave function by employing the concept of Brueckner orbitals first introduced by Nesbet into quantum chemistry [16]. In contrast to the optimized orbitals, the Brueckner orbitals do not arise from a variational criterion but from the projective condition $\langle \Phi_i^a|\hat{H}|\Psi\rangle = 0$ which eliminates the amplitudes of the singles rather than omitting them a priori as in orbital optimized methods. It has been shown that the Brueckner condition yields a reference determinant which has maximum overlap with the exact wave function in the full CI case [39]. For methods limited to the amplitudes of double excitations like CID (BCID) or CCD (BCCD) the Brueckner condition reads

$$\langle \Phi_i^a|\hat{H}|\Phi_0 + \frac{1}{2}\sum_{\substack{kl\\cd}} C_{cd}^{kl}\Phi_{kl}^{cd}\rangle = 0. \tag{46}$$

Evaluating the matrix elements, Eq. (46) can be rewritten as

$$f_{ia}^{B} = 0 \tag{47}$$

with

$$\begin{aligned} f_{ia}^{B} = {} & F_{ia} + \sum_{\substack{j\\b}} \tilde{C}_{ab}^{ij} F_{jb} + \sum_{\substack{j\\bc}} \tilde{C}_{bc}^{ij}\langle \psi_b\psi_c|\psi_a\psi_j\rangle \\ & - \sum_{\substack{jk\\b}} \tilde{C}_{ab}^{jk}\langle \psi_j\psi_k|\psi_i\psi_b\rangle. \end{aligned} \tag{48}$$

Although the functionals discussed in this contribution do no longer correspond to a wave function approach, one can still determine Brueckner orbitals according to Eq. (48) if the definition Eq. (18) for intermediately normalized coefficients is used.

Noting that the matrix elements F_{ia} which vanish for HF orbitals are still rather small for Brueckner orbitals, it can be assumed that the first, third, and fourth term dominate the right-hand side of Eq. (48). Comparing the Brueckner condition equation (48) with the variational condition equation (44) for the optimized orbitals, it can be seen that these terms reappear in the latter if we assume $b_{0,ij} \approx 1$ which is a reasonable approximation for the single reference case. Since the remaining terms in Eq. (44) are of higher order in the amplitudes of the doubles, there is some similarity between the Brueckner condition equation (48) and the variational condition equation (44). That projected Brueckner orbitals might be close to variationally optimized orbitals has been conjectured by Kutzelnigg and Smith [40] and, in the case of the CCD method, by Sherill et al. [41].

The difference between Brueckner and variationally optimized orbitals has been discussed by several authors [16, 42, 43]. First, it should be noted that the two sets of orbitals are completely identical for a full CI wave function which is invariant with respect to any orbital transformation. Thus, an orbital rotation eliminating the singles will still correspond to the variational minimum of the energy so that the Brueckner orbitals are also variationally optimized in this case. It may also be argued that the orbital optimization is no longer clearly defined if the wave function approaches the exact wave function while the Brueckner condition ($\langle \Phi_i^a|\hat{H}|\Psi\rangle = 0$) always uniquely defines a certain reference determinant. For limited CI wave functions, however, the Brueckner orbitals are different from the variationally optimized orbitals. Dykstra [42] has compared the stability conditions for CISD wave functions including and excluding single excitations and has found that in the former case the fulfillment of the Brueckner condition would be a poorer approximation to the variational condition for the orbitals than for wave functions without the explicit inclusion of singles. Moreover, he has shown that the energy of the BCID method is always slightly higher than the energy obtained from the CISD method based on a HF reference determinant. Orbital optimization in CC theory can be performed by defining a Lagrange function including the equations for the CC amplitudes as constraints in the CC energy expression [36, 41, 43, 44]. The Lagrangian can be considered as a kind of CC energy functional [44]. For a truncated cluster operator, one can expect the optimized orbitals to be different from the Brueckner orbitals [43]. Moreover, Köhn and Olsen [43] found that orbital optimized CC, in contrast to Brueckner CC, does not converge to the full CI limit. In the light of these discussions, it might be of interest to compare the optimized orbitals to Brueckner orbitals.

3 Numerical results

Various formalisms based on Eqs. (7) and (9) with and without orbital optimization have been implemented in the MOLPRO program package [45] for the single-reference case. To distinguish the versions including orbital optimization from those without orbital relaxation, the suffix “O” is appended (ACPFO, VCEPAO). The optimized orbitals are determined in complete analogy to the Brueckner orbitals as described by Hampel et al. [32] except that the matrix elements arising from the Brueckner condition equation (48) have been replaced by those corresponding to the orbital gradient (see Eq. 44). In the case of CEPA, the prefix “V” indicates that a variational version is used. The difference to the original CEPA approach has been discussed in Sect. 2.4. In the following, all references to CEPA tacitly assume that the contraction factor equation (10) corresponding to CEPA(1) has been used.

The geometrical data for a small test set of molecules have been taken from the Computational Chemistry Comparison and Benchmark Database.[1] These geometries have been used in all tables referring to single point calculations in the following sections. Core electrons are kept frozen in all calculations and the aug-cc-pVQZ basis set has been used throughout [46].

The following results are mainly intended to demonstrate the advantage arising from the replacement of single excitations by orbital optimization and are obtained using the functionals ACPF and VCEPA. The difference between the optimized and the Brueckner orbitals will also be illustrated by numerical results.

Table 1 Electronic energies in atomic units for some small molecules as obtained from the CCSD, VCEPA, VCEPAO, ACPF, and ACPFO methods with the aug-cc-pVQZ basis set

	CCSD	VCEPA	VCEPAO	ACPF	ACPFO
H_2O	−76.354	−76.355	−76.355	−76.356	−76.355
NH_3	−56.487	−56.489	−56.488	−56.489	−56.488
HF	−100.369	−100.370	−100.369	−100.370	−100.369
LiF	−107.294	−107.295	−107.294	−107.295	−107.294
CO	−113.172	−113.176	−113.174	−113.177	−113.174
N_2	−109.387	−109.391	−109.390	−109.392	−109.390
H_2CO	−114.354	−114.358	−114.356	−114.359	−114.357
HCN	−93.284	−93.288	−93.287	−93.289	−93.287
RMS		3.0	1.9	3.7	2.0
MAE		2.6	1.5	3.3	1.6

The last two lines display the route mean square (RMS) error and the mean absolute error (MAE) with respect to the CCSD reference results for each method in units of 10^{-3} a.u.

3.1 Energies and dipole moments

The electronic energies obtained from both ACPF and VCEPA as well as from their modified counterparts ACPFO and VCEPAO with the single excitations being replaced by orbital rotations are shown in Table 1. The CCSD values are given as a reference. The energies obtained from the orbital optimized approaches are consistently higher than those resulting from the original methods thus being slightly closer to the CCSD energy. Nonetheless, the effect of the replacement of single excitations by orbital optimization is rather small for these simple molecules.

The dipole moments for the same set of molecules are shown in Table 2. They point in the direction of the z axis which represents the rotation axis for all molecules shown in Table 2. Assuming this axis to point from the left to the right, the H atoms are located to the right of the heavy atoms for H_2O, NH_3, and HF. The same holds for Li in LiF. The C atom is to the left of the O atom in both CO and H_2CO and to the left of the N atom in HCN. For the original CISD and ACPF methods the dipole moments are calculated both as an expectation value using the density matrices equation (28) and a response to an external electric dipole field using a finite field approach with the dipole field strength being set to 0.005 a.u. in all calculations. The distinction between expectation values and response values is not necessary for the modified method ACPFO where the expectation and response values are identical because the density matrix from which the expectation value is calculated is fully relaxed in this case. This statement does not hold strictly for VCEPAO where the orbital invariance of the energy is violated for the space spanned by the occupied orbitals. In practice, however, we did not observe a significant difference between response and expectation values for VCEPAO. This difference can get quite large for VCEPA and ACPF in some cases, e.g., CO and formaldehyde. This indicates that the first-order density matrices obtained from Eq. (28) can deviate significantly from the relaxed density matrices determining properties in the case of HF orbitals. Thus, the former are often not very accurate given for example the relatively large deviation of the expectation value of the dipole moment of CO from the experimental value of 0.04 a.u. Note the fairly good agreement of the dipole moments obtained from ACPFO and VCEPAO with the CCSD reference values. This observation is corroborated if the dipole moment of CO is considered as a function of the bond length as presented in Fig. 1 which shows only the ACPF values. The ACPFO results agree well with CCSD in contrast to the ACPF expectation values. The ACPF response values are closer to CCSD than the ACPF expectation values but the corresponding relaxed density matrices can only be obtained after solving coupled-perturbed HF equations.

CO is just one example to demonstrate the superiority of the orbital optimized methods with respect to molecular properties. The sensitivity of the dipole moment of CO with respect to the orbitals has already been noted by Ernzerhof et al. who conclude that the orbitals should carefully be tuned to the electron correlation treatment which is used [47]. However, there are molecules where orbital relaxation plays an even more pronounced role. A remarkable example of this kind is CuF. It has been shown that the QCI method [15] which in most cases gives results very close to those obtained from CCSD calculations fails for CuH and to an even larger extent for CuF [29]. This indicates the importance of orbital relaxation because QCI

---

[1] http://srdata.nist.gov/cccbdb.

Table 2 Dipole moments in atomic units for some small molecules as obtained from the CCSD, VCEPA, VCEPAO, ACPF, and ACPFO methods with the aug-cc-pVQZ basis set

	CCSD^b	VCEPA^a	VCEPA^b	VCEPAO	ACPF^a	ACPF^b	ACPFO
$H_2\overline{O}$	0.736	0.722	0.732	0.735	0.722	0.732	0.735
$\overline{N}H_3$	0.605	0.597	0.601	0.604	0.596	0.601	0.604
$H\overline{F}$	0.714	0.700	0.711	0.714	0.700	0.711	0.713
$Li\overline{F}$	2.495	2.473	2.490	2.498	2.472	2.490	2.497
$\overline{C}O$	0.023	0.105	0.028	0.022	0.116	0.033	0.026
$\overline{H}_2\overline{C}O$	−0.963	−0.885	−0.948	−0.951	−0.868	−0.942	−0.944
$\overline{HC}N$	−1.202	−1.165	−1.194	−1.195	−1.161	−1.192	−1.193
RMS		46.5	7.4	5.4	53.9	10.0	8.1
MAE		36.4	6.3	3.6	41.3	8.1	5.1

The last two lines display the RMS error and the MAE with respect to the CCSD reference results for each method in units of 10^{-3} a.u. Atoms on the negative half of the *z*-axis are marked with an overline

[a] Expectation value

[b] Response property

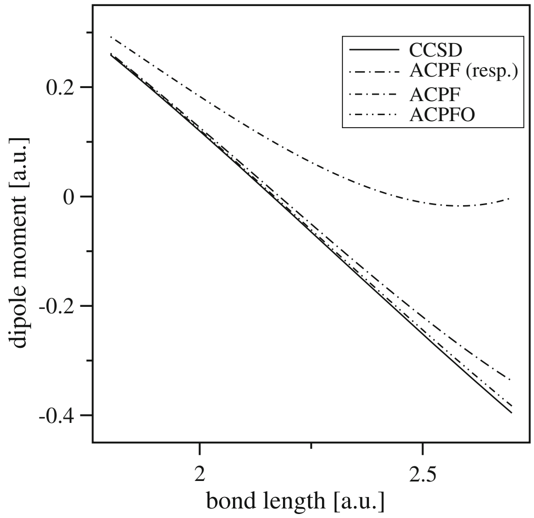

Fig. 1 Dipole moment of CO as a function of the C–O distance obtained from various methods using an aug-cc-pVQZ basis set

linearizes the single excitation operator whereas CCSD uses the full exponential thus being much less sensitive to the choice of the underlying MO basis than QCI. The relationship between application of the exponential of a single excitation operator and orbital relaxation has already been discussed in Sect. 2.5. The example of CuF shows that the linear approximation of the exponential is not always appropriate. This molecule should therefore be well-suited to demonstrate the effect of orbital optimization. The cc-pVQZ-PP basis set in connection with an effective core potential has been used for Cu [48]. The electronic energy and the dipole moment as a function of the Cu–F bond length for various methods are shown in Fig. 2. It can be seen that the energy curve obtained from ACPFO runs nicely parallel to the CCSD curve. The deviation of the conventional ACPF from the CCSD results is more pronounced and the energy minimum is shifted to the left. Much more interesting is again the dipole moment also shown in Fig. 2 with the Cu atom being located to the left of the F atom. We note the very good agreement between the CCSD and ACPFO results for all bond lengths. The conventional ACPF method, on the other hand, fails completely. The deviation is so large that even the calculation as a response property instead of an expectation value does not lead to a significant improvement. The error is particularly pronounced in the region near the equilibrium bond distance of about 3.25 Å. QCISD results are also shown in Fig. 2 indicating the failure of this method.

3.2 Geometries

Geometry optimizations for the molecular test set already shown in the preceding tables have also been performed. The results are given in Table 3. The differences between the orbital optimized methods and their unmodified counterparts are not very pronounced. Note, however, the excellent agreement of the bond lengths obtained from the orbital optimized methods with the CCSD reference values, especially for VCEPAO.

3.3 Spectroscopic constants for diatomic molecules

Spectroscopic constants for some diatomic molecules are presented in Table 4 which also shows the experimental values given by Huber and Herzberg [49]. We have also added results obtained from the perturbative inclusion of triples. These can be taken into account in analogy to

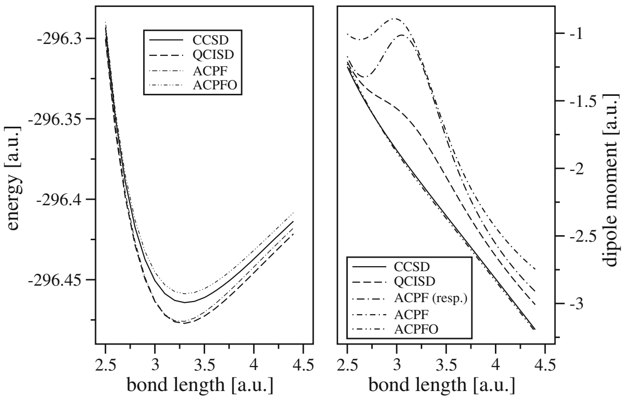

Fig. 2 Energy and dipole moment of CuF as a function of the Cu–F distance obtained from various methods using an aug-cc-pVQZ basis set

CCSD(T) [50] for the coupled-pair functionals. In the case of orbital optimization, the perturbation theory treatment requires a block diagonalization of the occupied-occupied and virtual–virtual subblocks of the Fock matrix.

Except for F_2, the replacement of single excitations by orbital optimization in the coupled-pair functionals shifts all results close to the corresponding CCSD or CCSD(T) reference values. This effect is again particularly pronounced for CuF where orbital relaxation plays an important role. Moreover, the perturbative inclusion of the triples leads to very good agreement with the experimental results. The case of F_2 is critical because this molecule exhibits an increased multireference character. While all methods considered here refer to a single reference determinant, the coupled-pair functionals deteriorate apparently faster than CCSD with increasing multireference character of the wave function. This deterioration is more pronounced for ACPF than for VCEPA. In the case of ACPFO(T), the energy curve for F_2 does not even exhibit a minimum in the range of bond lengths considered here.

Table 3 Optimized bond lengths and bond angles for some small molecules as obtained from the CCSD, VCEPA, VCEPAO, ACPF, and ACPFO methods with the aug-cc-pVQZ basis set

	CCSD	VCEPA	VCEPAO	ACPF	ACPFO	Exp.
H_2O						
l_{OH}	1.807	1.808	1.807	1.808	1.807	1.810
$\angle$HOH	104.55	104.53	104.59	104.56	104.57	104.48
NH_3						
l_{NH}	1.909	1.911	1.910	1.910	1.910	1.912
$\angle$HNH	106.82	106.68	106.73	106.72	106.71	106.67
N_2						
l_{NN}	2.066	2.069	2.066	2.071	2.068	2.075
CO						
l_{CO}	2.125	2.130	2.125	2.131	2.125	2.132
HF						
l_{HF}	1.729	1.730	1.729	1.730	1.729	1.733
LiF						
l_{HF}	2.979	2.982	2.978	2.980	2.978	2.955
H_2CO						
l_{CO}	2.269	2.274	2.270	2.277	2.272	2.277
l_{CH}	2.079	2.080	2.079	2.079	2.078	2.099
$\angle$OCH	121.74	121.72	121.67	121.69	121.66	121.90
HCN						
l_{CN}	2.172	2.176	2.173	2.177	2.174	2.184
l_{CH}	2.013	2.014	2.013	2.013	2.013	2.011
RMS						
l		3.0	0.6	3.9	1.4	
MAE						
l		2.6	0.4	2.8	1.0	
RMS						
$\angle$		0.08	0.07	0.06	0.08	
MAE						
$\angle$		0.06	0.07	0.05	0.07	

The RMS error and the MAE for various functionals with respect to the CCSD reference values are shown for the bond lengths (in units of 10^{-3} a.u.) and bond angles

3.4 Are the variationally optimized orbitals close to Brueckner orbitals?

The orbital optimized and the Brueckner approach share the common feature that single excitations do not appear. The differences between the two sets of orbitals have been discussed in Sects. 2.5 and 2.6. Both approaches refer to the same form of the energy functional which is obtained by omitting the singly excited states from Eq. (7) so that it might be of interest to compare the two sets of orbitals. It follows from the variational principle that the orbital optimized methods yield a lower electronic energy than the Brueckner method but the difference is very small and does not exceed 1 mH for our small test set of molecules. A possible difference between the two orbital sets may be detected in several ways. If the hypothesis that the Brueckner orbitals are close to the optimized orbitals is correct the total density matrices (Eqs. 28 and 29) obtained with the former should be almost fully relaxed, i.e., the dipole moments calculated as an expectation value should not deviate strongly from the corresponding value obtained as a response to an external dipole field. These values along with the Brueckner CCD (BCCD) results are given in Table 5. It can be seen that there is a considerable difference between the response and the expectation value in the case of CO.

The difference between Brueckner and optimized orbitals must also show up in the dipole moments obtained as

Table 4 Spectroscopic constants for some diatomic molecules as obtained from various methods with the aug-cc-pVQZ basis set

Method	Energy	r_e	B_e	α_e	ω_e	$\omega_e\chi_e$
N_2						
CCSD	−109.386848	1.093	2.015	0.0160	2,434.5	12.9
ACPF	−109.392460	1.096	2.005	0.0166	2,401.5	13.8
ACPFO	−109.390492	1.094	2.011	0.0163	2,423.0	13.4
VCEPA	−109.391467	1.095	2.008	0.0164	2,412.5	13.4
VCEPAO	−109.389574	1.093	2.014	0.0161	2,432.5	13.1
CCSD(T)	−109.407243	1.101	1.988	0.0170	2,354.6	13.9
ACPF(T)	−109.414832	1.105	1.972	0.0184	2,293.5	15.9
ACPFO(T)	−109.412220	1.102	1.981	0.0177	2,328.5	15.2
VCEPA(T)	−109.413551	1.104	1.976	0.0179	2,310.7	15.2
VCEPAO(T)	−109.411047	1.101	1.985	0.0173	2,343.1	14.5
Exp.		1.098	1.998	0.0173	2,358.6	14.3
CO						
CCSD	−113.171641	1.125	1.944	0.0163	2,231.4	12.1
ACPF	−113.176800	1.128	1.934	0.0172	2,193.0	13.4
ACPFO	−113.174071	1.125	1.944	0.0163	2,234.5	12.0
VCEPA	−113.176225	1.127	1.936	0.0171	2,199.7	13.2
VCEPAO	−113.173647	1.124	1.945	0.0162	2,237.2	12.0
CCSD(T)	−113.190371	1.132	1.920	0.0173	2,160.3	13.1
ACPF(T)	−113.198363	1.139	1.895	0.0203	2,062.6	17.7
ACPFO(T)	−113.194096	1.133	1.917	0.0174	2,152.5	13.3
VCEPA(T)	−113.197515	1.138	1.899	0.0198	2,077.1	16.9
VCEPAO(T)	−113.193520	1.132	1.918	0.0174	2,157.6	13.2
Exp.		1.128	1.931	0.0175	2,169.8	13.3
HF						
CCSD	−100.369106	0.915	21.046	0.7786	4,189.4	88.2
ACPF	−100.370065	0.916	21.012	0.7898	4,169.6	90.3
ACPFO	−100.369265	0.915	21.046	0.7860	4,183.7	89.8
VCEPA	−100.369900	0.915	21.020	0.7866	4,174.1	89.6
VCEPAO	−100.369111	0.915	21.053	0.7831	4,188.0	89.2
CCSD(T)	−100.377384	0.918	20.918	0.7877	4,142.1	89.5
ACPF(T)	−100.378840	0.919	20.859	0.8044	4,110.4	92.5
ACPFO(T)	−100.377807	0.918	20.907	0.7972	4,131.5	91.4
VCEPA(T)	−100.378645	0.919	20.868	0.8001	4,116.1	91.6
VCEPAO(T)	−100.377628	0.918	20.915	0.7933	4,136.7	90.6
Exp.		0.917	20.956	0.7980	4,138.3	89.9
F_2						
CCSD	−199.344390	1.390	0.918	0.0104	1,016.8	8.7
ACPF	−199.354609	1.428	0.871	0.0192	813.9	22.8
ACPFO	−199.352395	1.424	0.875	0.0200	818.5	25.4
VCEPA	−199.351272	1.407	0.897	0.0121	941.0	10.8
VCEPAO	−199.349153	1.404	0.901	0.0122	949.2	11.1
CCSD(T)	−199.365737	1.413	0.889	0.0125	921.5	11.4
ACPF(T)	−199.507134	2.083	0.409	−0.0041	2,527.4	39.8
ACPFO(T)	–	–	–	–	–	–
VCEPA(T)	−199.376055	1.450	0.844	0.0207	747.1	23.7
VCEPAO(T)	−199.373099	1.443	0.853	0.0204	768.1	24.4
Exp.		1.412	0.890	0.0138	916.6	11.2

Table 4 continued

Method	Energy	r_e	B_e	α_e	ω_e	$\omega_e\chi_e$
CuF						
CCSD	−296.464270	1.751	0.377	0.0031	613.7	3.4
QCISD	−296.477179	1.739	0.382	0.0032	667.6	4.8
ACPF	−296.476079	1.726	0.388	0.0038	709.4	7.2
ACPFO	−296.458737	1.751	0.377	0.0031	608.8	3.2
VCEPA	−296.472591	1.738	0.382	0.0031	673.8	5.1
VCEPAO	−296.458505	1.751	0.377	0.0031	608.8	3.3
CCSD(T)	−296.500440	1.743	0.380	0.0032	619.1	3.5
QCISD(T)	−296.489367	1.757	0.374	0.0037	445.7	−7.7
ACPF(T)	−296.557422	1.693	0.403	0.0026	1,103.8	15.6
ACPFO(T)	−296.497712	1.738	0.382	0.0032	620.3	3.4
VCEPA(T)	−296.539415	1.718	0.392	0.0017	914.5	9.2
VCEPAO(T)	−296.497351	1.739	0.382	0.0033	620.3	3.5
Exp.		1.745	0.379	0.0032	622.6	4.0

Experimental values are also shown. The energies are given in atomic units, bond lengths r_e in Ångström, whereas the equilibrium rotational constant B_e, the vibration–rotation interaction constant α_e, the harmonic frequency ω_e, and the anharmonicity $\omega_e\chi_e$ are given in cm^{-1}

Table 5 Dipole moments in atomic units for some small molecules as obtained from the BCCD, BACPF and ACPFO methods with the aug-cc-pVQZ basis set

	BCCD[a]	BACPF[a]	BACPF[b]	ACPFO
$H_2\overline{O}$	0.737	0.736	0.724	0.735
$\overline{N}H_3$	0.606	0.604	0.599	0.604
$H\overline{F}$	0.715	0.714	0.701	0.713
$Li\overline{F}$	2.499	2.499	2.480	2.497
$\overline{C}O$	0.020	0.025	0.089	0.026
$\overline{H_2}\overline{C}O$	−0.966	−0.945	−0.901	−0.944
$\overline{HC}\ N$	−1.203	−1.193	−1.168	−1.193

In the case of BACPF, both the expectation and the response value are given. Atoms on the negative half of the *z*-axis are marked with an overline

[a] Response property

[b] Expectation value

Table 6 Dipole moments in atomic units for some small molecules as obtained from single determinant wave functions formed with the HF, BCCD, BACPF, and ACPFO orbitals

	HF	BCCD	BACPF	ACPFO
$H_2\overline{O}$	0.780	0.741	0.740	0.751
$\overline{N}H_3$	0.637	0.610	0.609	0.614
$H\overline{F}$	0.756	0.717	0.716	0.728
$Li\overline{F}$	2.540	2.491	2.491	2.508
$\overline{C}O$	−0.104	0.053	0.056	−0.007
$\overline{H_2}\overline{C}O$	−1.116	−0.961	−0.949	−0.993
$\overline{HC}N$	−1.295	−1.209	−1.202	−1.227

Atoms on the negative half of the *z*-axis are marked with an overline

an expectation value from the corresponding reference determinants. These are given in Table 6 including the dipole moments arising from the Brueckner coupled cluster doubles (BCCD) reference determinant. The good agreement of the latter with the BACPF values indicates a close resemblance between the BACPF and the BCCD orbitals. The fairly large difference between the ACPFO and BACPF values in cases like CO leads again to the conclusion that the difference between the two sets of orbitals can not in general be neglected.

It may also be noted that the dipole moments obtained from the Brueckner determinants are clearly superior to the HF values. The agreement of the values obtained from the BCCD reference determinant shown in Table 6 and the corresponding CCSD values in Table 2 is fairly good. In the case of CO, there is not only a sign change but also the largest difference between HF and BCCD values for all molecules shown in Table 6. It has been observed before that Brueckner orbitals are more appropriate for the calculation of molecular properties than HF orbitals [51]. This can be ascribed to the fact that the Brueckner determinant is the determinant which has maximum overlap with the total wave function thus being closer to it than the determinant formed with any other set of orbitals.

4 Conclusion

The role of orbital transformations in coupled-pair energy functionals has been discussed. The most striking property of the orbital optimized ACPF functional is its fully variational nature with respect to all variables, i.e, both the orbital coefficients and the amplitudes of the double excitations. Thus, fully relaxed density matrices are directly obtained without the necessity to solve coupled-perturbed equations. This advantage can hardly be overestimated with respect to the calculation of response properties. It has also been demonstrated that orbital optimized coupled-pair functionals lead to improved results as compared to their unmodified counterparts including single excitations. This improvement is particularly pronounced in cases with strong orbital relaxation effects. Taking CuF as an example, it has been shown that the conventional ACPF method fails completely in this case whereas the ACPF with orbital optimization is still well-behaved. The agreement with the CCSD reference values is in general very good and clearly better than for the conventional ACPF method. Moreover, the elimination of the single excitations removes an ambiguity indicated by the difference between the ACPF [20], the ACPF-2 [30], and the NACPF [25] methods. Since the solution of the *Z*-vector equations [22] necessary to obtain relaxed density matrices for CCSD is as costly as solving the CCSD equations itself, we conclude that the orbital optimized methods presented here offer a considerably cheaper alternative for obtaining relatively accurate density matrices. The direct availability of correlated densities and first and second-order density matrices is not only advantageous for the calculation of molecular properties but could also be exploited to determine intermolecular electrostatic and first-order exchange energies in the framework of intermolecular perturbation theories, see e.g., Refs. [52, 53].

Finally, a word with respect to the computational efficiency of the orbital optimized methods might be appropriate. The scaling is the same as for the conventional methods with the most expensive step scaling as m^2N^4 if N is the number of basis functions and m the number of valence orbitals. However, it has to be admitted that our present implementation is rather slow. For the small molecules considered here, the CPU times are increased by a factor of roughly 2.5 as compared to the corresponding methods without orbital optimization. The bottleneck is the integral transformation of the electron repulsion integrals which has to be performed in each iteration cycle in the case of orbital optimized methods and takes more than one half of the time per iteration cycle for all molecules considered here. In particular, our present implementation performs the integral transformation for integrals with up to three external indices leading to mN^4 scaling of this step. This seems to be cheap compared to the aforementioned m^2N^4 scaling arising from the most unfavorable term in the residuals, i.e., the one involving integrals with four external indices but the prefactor is apparently very unfavorable. Thus, the integral transformation has to be avoided for the integrals with three external indices in an efficient implementation. This can be achieved by performing the corresponding contractions in the AO basis as described by Hampel et al. [32] and will be considered in future implementations. Moreover the additional cost in orbital optimized methods due to the integral transformation step can greatly be reduced with density-fitting methods, see e.g. Ref. [54].

Acknowledgment C. K. would like to thank F. Neese and H.-J. Werner for stimulating discussions.

References

1. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8:61
2. Davidson ER, Silver DW (1977) Chem Phys Lett 52:403
3. Bartlett RJ, Shavitt I (1977) Int J Quantum Chem Quantum Chem Symp 11:165
4. Siegbahn PEM (1978) Chem Phys Lett 55:386
5. Meissner L (1988) Chem. Phys Lett 146:204
6. Pople JA, Seeger R, Krishnan R (1977) Int J Quantum Chem Quantum Chem Symp 11: 149
7. Møller C, Plesset MS (1934) Phys Rev 46:618
8. Meyer W (1973) J Chem Phys 58:1017
9. Kelly HP (1964) Phys Rev 134:A1450
10. Ahlrichs R (1979) Comp Phys Commun 17:31
11. Kutzelnigg W (1977) In: Methods of electronic structure theory. Schaefer HF III (ed) Plenum Press, New York, pp 129–188
12. Čižek J (1966) J Chem Phys 5:4256
13. Čižek J (1969) Adv Chem Phys 14:35
14. Bartlett RJ (1981) Annu Rev Phys Chem 32:359
15. Pople JA, Head-Gordon M, Raghavachari K (1987) J Chem Phys 87:5968
16. Nesbet RK (1958) Phys Rev 109:1632
17. Handy NC, Pople JA, Head-Gordon M, Raghavachari K, Trucks GW (1989) Chem Phys Lett 164:185
18. Pulay P (1983) Int J Quantum Chem Quantum Chem Symp 17:257
19. Ahlrichs R, Scharf P, Ehrhardt C (1985) J Chem Phys 82:890
20. Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413
21. Szalay PG, Bartlett RJ (1993) Chem Phys Lett 214:481
22. Handy NC, Schaefer HF III (1984) J Chem Phys 81:5031
23. Kollmar C (2006) J Chem Phys 125:084108
24. Nooijen M, Le Roy RJ (2006) J Mol Struct (Theochem) 768:25
25. Wennmohs F, Neese F (2008) Chem Phys 343:217
26. Bak KL, Jørgensen P, Ohlsen J, Helgaker T, Klopper W (2000) J Chem Phys 112:9229
27. Neese F, Hansen A, Wennmohs F, Grimme S (2008) Acc Chem Res 42:641
28. Ahlrichs R, Driessler F, Lischka H, Staemmler V, Kutzelnigg W (1975) J Chem Phys 62:1235
29. Hrušák J, Ten-no S, Iwata S (1997) J Chem Phys 106:7185
30. Gdanitz RJ (2001) Int J Quantum Chem 85:281
31. Pulay P, Saebø S, Meyer W (1997) J Chem Phys 81:1901
32. Hampel C, Peterson KA, Werner HJ (1992) Chem Phys Lett 190:1
33. Eugene DePrince A III, Mazziotti DA (2007) Phys Rev A 76:042501
34. DePrince AE III, Mazziotti DA (2007) Phys Rev A 76:042501
35. Mazziotti DA (2008) Phys Rev Lett 101:253002
36. Scuseria GE, Schaefer HF III (1987) Chem Phys Lett 142:354
37. Jørgensen P, Simons J (1981) Second quantization based methods in quantum chemistry. Academic Press, New York, pp 10–13

38. Levy B (1969) Chem Phys Lett 4:17
39. Brenig W (1957) Nucl Phys 4:363
40. Kutzelnigg W, Smith V (1964) The independent-particle model for many–electron systems. I. Comparison of different independent particle model approximations. Preprint No. 130, Quantum Chemistry Group, Uppsala
41. Sherill CD, Krylov AI, Byrd EFC, Head-Gordon M (1998) J Chem Phys 109:4171
42. Dykstra CE (1977) Chem Phys Lett 45:466
43. Köhn A, Olsen J (2005) J Chem Phys 122:084116
44. Bartlett RJ, Musial M (2007) Rev Mod Phys 79:291
45. Werner HJ, Knowles PJ, Lindh R, Manby FR, Schütz M et al (2006) Molpro, version 2006.1, a package of ab initio programs. See http://www.molpro.net
46. Dunning TH Jr (1989) J Chem Phys 90:1007
47. Ernzerhof M, Marian CM, Peyerimhoff SD (1993) Chem Phys Lett 204:59
48. Peterson KA, Puzzarini C (2005) Theor Chem Accts 114:283
49. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure. IV. Constants of diatomic molecules. Van Nostrand Reinhold, New York
50. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) J Chem Phys 157:479
51. Heßelmann A, Jansen G (1999) Chem Phys Lett 315:248
52. Korona T, Jeziorski B (2006) J Chem Phys 125:184109
53. Korona T (2006) J Chem Phys 128:224104
54. Werner HJ, Manby FR, Knowles PJ (2003) J Chem Phys 118:8149