

Excited states theory for optimized orbitals and valence optimized orbitals coupled-cluster doubles models

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We introduce an excited state theory for the optimized orbital coupled cluster doubles (OO-CCD) and valence optimized orbital coupled cluster doubles (VOO-CCD) models. The equations for transition energies are derived using a similarity transformed Hamiltonian. The effects of orbital relaxation are discussed. We present results for several single-reference molecules (H_2O , CH_2O , $\text{C}_2\text{H}_4\text{O}$, C_2H_4 , BeO), as well as for molecules with significant nondynamical correlation in the ground state (CH^+ , BH , $\tilde{A}^1A_1 \text{CH}_2$), and for rectangular O_4^+ . We find that: (i) OO-CCD excitation energies are very close to CCSD excitation energies; (ii) similarly to the complete active space SCF (CASSCF) model, the effects of orbital relaxation are very important for VOO-CCD excited states such that the excitation energies calculated by VOO-CCD and CASSCF with orbitals optimized for the ground state are very close to each other and unsatisfactory; (iii) the VOO-CCD model with an approximate treatment of orbital relaxation describes singly (valence and Rydberg) and doubly (valence) excited states within errors of 0.2–1.0 eV at equilibrium geometries and along bond-breaking coordinates; (iv) the above accuracy of the VOO-CCD model does not degrade as molecules or basis sets grow in size; (v) the shapes of potential energy surfaces around excited states minima are reproduced well by VOO-CCD model suggesting the use of this method for excited states geometry optimization. © 2000 American Institute of Physics. [S0021-9606(00)30540-2]

I. INTRODUCTION

Recently, we have reported an optimized orbital coupled-cluster doubles (OO-CCD) electronic structure model in which the orbitals are obtained variationally by minimizing the energy with respect to orbital rotations between occupied and virtual subspaces.¹ This model had been considered before,^{2,3} although previously no practical algorithm had been reported. The orbitals obtained by this procedure¹ may be considered approximate Brueckner orbitals, in the sense that they approximate the “true” Brueckner orbitals^{4,5} of the full configuration interaction wave function. This approach contrasts with the typical Brueckner CCD (B-CCD) method,⁶ which obtains approximate Brueckner orbitals by a projection equation involving singly substituted determinants. For the well-behaved molecules, both B-CCD and OO-CCD ground state energies are very close to those of coupled cluster singles and doubles (CCSD) model. However, for certain symmetry breaking cases, e.g., the $^4B_{1g}$ state of rectangular O_4^+ , B-CCD, and OO-CCD are superior to CCSD for the prediction of harmonic vibrational frequencies. The variationally determined approximate Brueckner orbitals simplify analytic gradients and, as has been recently re-emphasized,⁷ do not give unphysical second-order poles in the linear response functions.^{8,9}

Moreover, the variational definition of Brueckner orbit-

als was generalized by Krylov *et al.*¹⁰ for the case when all nonvalence orbitals are made inactive, or restricted. The resulting valence optimized orbitals CCD (VOO-CCD) model has been shown^{10,11} to be an accurate and size-consistent approximation to a full valence active space complete active space SCF (CASSCF) model for such multireference cases as single bond dissociation and diradicals. The computational cost of the VOO-CCD model is proportional to the sixth power of molecule size, which breaks a factorial bottleneck of CASSCF and therefore allows us to perform calculations in a full valence space for much larger molecules (up to a bound 10 heavy atoms). The attractive property of the VOO-CCD model is that it is free of arbitrariness in the selection of configurations and in the choice of orbital space (since the variationally optimized full valence active space is uniquely defined), and therefore it satisfies the requirements of a *theoretical model chemistry*.¹² Its principal limitation is that VOO-CCD cannot correctly break multiple bonds, due to the restriction to double substitutions.

In this work we present an excited state theory for the OO-CCD and VOO-CCD models. There are several alternative recipes for calculating excited states for the given approximate ground state wave function (see, for example, Ref. 13), such as (i) calculate transition energies as linear response of the given ground state wave function perturbed by

an oscillating electric field; (ii) propagators and Green functions methods; and (iii) equation of motion (EOM) method. The resulting equations for transition energies are very similar. As far as further approximations are concerned, the Tamm–Dancoff approximation^{14,15} is often employed which simplifies the equations and usually does not considerably affect the quality of the excitation energies. The quality of transition energies calculated in these ways is closely related to the quality of the ground state wave function. Below we briefly review several widely used excited state theories.

The configuration interaction singles (CIS) (Refs. 16,17) model based on the Hartree–Fock ground state wave function is very inexpensive (as the Hartree–Fock model itself), and can give qualitatively accurate results for closed shell molecules at equilibrium geometry (errors of 0.5–2 eV). The important limitations of CIS model are: (i) doubly excited electronic states cannot be described; (ii) errors for valence states of some radicals can become very large (more than 2 eV); (iii) just like the Hartree–Fock model itself, CIS cannot describe potential energy surfaces (PES’s) along bond-breaking coordinates. The equation-of-motion CC singles and doubles (EOM-CCSD) or linear response CC (CCSDLR) models^{18,19} can describe singly excited states at equilibrium geometry with remarkable accuracy (0.1–0.3 eV). However, doubly excited electronic states are approximated much more poorly (errors of 1 eV and more). Finally, these methods cannot give reliable PES’s since CCSD is a single-reference model. Models based on multireference wave functions,^{20–46} such as CASSCF (Refs. 20–25) and CASSCF augmented by second-order perturbation theory corrections for dynamical correlation (CASPT2),^{26,27} multireference configuration interaction (MRCI),^{29,30} and multireference CC (MRCC) (Refs. 32–46) are capable of describing excited state PES’s and doubly excited states. Unfortunately, careful selection of the active orbital space and of important configurations has to be performed for each individual molecule and each particular chemical process when using these ‘‘molecule-at-a-time’’ models.

The theoretical treatment of the excited states is more difficult than the multireference ground state problem. One of the reasons is that for the ground state we can consider a CASSCF wave function defined in a full valence active space as a qualitatively correct (and size-consistent) ground state wave function, and then approximate it either by reducing the active space based on physical considerations, or, as we advocate, approximating the full configuration interaction expansion in the active space by a CC expansion.¹⁰ However, the active space required for the excited state calculations does not necessarily coincide with the full valence space; consider, for example, Rydberg excited states, where the Rydberg orbital is certainly not valence-like. Therefore different active spaces for each group of excited states are often used in multireference calculations, e.g., six different active spaces have been employed in a CASSCF study of excited states of formaldehyde.⁴⁷

Our goal here is to investigate an alternative approach, which does not require a case-by-case selection of orbital space and important configurations and thus can be applied in a general fashion. Given these considerations, our target

excited state wave function can be defined as the linear response of a ground state full valence active space CASSCF wave function with an explicit treatment of orbital relaxation. We approximate this target theory by replacing the CASSCF wave function with the much more economical VOO-CCD approach.

Here we derive equations for the (V)OO-CCD transition energies by using the EOM formalism.^{48,19} We also present an alternative (EOM) derivation of the (V)OO-CCD equations,¹ which re-emphasizes the similarity between the multiconfigurational SCF (MCSCF) and VOO-CCD models by employing biorthogonal properties of the EOM formalism.¹⁹ Coupled cluster response functions and calculation of transition energies have been discussed by many authors.^{49,50,48,51,18,19,52,8,9,53,54,7} Recently, Koch and co-workers⁷ presented a derivation of OO-CCD response equations by using a time-dependent coupled-cluster Lagrangian. The applications of the response formalism for MCSCF wave functions for excited state calculations have also been discussed.^{55–58}

The structure of the paper is the following: in Sec. II we present excited state equations for the (V)OO-CCD model; Sec. III presents transition energies calculated by OO-CCD and VOO-CCD models for several single-reference molecules (H₂O, CH₂O, C₂H₄O, C₂H₄, BeO), as well as for molecules with significant nondynamical correlation in the ground state (CH⁺, BH, CH₂), and for rectangular O₄⁺; and a comparison with other excited state models. Programmable expressions for the excited state equations and details of computational implementation are presented in the Appendix. Our final remarks and conclusions are given in Sec. IV.

II. GENERAL THEORY

In this section, we derive equations for the (V)OO-CCD transition energies using the EOM formalism.^{48,19} We also present an alternative (EOM) derivation of (V)OO-CCD equations,¹ which re-emphasizes the similarity between MCSCF and VOO-CCD models by employing biorthogonal properties of the EOM formalism.¹⁹

Following Bartlett and co-workers,^{48,19} we start with the following ansatz for the wave function:

$$|\Psi\rangle = R e^T |\Phi_0\rangle, \quad (1)$$

$$R = R_0 + R_1 \cdots + R_n, \quad (2)$$

$$T = T_1 + \cdots + T_n, \quad (3)$$

where $|\Phi_0\rangle$ is a reference Slater determinant and R_k , T_k are k -fold excitation operators from this reference,

$$R_0 = r_0, \quad R_1 = \sum_{ia} r_i^a a^+ i, \quad R_2 = \frac{1}{4} \sum_{ijab} r_{ij}^{ab} a^+ b^+ j i, \\ \dots \quad (4)$$

$$T_1 = \sum_{ia} a_i^a a^+ i, \quad T_2 = \frac{1}{4} \sum_{ijab} a_{ij}^{ab} a^+ b^+ j i, \\ \dots$$

By inserting Eq. (1) into the Schrödinger equation we obtain

$$H \text{Re}^T |\Phi_0\rangle = E \text{Re}^T |\Phi_0\rangle. \quad (5)$$

Since R and T commute (both are excitation operators), Eq. (5) can be rewritten as an eigenvalue problem for an effective, i.e., similarity transformed Hamiltonian \bar{H} ,

$$\bar{H}R |\Phi_0\rangle = ER |\Phi_0\rangle, \quad (6)$$

$$\bar{H} = e^{-T} H e^T. \quad (7)$$

Since Hamiltonian \bar{H} is not a Hermitian operator, the bra eigenstates of \bar{H} are not Hermitian conjugates of its ket eigenstates, but a contravariant set such that bra's and ket's form a biorthogonal set. This means that operator L is inverse of R ,

$$\langle \Phi_0 | L \bar{H} = E \langle \Phi_0 | L, \quad (8)$$

$$L = L_0 + L_1 + \dots + L_n, \quad (9)$$

$$\langle \Phi_0 | LR |\Phi_0\rangle = \hat{1} \quad (L = R^{-1}), \quad (10)$$

where we have chosen the normalization constant to be unity, and where L_k are de-excitation operators,

$$L_1 = \sum_{ia} l_i^a i^+ a, \quad L_2 = \frac{1}{4} \sum_{ijab} l_{ij}^{ab} i^+ j^+ b a, \quad (11)$$

...

If no truncation has been made to R and L , the solution of Eqs. (6) and (8) would give an exact energies, since a similarity transformation does not change the eigenvalues of the Hamiltonian. Moreover, the energies from Eqs. (6) and (8) would be invariant with respect to any unitary transformation of orbitals, no matter whether the reference state changes or not as result of this transformation.

At this point we introduce approximations by truncating R and L to single and double substitutions, and T to double substitutions only. With this approximation, the eigenenergies of \bar{H} do vary upon orbital transformations. We are going to find such a unitary transformation which minimizes the total energy.¹

Consider unitary transformation of molecular orbitals (MO's) given by the unitary matrix U ,

$$C = C^0 U, \quad (12)$$

where $C_{\mu p}$ and $C_{\mu p}^0$ are coefficients giving the contribution of the μ th atomic orbital (AO) to the p th MO for a transformed, $\{|p\rangle\}$, and for some initial, $\{|p^0\rangle\}$, set of orbitals, respectively. The corresponding transformation \mathcal{U} of the Fock space is a unitary one, $\mathcal{U}\mathcal{U}^+ = 1$, defined by the following equations:¹³

$$p^+ = \mathcal{U} p^0 + \mathcal{U}^+ = \sum_q q^0 + U_{qp}, \quad (13)$$

$$p^{0+} = \mathcal{U}^+ p^+ \mathcal{U} = \sum_q U_{pq} q^+, \quad (14)$$

$$\mathcal{U}|\rangle = |\rangle, \quad (15)$$

where p^+ 's stand for creation operators and the last equation states the vacuum invariance.

The effect of this transformation is to replace the initial orbitals with the transformed ones in every determinant,

$$\begin{aligned} \mathcal{U}|\Phi^0\rangle &= \mathcal{U} p^{0+} q^{0+} \dots r^{0+} |\rangle \\ &= \mathcal{U} p^{0+} \mathcal{U}^+ \mathcal{U} q^{0+} \mathcal{U}^+ \dots \mathcal{U} r^{0+} \mathcal{U}^+ |\rangle = |\Phi\rangle. \end{aligned} \quad (16)$$

As a next step consider variations of \mathcal{U} and a convenient parameterization for \mathcal{U} . Allowed variations of \mathcal{U} preserve the unitarity of \mathcal{U} , and therefore

$$\delta\mathcal{U}\mathcal{U}^+ + \mathcal{U}\delta\mathcal{U}^+ = 0 \quad (17)$$

which means that the operator $\delta\mathcal{U}\mathcal{U}^+$ is anti-Hermitian,

$$\delta\mathcal{U}\mathcal{U}^+ = \Lambda, \quad \Lambda^+ = -\Lambda, \quad (18)$$

which gives the following expression for the variation $\delta\mathcal{U}$:

$$\delta\mathcal{U} = \Lambda\mathcal{U}, \quad \delta\mathcal{U}^+ = -\mathcal{U}^+\Lambda. \quad (19)$$

Operator Λ can be parameterized as

$$\Lambda = \sum_{rs} \Delta_{rs} r^+ s, \quad (20)$$

where Δ is antisymmetric matrix.

Such parameterization is equivalent to parameterizing transformation \mathcal{U} as: $\mathcal{U} = e^{\Lambda}\mathcal{U}^c$, where \mathcal{U}^c is some (current) transformation. It allows us to consider small variations $\delta\mathcal{U}$ when the transformation itself can be *large*.

Consider now the energy of the wave function (1) and its variation with the orbital transformation:

$$E = \langle \Psi_L | H | \Psi_R \rangle = \langle \Psi_L^0 | \mathcal{U}^+ H \mathcal{U} | \Psi_R^0 \rangle, \quad (21)$$

$$\begin{aligned} \delta E &= \langle \Psi_L^0 | \delta\mathcal{U}^+ H \mathcal{U} + \mathcal{U}^+ H \delta\mathcal{U} | \Psi_R^0 \rangle \\ &= \langle \Psi_L^0 \mathcal{U}^+ | [H, \Lambda] | \mathcal{U} \Psi_R^0 \rangle = \langle \Psi_L | [H, \Lambda] | \Psi_R \rangle. \end{aligned} \quad (22)$$

To solve for the ground state we are going to determine amplitudes T_2 and the transformation \mathcal{U} such that the ket ground state of Eq. (6) is simply $|\Phi_0\rangle$ and its energy is minimal with respect to orbital rotations ($\delta E = 0$). To ensure the biorthogonality condition (10), the bra ground state must be taken as $\langle \Phi_0 | (1 + Z_2) e^{-T_2} = \langle \Psi_L |$, where the de-excitation operator Z_2 is equivalent to the Z -vector appearing in the coupled-cluster response theory. This yields the following set of equations:

$$\begin{aligned} E &= \langle \Phi_0 | (1 + Z_2) e^{-T_2} | H | e^{T_2} \Phi_0 \rangle \\ &= \langle \Phi_0 | H | (1 + T_2) \Phi_0 \rangle, \end{aligned} \quad (23)$$

$$0 = \delta E = \langle \Phi_0 | (1 + Z_2) e^{-T_2} | [H, \Lambda] | e^{T_2} \Phi_0 \rangle. \quad (24)$$

$$\langle \Phi_{ij}^{ab} | (\bar{H} - E) | \Phi_0 \rangle = 0, \quad (25)$$

$$\langle \Phi_0 | (1 + Z_2) | (\bar{H} - E) | \Phi_{ij}^{ab} \rangle = 0, \quad (26)$$

where Eq. (23) defines the energy, and Eqs. (25) and (26) define amplitudes T_2 and Z_2 . The resulting equations for the amplitudes are the same as equations derived in Ref. 1 by using a response approach.

Equation (24) is an alternative form for the stationary condition of energy with respect to orbital rotations. This form allows us to re-emphasize the similarity between the MCSCF and (V)OO-CCD models, and to derive Eqs. (31)–

(34) from Ref. 1 in a simpler way. Moreover, this form allows us to describe orbital relaxation for the excited states in the same fashion.

Following the derivations of the MCSCF equations as given by McWeeny,¹³ in order to derive equations for the orbital rotation gradient, $\partial E/\partial U_{rs}$, we rewrite commutator $[H, \Lambda]$ as

$$\begin{aligned} [H, \Lambda] &= \sum_{st} \Delta_{st} (s^+ [H, t] + [H, s^+] t) \\ &= \sum_{st} \Delta_{st} \left(- \sum_q \langle q|h|t \rangle s^+ q + \sum_q \langle s|h|q \rangle q^+ t \right. \\ &\quad - \frac{1}{2} \sum_{quv} \langle uv||qt \rangle s^+ q^+ uv \\ &\quad \left. + \frac{1}{2} \sum_{pqu} \langle su||pq \rangle p^+ q^+ ut \right). \end{aligned} \quad (27)$$

By defining the one- and two- electron density matrices,¹⁹

$$\rho_{pq} = \langle \Psi_L | p^+ q | \Psi_R \rangle, \quad \pi_{pqrs} = \langle \Psi_L | p^+ q^+ sr | \Psi_R \rangle, \quad (28)$$

the energy variation assumes the following form:

$$\begin{aligned} \delta E &= \langle \Psi_L | [H, \Lambda] | \Psi_R \rangle \\ &= \text{Tr} \{ \Delta^+ ([h, \rho] + \frac{1}{2} [\Pi, \pi]) \} \\ &= \sum_{st} \Delta_{st} \left(\sum_q (-\rho_{sq} \langle q|h|t \rangle + \langle s|h|q \rangle \rho_{qt}) \right. \\ &\quad \left. + \frac{1}{2} \sum_{pqu} (-\pi_{supq} \langle qp||ut \rangle + \langle su||pq \rangle \pi_{qpqt}) \right), \end{aligned} \quad (29)$$

where Π denotes the supermatrix of two-electron integrals.

Since Δ is an antisymmetric matrix, Eq. (29) can be rewritten as

$$\begin{aligned} \delta E &= \text{Tr} \{ \Delta^+ (2\gamma h + \Gamma \Pi) \} \\ &= \sum_{st} \Delta_{st} \left(2 \sum_q \gamma_{sq} \langle q|h|t \rangle + \sum_{quv} \Gamma_{squv} \langle uv||qt \rangle \right), \end{aligned} \quad (30)$$

where γ and Γ are symmetrized density matrices,

$$\gamma_{pq} = \frac{1}{2} (\rho_{pq} + \rho_{qp}), \quad \Gamma_{pqrs} = \frac{1}{2} (\pi_{pqrs} + \pi_{rspq}). \quad (31)$$

By using properties of the trace,

$$\begin{aligned} \delta E &= \text{Tr} \left\{ \delta U^+ \frac{\partial E}{\partial U} \right\} = \text{Tr} \{ U \Delta^+ (2\gamma h + \Gamma \Pi) U^+ \} \\ &= \sum_{st} (\Delta U)_{st} \left(2 \sum_q \gamma_{sq} \langle q|h|t^0 \rangle \right. \\ &\quad \left. + \sum_{quv} \Gamma_{squv} \langle uv||qt^0 \rangle \right). \end{aligned} \quad (32)$$

Thus, the orbital gradient $\partial E/\partial U$ is given by

TABLE I. Effective one- and two-electron density matrices defined by Eqs. (28) and (31).^a

$\gamma_{ij} = \tilde{\gamma}_{ij} + \delta_{ij}$
$\gamma_{ab} = \tilde{\gamma}_{ab}$
$\Gamma_{ijkl} = 4\tilde{\Gamma}_{ijkl} - \delta_{il}\tilde{\gamma}_{jk} - \delta_{jk}\tilde{\gamma}_{il} + \delta_{jl}\tilde{\gamma}_{ik} + \delta_{ik}\tilde{\gamma}_{lj} + \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$
$\Gamma_{abcd} = 4\tilde{\Gamma}_{abcd}$
$\Gamma_{ijab} = 2\tilde{\Gamma}_{ijab}$
$\Gamma_{iajb} = \tilde{\Gamma}_{iajb} + \delta_{ij}\gamma_{ab}$

^a $\tilde{\gamma}$ and $\tilde{\Gamma}$ denote density matrices from Ref. 1.

$$\begin{aligned} \frac{\partial E}{\partial U_{sr}} &= 2 \sum_q \gamma_{rq} \langle q|h|s^0 \rangle + \sum_{upq} \Gamma_{rupq} \langle qp||us^0 \rangle \\ &= 2 \sum_q \gamma_{rq} \langle s^0|h|q \rangle + \sum_{upq} \Gamma_{rupq} \langle s^0 u||pq \rangle. \end{aligned} \quad (33)$$

For the ground (V)OO-CCD state, Eqs. (31)–(34) from Ref. 1 are easily retrieved from Eq. (33) by establishing the relationships between density matrices defined by Eqs. (28), (31) and density matrices defined in Table I of Ref. 1. These relations are given in Table I. Table II contains effective density matrices for the excited states. For the ground state, density matrices defined by Eqs. (28) and (31) are equivalent to density matrices derived by response theory. For excited states, however, density matrices from Eqs. (28), (31) and Table II do not describe the response of orbitals and amplitudes T_2 to a perturbation, and thus represent an approxima-

TABLE II. Excited state's effective one- and two-electron density matrices defined by Eqs. (28) and (31).^a

$t_{ij}^{ab} = r_{ij}^{ab} + \frac{1}{2} r_0 a_{ij}^{ab}$
$u_{ij}^{ab} = r_{ij}^{ab} + r_0 a_{ij}^{ab}$
$\gamma_{ij} = \tilde{\gamma}_{ij} + \delta_{ij}$
$\tilde{\gamma}_{ij} = -\frac{1}{2} \sum_a (l_i^a r_j^a + l_j^a r_i^a) - \frac{1}{4} \sum_{kab} (l_{ik}^{ab} u_{jk}^{ab} + l_{jk}^{ab} u_{ik}^{ab})$
$\gamma_{ia} = \frac{1}{2} r_0 l_i^a + \frac{1}{2} \sum_{jb} (l_j^b u_{ij}^{ab} + l_{ij}^{ab} r_j^b) + \frac{1}{2} \sum_{jkb} l_{jk}^{bc} (a_{ij}^{ab} r_k^c + \frac{1}{2} a_{ij}^{bc} r_k^c + \frac{1}{2} a_{jk}^{ab} r_i^c)$
$\gamma_{ab} = \frac{1}{2} \sum_i (l_i^a r_i^b + l_i^b r_i^a) + \frac{1}{4} \sum_{ijc} (l_{ij}^{ac} u_{ij}^{bc} + l_{ij}^{bc} u_{ij}^{ac})$
$\Gamma_{ijkl} = \tilde{\Gamma}_{ijkl} - \delta_{il}\delta_{kj} + \delta_{ki}\delta_{lj} - \delta_{li}\tilde{\gamma}_{jk} + \delta_{ki}\tilde{\gamma}_{jl} + \delta_{lj}\tilde{\gamma}_{ik} - \delta_{kj}\tilde{\gamma}_{il}$
$\tilde{\Gamma}_{ijkl} = \frac{1}{4} \sum_{ab} (l_{ki}^{ab} u_{ij}^{ab} + l_{ij}^{ab} u_{kl}^{ab})$
$\Gamma_{abcd} = \frac{1}{4} \sum_{ij} (l_{ij}^{ab} u_{ij}^{cd} + l_{ij}^{cd} u_{ij}^{ab})$
$\Gamma_{ijka} = \tilde{\Gamma}_{ijka} - \delta_{kj}\gamma_{ia} + \delta_{ki}\gamma_{ja}$
$\tilde{\Gamma}_{ijka} = \frac{1}{2} \sum_b (l_k^b u_{ij}^{ab} + l_{ij}^{ab} r_k^b) + \frac{1}{2} \sum_{lbc} l_{kl}^{bc} (a_{ij}^{ab} r_l^c + a_{jl}^{ab} r_i^c - a_{il}^{ab} r_j^c - \frac{1}{2} a_{il}^{bc} r_j^a + \frac{1}{2} a_{jl}^{bc} r_i^a + \frac{1}{2} a_{ij}^{bc} r_l^a)$
$\Gamma_{ijab} = \frac{1}{2} (a_{ij}^{ab} + r_0 l_{ij}^{ab}) - \frac{1}{2} \sum_{kc} l_{kc}^{bc} (-a_{ic} r_k^b + a_{jk}^{ac} r_i^b + a_{ij}^{ac} r_k^b + a_{bc} r_i^a - a_{jk}^{bc} r_i^a - a_{ij}^{bc} r_k^a + a_{ik} r_j^c - a_{jk} r_i^c) - \frac{1}{2} \sum_{klcd} l_{kl}^{cd} (\frac{1}{2} a_{ik}^{cd} l_{jl} - \frac{1}{2} a_{jk}^{cd} l_{il} - \frac{1}{4} a_{ij}^{cd} l_{kl} + \frac{1}{2} a_{ik}^{ac} l_{jl} + a_{jk}^{bd} l_{il} + \frac{1}{2} a_{ij}^{ac} l_{kl} - \frac{1}{2} a_{kl}^{bc} l_{ij} + a_{bc} l_{kl}^{ad} - a_{jk}^{ad} l_{il} - \frac{1}{2} a_{ij}^{bc} l_{kl} - \frac{1}{4} a_{kl}^{ab} l_{ij} + \frac{1}{2} a_{ik}^{cd} l_{jl} - \frac{1}{2} a_{jk}^{cd} l_{il})$
$\Gamma_{iajb} = \tilde{\Gamma}_{iajb} + \delta_{ij}\gamma_{ab}$
$\tilde{\Gamma}_{iajb} = -\frac{1}{2} (l_i^b r_j^a + l_j^b r_i^a) - \frac{1}{2} \sum_{kc} (l_{ik}^{bc} u_{jk}^{ac} + l_{jk}^{bc} u_{ik}^{ac})$
$\Gamma_{iabc} = \frac{1}{2} \sum_j (l_j^a u_{ij}^{bc} + l_{ij}^{bc} r_j^a) - \frac{1}{2} \sum_{jkd} l_{jk}^{ad} (\frac{1}{2} a_{jk}^{bd} r_i^c + a_{ij}^{bd} r_k^c - \frac{1}{2} a_{jk}^{cd} r_i^b - a_{ij}^{cd} r_k^b - \frac{1}{2} a_{jk}^{bc} r_i^d - a_{ij}^{bc} r_k^d)$

^aHere it is assumed that left and right excited states are biorthogonalized such that $\sum_i l_i^a r_i^a + \frac{1}{4} \sum_{ijab} l_{ij}^{ab} r_{ij}^{ab} = 1$, and factor r_0 insures orthogonality of the right excited states to the left ground state, and thus is $r_0 = -\frac{1}{4} \sum_{ijab} z_{ij}^{ab} r_{ij}^{ab}$. Excited left states do not mix with the reference, thus $l_0 = 0$.

tion to fully relaxed density matrices from response theory. Stanton and Bartlett¹⁹ have compared calculation of certain properties, e.g., excited state dipole moments and transition dipole moments, by using such unrelaxed density matrices and by using density matrices from response theory. Their results¹⁹ have demonstrated that neglect of orbital and T_2 relaxation has only a minor effect on properties. However, analytic nuclear gradients calculation would require calculation of fully relaxed density matrices.^{59,60}

A. Excited state equations

To obtain equations for the excited states, we rewrite Eq. (6) as follows:

$$[\bar{H}, R]|\Phi_0\rangle = \omega R|\Phi_0\rangle, \quad (34)$$

where ω is the transition energy,

$$\omega = E_{\text{ex}} - E_{\text{gs}} = \langle \Phi_0 | L \bar{H} R | \Phi_0 \rangle - \langle \Phi_0 | \bar{H} | \Phi_0 \rangle. \quad (35)$$

Such a definition of the transition energy ω is consistent only if ground state solution and excited states are noninteracting across the Hamiltonian, i.e., if the following is true:

$$\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0, \quad (36)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0. \quad (37)$$

For OO-CCD model, Eq. (37) is satisfied by Eq. (25). However, Eq. (36), which would be satisfied for projective B-CCD, is not exactly satisfied for OO-CCD. Thus, EOM-OO-CCD excited states interact across the Hamiltonian with the ground state. However, since variationally optimized orbitals are very nearly equivalent to the projective Brueckner orbitals,¹ the corresponding matrix elements are very small. We also note that a linear response treatment allowing time-dependence in the orbitals and the amplitudes would be formally consistent and the present approach is expected to be like a Tamm–Dancoff approximation to this full result.

As the next step, we project Eq. (34) with the singly, Φ_i^a , and doubly, Φ_{ij}^{ab} , excited determinants. Equations for right eigenvectors, $(R_1 \ R_2)$, and left ones, $(L_1 \ L_2)$, can be written in a matrix form as follows:

$$\begin{pmatrix} A & X \\ Y & B \end{pmatrix} \begin{pmatrix} R_1 \\ R_2 \end{pmatrix} = \omega \begin{pmatrix} R_1 \\ R_2 \end{pmatrix}, \quad (38)$$

$$(L_1 \ L_2) \begin{pmatrix} A & X \\ Y & B \end{pmatrix} = \omega (L_1 \ L_2), \quad (39)$$

where A , B , X , Y are different blocks of the transformed Hamiltonian. We solve Eqs. (38) and (39) by using a generalization of Davidson's iterative diagonalization procedure,^{61,62} which requires calculation of products of the transformed Hamiltonian matrix with trial vectors,

$$\begin{aligned} \sigma_i^a &= (AR_1)_i^a + (XR_2)_i^a, \\ \sigma_{ij}^{ab} &= (YR_1)_{ij}^{ab} + (BR_2)_{ij}^{ab}, \end{aligned} \quad (40)$$

$$\begin{aligned} \tilde{\sigma}_i^a &= (L_1A)_i^a + (L_2Y)_i^a, \\ \tilde{\sigma}_{ij}^{ab} &= (L_1X)_{ij}^{ab} + (L_2B)_{ij}^{ab}. \end{aligned} \quad (41)$$

Expressions for different blocks are given by

$$\begin{aligned} (AR_1)_i^a &= \langle \Phi_i^a | H | (R_1 + R_1 T_2) \Phi_0 \rangle - r_i^a E \\ (XR_2)_i^a &= \langle \Phi_i^a | H | R_2 \Phi_0 \rangle, \\ (YR_1)_{ij}^{ab} &= \langle \Phi_{ij}^{ab} | H | (R_1 + R_1 T_2) \Phi_0 \rangle, \\ (BR_2)_{ij}^{ab} &= \langle \Phi_{ij}^{ab} | H | (R_2 + R_2 T_2) \Phi_0 \rangle - r_{ij}^{ab} E, \\ (L_1A)_i^a &= \langle \Phi_0 | L_1 | H | (1 + T_2) \Phi_i^a \rangle - l_i^a E, \\ (L_2Y)_i^a &= \langle \Phi_0 | L_2 | H | (1 + T_2) \Phi_i^a \rangle, \\ (L_1X)_{ij}^{ab} &= \langle \Phi_0 | L_1 | H | \Phi_{ij}^{ab} \rangle, \\ (L_2B)_{ij}^{ab} &= \langle \Phi_0 | L_2 | H | (1 + T_2) \Phi_{ij}^{ab} \rangle - l_{ij}^{ab} E. \end{aligned} \quad (42)$$

Programmable expressions, intermediates, and details of implementation are given in the Appendix.

B. Orbital relaxation

If the orbital relaxation is significant, one can explicitly optimize the energies of excited states with respect to the orbital rotation by using Eq. (33) and excited state density matrices defined by Eqs. (28), (31) and given in Table II. This is similar to the CASSCF method, when orbitals are optimized individually for each state. In this work we do not consider such explicit orbital relaxation. It is desirable in principle, but computationally very demanding in practice. Instead, we are going to qualitatively analyze the effect of orbital relaxation for excited states and include the effects of orbital relaxation in an approximate way. The approximate description is based on considering the first variation of the energy with respect to orbital rotation. The energy variation is given by Eq. (22), and equals the expectation value of commutator of the Hamiltonian and operator Λ describing small orbital rotations and defined by Eq. (20) on the CC wave function.

To proceed with the analysis, we rewrite Λ such that only non-redundant terms are left. For OO-CCD model, only mixing between occupied and virtual orbital subspaces affects the energy,

$$\Lambda = \sum_{ia} \Delta_{ai} (a^+ i - i^+ a). \quad (43)$$

When acting on the operators $R = R_0 + R_1 + R_2$, Λ generates single, double, and triple excitations (the appearance of triple excitations in EOM-CCSD equations when orbital relaxation is accounted for has been discussed by Sekino and Bartlett⁴⁸). Single and double excitations are already present in the excited state wave function, and therefore, orbital relaxation for the singly excited states is approximately described. However, since triple excitations are omitted in EOM-CCSD/OO-CCD excited state theory, orbital relaxation for doubly excited states is not well described. Since excitation of two electrons can cause considerable changes in orbitals, and since the relaxation effects are totally disregarded, one can expect larger errors for doubly excited states in EOM-CCSD/OO-CCD theory with unrelaxed orbitals. This is an alternative explanation of the poor performance of EOM-CCSD/OO-CCD for doubly excited states.

For the VOO-CCD model, there are four different orbital subspaces,¹⁰ i.e., restricted core, active occupied (valence), active virtual (valence), and restricted virtual spaces. The non-redundant terms in Λ are then

$$\Lambda = \sum_{ia} \Delta_{ai}(a^+i - i^+a) + \sum_{i''j'} \Delta_{i''j'}(i''^+j' - j'^+i'') \\ + \sum_{a'b''} \Delta_{b''a'}(b''^+a' - a'^+b''), \quad (44)$$

where " and ' are used to distinguish between restricted and active orbitals, respectively. If one is interested in valence excited states, operators R_1 and R_2 would be restricted to the valence space. If orbital relaxation was explicitly described, such a wave function is an approximation of the CASSCF wave function. When Λ acts on R_0 and valence space R_1 and R_2 , it generates the following terms: (i) From R_0 —all single excitations; (ii) from R_1 —single excitations from core orbitals to valence virtuals, single excitations from valence occupied orbitals to the restricted virtual orbitals, and double excitations where one electron is excited within the active space, and a second electron is excited from any occupied to any virtual; (iii) from R_2 —double excitations where one electron is excited from a core orbital, and the second from an active orbital, both to the active orbitals; double excitations where both electrons are excited from valence orbitals so that one electron is excited to valence virtual, and the second to a restricted virtual orbital; and triple excitations such that two electrons are excited within the valence space, and a third electron is excited from any occupied orbital to any virtual orbital.

Thus, for singly excited valence states an approximate description of orbital relaxation can be given by allowing single excitations in the whole space, as it is done in the multiconfigurational linear response (MCLR) (Refs. 55–58) model. However, the description of Rydberg states would be less accurate, because for these states single excitations outside the valence space are required to describe the state itself. Relaxation of doubly excited states would be completely neglected by this model. One can improve the model by allowing selected double excitations from the valence space, when one of the electrons is excited within the active space. It is appropriate to employ terminology from multireference theory⁶³ and call excitations restricted to the active space as internal excitations and excitations with one excitation restricted to the active space as semi-internal excitations. This classification has been also used in coupled-cluster theory when an active space is introduced.⁶⁴

In this work we consider two models which provide an approximate treatment of orbital relaxation. In the first model, we restrict operator R_2 to the valence space only (internal doubles), and operator R_1 is defined in the whole space. This model can be considered as an approximation to a MCLR (Refs. 55–58) wave function with the MCSCF reference being the full valence space CASSCF wave function. We expect that such a wave function would give its most accurate results for valence single excited states, and will be poorer for Rydberg states and doubly excited states. A second model allows for double excitations from the valence

space such that one electron is excited within the active space and a second electron is excited either from a core orbital to the valence space or from a valence orbital to a restricted orbital (internal and semi-internal doubles).

For both models Eq. (36) is not satisfied, though corresponding coupling elements are small. Potentially more serious effects can be caused by the fact that for that second model, i.e., with semi-internal doubles, Eq. (37) is no longer satisfied either. The definition of the transition energy by Eq. (35) could cause an unbalanced description of ground and excited states: semi-internal doubles would partially describe dynamical correlation effects for the excited states, while dynamical correlation is not present in the ground state VOO-CCD wave function. The extent to which these formal concerns have practical chemical consequences will be assessed by numerical tests in the following section.

III. RESULTS AND DISCUSSION

In this section we present transition energies calculated by EOM-OO-CCD and EOM-VOO-CCD models for several single-reference molecules (H_2O , CH_2O , $\text{C}_2\text{H}_4\text{O}$, C_2H_4 , BeO), as well as for molecules with a significant nondynamical correlation in the ground state (CH^+ , BH , $\tilde{A}^1A_1 \text{CH}_2$), and for symmetry-breaking rectangular O_4^+ . The results are compared with other excited state models. For the sake of brevity, we will further refer to the EOM-(V)OO-CCD transition energies as to (V)OO-CCD transition energies.

All electrons are correlated for the OO-CCD calculations. All VOO-CCD and CASSCF ground state calculations were performed in the full valence active space, with core orbitals being restricted. For the VOO-CCD model, we report excitation energies calculated with (i) no orbital relaxation, i.e., internal R_2, L_2 and R_1, L_1 defined in the whole space; and (ii) approximate treatment of orbital relaxation, i.e., internal and semi-internal R_2, L_2 .

We compare the internal (unrelaxed) VOO-CCD model with CASSCF calculations where orbitals are optimized for the ground state only. The purpose here is to address the question of the relative importance of orbital relaxation for the excited states vs nondynamical correlation. We want to understand whether the VOO-CCD excited state wave function is flexible enough to give results of CASSCF quality with individually optimized orbitals, or whether the omitted higher excitations are an essential limitation of the model which cannot be recovered by orbital optimization. Semi-internal VOO-CCD is compared with CASSCF with individually optimized orbitals in order to demonstrate the performance of this approximate treatment of orbital relaxation.

Calculations were performed using two *ab initio* packages: Q-CHEM (Ref. 65) and PSI.⁶⁶ Our program for (V)OO-CCD ground and excited states calculations is linked to both platforms, and soon will become available through a new release of Q-CHEM.⁶⁷ Full CI results were obtained using the determinant-based CI program DETCI,^{68,69} and all CASSCF calculations were performed using a new program written by C.D.S., which has been interfaced to DETCI. CCSD results were obtained using the ACESII *ab initio* program.⁷⁰ Some

TABLE III. Vertical excitation energies (eV) for water (DZ basis set).

State	FCI ^a	CCSD ^b	OO-CCD ^c	CIS ^b	CASSCF ^{d,e}	VOO-CCD ^{e,f}	CASSCF ^{d,g}	VOO-CCD ^{f,h}
1 ¹ B ₁	8.696	8.58	8.55	9.57	17.03	9.55	8.74	8.10
1 ¹ A ₂	10.798	10.72	10.69	11.38	17.64	11.52	10.81	10.17
2 ¹ A ₁	10.840	10.74	10.71	11.63	27.13	11.90		10.49
1 ¹ B ₂	13.272	13.21	13.19	13.76	21.37	14.26	13.48	12.99

^aReference 72.^bReference 52.^cOO-CCD total energy is $-76.155\,940$ hartree.^dCASSCF total energy is $-76.064\,997$ hartree.^eOrbitals are optimized for the ground state.^fVOO-CCD total energy is $-76.064\,893$ hartree.^gIndividually optimized orbitals.^hOrbital relaxation is approximately described by semi-internal double excitations.

basis sets used in this work were obtained from the EMSL database.⁷¹

A. H₂O

Our first test case is the H₂O molecule. Water does not exhibit significant nondynamical correlation at equilibrium geometry, and its lowest excited states are one-electron excitations. Two sets of calculations have been performed: (i) using a small basis set, such that comparison against FCI calculations⁷² is possible; and (ii) using a very large basis set,¹⁸ such that comparison with experimental results is possible. The comparison between (i) and (ii) elucidates the question of the basis set dependence of the results.

Table III shows excitation energies calculated using the double- ζ (DZ) basis and geometry of the FCI benchmark paper of Saxe *et al.*⁷² CIS and CCSD results are taken from Rico and Head-Gordon.⁵² Experimental results are cited from Ref. 18.

The OO-CCD and CCSD energies are very close: the difference between the two models does not exceed 0.03 eV. Both models approximate FCI energies closely, within 0.1 eV. By contrast, the VOO-CCD model with internal doubles gives errors of 0.7–1.0 eV, which exceeds errors even of the CIS model (0.5–0.9 eV). To investigate the source of these errors, we performed model CASSCF calculations, where orbitals were optimized for the ground state. This model completely disregards orbital relaxation for excited states, and so calculated excitation energies are, as expected, very poor and errors are of the same order of magnitude as excitation energies. The errors of this model are much larger than errors of the internal VOO-CCD model, because single excitations outside the active space which are allowed in the latter partially describe relaxation effects. An important observation, however, can be made by comparing the *trend* in the error behavior: for both models the errors, though are very different in magnitude, are parallel, as demonstrated in Fig. 1. This suggests that the source of large VOO-CCD errors is an insufficient treatment of orbital relaxation, rather than omitted higher excitations. When we correct the VOO-CCD model by including semi-internal double excitations, the performance is improved. Overall errors for VOO-CCD with such approximate treatment of orbital relaxation are negative, within 0.3–0.6 eV. The CASSCF model with individually optimized orbitals exhibits very tiny errors of 0.01–

0.2 eV. We expect that explicit orbital optimization for the VOO-CCD excited states would make VOO-CCD excitation energies close to CASSCF excitation energies.

Table IV shows results of calculations performed with a large basis set from Ref. 18, and experimental excitation energies. The contraction scheme is $(12s8p4d)/[8s6p4d]$ for oxygen and $(6s4p)/[4s3p]$ for hydrogen. Six Cartesian *d*-functions as in Ref. 52 have been used. Calculations have been performed at the experimental geometry: $r_{\text{OH}}=1.809$ bohr and $\alpha_{\text{HOH}}=104.5^\circ$ (the nuclear repulsion and Hartree–Fock energies are 9.194 180 and $-76.054\,115$ hartree, respectively). There is a small discrepancy between the geometry used in the previous papers,^{18,52} and in this work: we

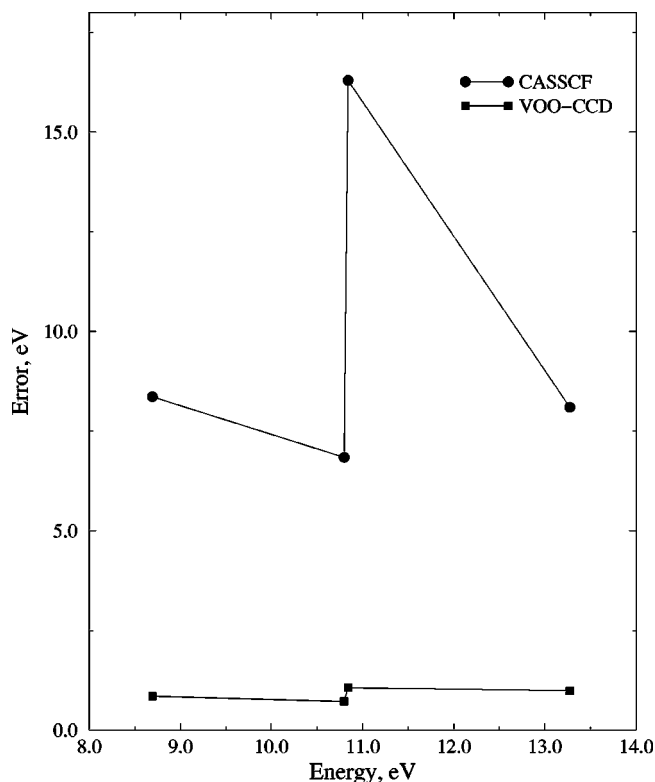


FIG. 1. VOO-CCD errors against FCI as functions of FCI excitation energies for the H₂O molecule, with the DZ basis set. CASSCF and VOO-CCD models with orbitals optimized for the ground are compared. Similar behavior of errors suggests that the source of VOO-CCD errors is in insufficient treatment of orbital relaxation.

TABLE IV. Vertical excitation energies (eV) for water (large basis set).

State	CCSD ^a	OO-CCD ^b	CIS ^c	VOO-CCD ^{d,e}	VOO-CCD ^{d,f}	Expt.
1 ¹ B ₁	7.49	7.47	8.66	8.76	6.80	7.4
2 ¹ B ₁	9.86	9.84		11.21	9.47	10.0
1 ¹ A ₂	9.23	9.22	10.33	10.49	8.58	9.1
2 ¹ A ₁	9.77	9.75	10.90	11.22	9.42	9.7
3 ¹ A ₁	10.09	10.08		11.67	9.85	10.17
1 ¹ B ₂	11.19	11.18	12.55	12.71	10.84	

^aCCSD total energy is $-76.316\,091$ hartree.

^bOO-CCD total energy is $-76.316\,436$ hartree.

^cReference 52.

^dVOO-CCD total energy is $-76.107\,121$ hartree.

^eOrbitals are optimized for the ground state.

^fOrbital relaxation is approximately described by semi-internal double excitations.

could not reproduce STO-3G results from Ref. 52. We have also noticed that CCSD results are different between Ref. 52 and Ref. 18. For these reasons, we have recalculated CCSD excitation energies.

Similarly to the small basis set, the difference between CCSD and OO-CCD excitation energies does not exceed 0.02 eV, and both models reproduce experimental excitation energies within 0.1–0.2 eV.

The errors of the VOO-CCD model with internal doubles becomes larger (1.2–1.5 eV), and, as in the small basis set, they are slightly larger than the errors of the CIS model. For this basis set, the valence active space CASSCF model with orbitals optimized for the ground state is irrelevant, since all the excited states except 1 ¹B₁ state are Rydberg states. The VOO-CCD model with internal and semi-internal doubles underestimates excitation energies by 0.3–0.6 eV (the largest error observed for the valence state). The fact that VOO-CCD errors do not increase in the large basis set is very encouraging, since it demonstrates that the potential imbalance introduced into the model by inclusion of semi-internal double excitations has only a minor numerical effect.

To explore what magnitude of errors could arise from the completely unbalanced treatment of dynamical correlation, we have performed calculations with a purposely unbalanced model, where the ground state was described by a VOO-CCD wave function, and excited states were described by single and double excitations in the whole orbital space. Such a model completely omits dynamical correlation for the ground state, but includes a significant part for the excited states, therefore it is expected to (i) underestimate excitation energies significantly and (ii) exhibit strong basis set dependence. For the H₂O molecule, such a model underestimates excitation energies by 0.3–1.2 eV in a DZ basis, and by 1.0–2.3 eV in the large basis set.

Another interesting observation has been made by us when we investigated the importance of core relaxation — it has been found to be very important for this particular system. Fig. 2 shows VOO-CCD errors (OO-CCD results with restricted core are quite similar) against experimental excitation energies as a function of excitation energy. Three models differ by a description of core orbital relaxation: model *a* completely neglects core relaxation (core is frozen for ex-

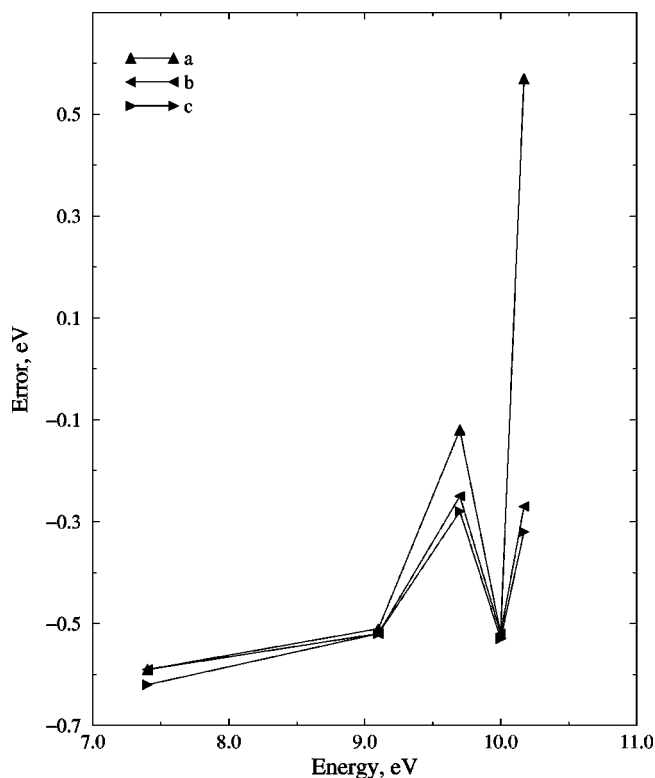


FIG. 2. Errors against experimental excitation energies as functions of experimental excitation energies for the H₂O molecule. Model *a* completely neglects core relaxation (core is frozen for excited state calculation). Model *b* allows single excitations from core orbital, i.e., describes partially core relaxation. Model *c* in addition to these single excitations, allows for double excitations where one electron is excited from core to the valence orbital, and second electron is excited from valence to valence orbital.

cited state calculation). Model *b* allows single excitations from the core orbital, i.e., it describes partially core relaxation. Model *c* in addition to these single excitations, allows for the semi-internal core-valence double excitations (when one electron is excited from core to the valence orbital, and second electron is excited from valence to valence orbital). As Fig. 2 demonstrates, core relaxation effects are very non-uniform, and for the 3 ¹A₁ state give as much as 0.8 eV difference! The 3 ¹A₁ state is a mixture of the excitations from 3b₁ and 2a₁ orbitals to high Rydberg orbitals. Since 2a₁ orbital is the lowest valence orbital, the hole created by excitation can strongly perturb core electrons, which explains the observed effects. Overall performance of the model is improved when core relaxation is accounted for; errors become smaller and more uniform. Similar effects have been also observed in the small (DZ) basis set. For other systems studied here core relaxation effects have been found to be less dramatic, but still considerable. Interestingly, core relaxation effects for water are insignificant for EOM-CCSD calculations with Hartree–Fock orbitals; apparently this effect arises as a result of using Brueckner orbitals.

B. CH₂O

Our second test case is the formaldehyde molecule, for which all the lowest excited states are single excitations. Our results are summarized in Table V. The CIS and CCSD en-

TABLE V. Vertical excitation energies (eV) for formaldehyde.

State	CCSD ^a	OO-CCD ^b	CIS ^a	VOO-CCD ^{c,d}	VOO-CCD ^{e,c}	CASSCF ^f	CPT2F ^f	Expt.
2 ¹ A ₁ (R)	8.00	8.00	9.66	10.07	7.75	7.63	8.09	8.14
3 ¹ A ₁ (R)	9.27	9.26	10.88	10.94	8.92	8.78	9.24	
4 ¹ A ₁ (R)	9.52 ^g	9.52		11.44	9.22			
5 ¹ A ₁ (V)	10.00	9.99	9.45	11.76	9.61	10.24	9.77	
1 ¹ A ₂ (V)	3.95	3.91	4.48	5.01	3.08	4.62	3.91	4.07,3.79
2 ¹ A ₂ (R)	8.23	8.22	9.78	10.24	7.99	8.17	8.32	8.37
3 ¹ A ₂ (R)	9.63 ^g	9.64		11.23	9.45	9.08	9.31	9.22
4 ¹ A ₂ (V)	10.38 ^g	10.41		11.59	9.60			
1 ¹ B ₂ (R)	7.06	7.06	8.63	8.91	6.72	6.88	7.30	7.11
2 ¹ B ₂ (R)	7.89	7.89	9.36	9.82	7.65	7.70	8.12	7.97
3 ¹ B ₂ (R)	9.07	9.07	10.61	10.99	8.80	8.56	9.13	8.88
4 ¹ B ₂ (R)	9.40	9.39	10.86	11.32	9.11	8.70	9.31	
1 ¹ B ₁ (V)	9.26	9.22	9.66	10.51	8.45	10.18	9.09	
2 ¹ B ₁ (R)	10.75 ^g	10.74		12.47	10.65	8.49	9.23	

^aReferences 73–75.^bOO-CCD total energy is $-114.291\,526$ hartree.^cVOO-CCD total energy is $-114.033\,762$ hartree.^dOrbitals are optimized for the ground state.^eOrbital relaxation is approximately described by semi-internal double excitations.^fReference 47.^gThis work.

ergies have been calculated with the 6-311(2+,2+)G** basis set and are from Refs. 73–75. CASSCF and CASPT2F calculations⁴⁷ have been obtained with an extended ANO basis set (C,O[4s3p1d]/H[2s1p]) with a 1s1p1d set of Rydberg functions contracted from a set of 8s8p8d primitives), and with four active electrons (the active space used for different states is different, its size varies from three to seven orbitals). Experimental energies are cited from Ref. 47. OO-CCD and VOO-CCD calculations of formaldehyde excitation energies have been performed with a 6-311(2+,2+)G** basis set (pure *d*-functions have been used), at the MP2 6-31G* optimized geometry reported by Hadad *et al.*:⁷⁶ $r_{CO} = 1.220$ Å, $r_{CH} = 1.104$ Å, $\alpha_{OCH} = 122.19^\circ$ (nuclear repulsion energy is 31.016 023 hartree).

OO-CCD energies are again very close to those of CCSD: the difference does not exceed 0.01 eV. Both models reproduce experimental values within 0.1–0.2 eV. The errors of CIS model vary from 0.4 eV for the lowest valence state to 1.5–1.7 eV for the Rydberg and higher valence states.

Similarly to the previous example, errors of VOO-CCD with internal doubles are quite large (larger than those of CIS). The error for the valence *A*₂ state is smaller than errors for Rydberg states, because for the valence state single excitations from the valence space are capable of approximately describing orbital relaxation, whereas for Rydberg states these single excitations are employed to describe the electron promotions and therefore cannot account for the orbital relaxation. Moreover, we expect orbital relaxation to become more important when the excited electron is promoted to a diffuse orbital, and the remaining core becomes more cation-like, as happens in Rydberg states.

Allowing semi-internal doubles improves results consistently, and makes them better than CIS. The resulting errors are very close to those of the CASSCF model. For most states the errors are negative and in the range of 0.2–0.4 eV.

The largest error has been observed for the lowest valence state; the excitation energy is underestimated by 0.7–0.99 eV. The CASSCF error for this state is also largest; the energy is overestimated by 0.55–0.8 eV. Excitation energies for the rest of the states are underestimated by CASSCF model by about 0.1–0.5 eV.

Therefore for formaldehyde the VOO-CCD model with an approximate description of orbital relaxation (internal and semi-internal doubles) performs similarly to CASSCF with state-average orbital optimization.⁴⁷ The important advantage of the VOO-CCD model, however, is that no selection of active space is required (since the whole valence space can be made active for much larger systems due to reduced computational demands), while the CASSCF calculations⁴⁷ have been performed with active spaces selected individually for each group of excited states.

C. CH₃CHO

Comparing results for formaldehyde with the larger acetaldehyde molecule can help to assess whether or not any potential imbalance in VOO-CCD (introduced by inclusion of semi-internal double excitations) would worsen as molecules grow in size. Calculations have been performed with a 6-311(2+)G* basis set (pure *d*-functions have been used), at the MP2 6-31G* optimized geometry reported by Hadad *et al.*:⁷⁶ (nuclear repulsion energy is 69.399 788 hartree), as in Ref. 75. The results are summarized in Table VI. CCSD, CIS, and experimental energies are cited from Ref. 75.

The errors of VOO-CCD with semi-internal doubles are only 0.1–0.2 eV, except for the valence 1 ¹A'' state, for which VOO-CCD underestimates the excitation energy by 0.8 eV. As for formaldehyde, VOO-CCD represents a considerable improvement over CIS. In this case at least, the performance of VOO-CCD does not degrade as the molecule

TABLE VI. Vertical excitation energies (eV) for acetaldehyde.

State	CCSD ^a	CIS ^b	VOO-CCD ^{c,d}	Expt.
2 ¹ A' (R)	6.78	8.51	6.66	6.82
3 ¹ A' (R)	7.49	9.22	7.39	7.46
4 ¹ A' (R)	7.68	9.30	7.62	7.75
5 ¹ A' (R)	8.39	10.19	8.35	8.43
6 ¹ A' (R)	8.51	10.26	8.44	8.69
1 ¹ A'' (V)	4.26	4.89	3.46	4.28
2 ¹ A'' (R)	7.64	9.37	7.55	
3 ¹ A'' (R)	8.57	10.31	8.53	
4 ¹ A'' (V)	9.23	9.78	9.06	

^aReferences 73 and 75.^bReference 76.^cVOO-CCD total energy is $-153.154\,287$ hartree.^dOrbital relaxation is approximately described by semi-internal double excitations.

grows in size. We expect this to be approximately true in general, because dynamical correlation originates primarily in *local* interactions. Using semi-internal double excitations which partly account for dynamical correlation should therefore not be artificially degraded by the addition of remote functional groups. More significant effects may arise in large molecules with highly delocalized excited states.

D. C₂H₄

The ethylene molecule is described well by single reference methods both in its ground and excited states, although it exhibits some nondynamical correlation arising from the $(\pi^*)^2$ configuration. Table VII summarizes the results of previously reported calculations, experimental excitation energies, and our OO-CCD and VOO-CCD calculations. The comparison with experimental values is problematic, because only for the valence 1^1B_{1u} ($\pi \rightarrow \pi^*$) state the reported experimental excitation energy corresponds to the vertical transition. Experimental energies and CIS results are cited from Ref. 77. CCSD energies are from Refs. 73 and 75. Calculation of ethylene excitation energies has been performed with a 6-311G(2+,2+)G** basis (five Cartesian *d*-functions have been used), at the geometry from Ref. 78.

Differences between OO-CCD and CCSD models do not exceed 0.05 eV, and for both models the errors against experiment are within 0.1–0.4 eV. The largest error for both models is for the valence 1^1B_{1u} ($\pi \rightarrow \pi^*$) state, probably because for this state the balanced description of nondynamical correlation is more important than for other states.

The performance of the VOO-CCD model with internal doubles is unsatisfactory. The VOO-CCD model with internal and semi-internal doubles performs well; most of the excitation energies are within 0.2–0.3 eV from the experimental values. The largest error of 1 eV against experiment, or 0.6 eV against OO-CCD, has been observed for the 3^1B_{1g} state. The error for the valence 1^1B_{1u} state (for which CCSD and OO-CCD give the error of 0.5 eV) is 0.2 eV, because the nondynamical correlation is described well by the VOO-CCD model.

E. BeO

BeO is a molecule that has large T_1 amplitudes in the ground state. The largest amplitude is 0.09, and the T_1 diagnostic^{79,80} is very large at 0.036 (a value above around 0.02 is frequently associated with substantial nondynamical correlation). The ground state electronic configuration is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$, with a contribution from $\pi \rightarrow \pi^*$ excitation (the value of the corresponding T_2 in VOO-CCD wave function is 0.09). As such, it is an interesting test case for comparing (V)OO-CCD against CCSD, since there are relatively large differences in the Brueckner orbitals relative to Hartree–Fock orbitals.

The calculations have been performed at the experimental geometry⁸¹ with a basis set derived from the augmented double- ζ ANO basis of Roos⁸² by uncontracting the two most diffuse *s* and *p* functions. The contraction scheme is $(14s9p4d)/[6s5p2d]$. Manifolds of five *d* functions have been used in this study. Test calculations with additional diffuse functions (one *s*-function on Be, and two *s*- and one *p*-functions on oxygen), have shown that extra diffuse functions have essentially no effect (about 0.01 eV for a couple of states) on the excitation energies reported here.

The results are given in Table VIII. MRCI calculations⁸³ have previously been performed in a DZP-quality basis set augmented by one diffuse *p*-function on oxygen. All the states from Table VIII have predominantly singly excited character. The leading excitation for the $2^1\Sigma^+$, $1^1\Sigma^-$, $1^1\Delta$, $1^1\Pi$, and $2^1\Pi$ states is valence. However, these states also exhibit significant Rydberg character. The $2^1\Sigma^+$ state is $4\sigma \rightarrow 1\sigma^*$ excitation; $1^1\Sigma^-$ and $1^1\Delta$ states are $\pi \rightarrow \pi^*$ excitations; $1^1\Pi$ and $2^1\Pi$ state are $\pi \rightarrow 1\sigma^*$ and $4\sigma \rightarrow \pi^*$ excitations, respectively. The rest of the states from Table VIII are Rydberg excitations of π -electrons.

CIS exhibits very large errors (up to 4 eV!) for some of the states, though it describes the character of these states correctly. Presumably because of the very large T_1 amplitudes in the ground state CCSD wave function, for this case we see the largest differences yet between OO-CCD and CCSD excitation energies. The OO-CCD excited states for BeO are generally about 0.1 eV below the EOM-CCSD results, the largest difference being 0.14 eV. Given that the accuracy of EOM-CCSD is about 0.2–0.3 eV, these differences between OO-CCD and CCSD excitation energies should still be considered fairly small. Nevertheless, in this case we see that OO-CCD reproduces excitation energies for the two experimentally known excited states even better than EOM-CCSD, with errors of 0.01 and 0.15 eV, compared to 0.13 and 0.27 eV for EOM-CCSD. For this molecule VOO-CCD with semi-internal doubles also performs very well—the maximum discrepancy between OO-CCD and VOO-CCD excitation energies is 0.25 eV.

F. CH⁺

In this section we investigate performance of OO-CCD and VOO-CCD models for the CH⁺ molecule. CH⁺ has a ground electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$ and a moderately large nondynamical correlation contribution originating

TABLE VII. Vertical excitation energies (eV) for ethylene, 6-311G(2+,2+)G(*,*) basis set.^a

State	CCSD ^b	OO-CCD ^c	CIS ^d	VOO-CCD ^{e,f}	VOO-CCD ^{e,g}	Expt.
2 ¹ A _g (R)	8.34	8.38	8.09	9.07	8.11	8.29
3 ¹ A _g (R)		10.52	10.29	11.14	10.23	
4 ¹ A _g (R)		11.54		12.77	11.50	
1 ¹ B _{1g} (R)	7.96	8.01	7.71	8.74	7.64	7.80
2 ¹ B _{1g} (R)	9.38	9.42	9.09	10.16	9.10	9.34
3 ¹ B _{1g} (V)		8.75	9.28	9.70	8.18	9.2
4 ¹ B _{1g} (R)		10.37	10.06	11.08	9.99	
1 ¹ B _{2g} (R)	7.99	8.04	7.68	8.89	7.73	8.01
2 ¹ B _{2g} (R)		9.46	9.19	10.24	9.16	
3 ¹ B _{2g} (RV)		9.87	9.56	10.63	9.59	
4 ¹ B _{2g} (RV)		10.24	10.26	11.22	9.73	
1 ¹ B _{3g} (R)		9.76		10.93	9.66	
2 ¹ B _{3g} (R)		11.31		12.51	11.28	
3 ¹ B _{3g} (R)		11.68		12.86	11.61	
4 ¹ B _{3g} (R)		11.90		13.09	11.85	
1 ¹ A _u (R)	9.01	9.05	8.77	9.85	8.76	
2 ¹ A _u (R)		9.95	9.65	10.72	9.65	
3 ¹ A _u (R)		10.84		12.01	10.80	
4 ¹ A _u (R)		11.37		12.18	11.01	
1 ¹ B _{1u} (V)	8.14	8.19	7.74	8.94	7.80	7.60
2 ¹ B _{1u} (R)	9.39	9.43	9.09	10.20	9.12	9.33
3 ¹ B _{1u} (R)		10.51		11.68	10.40	
4 ¹ B _{1u} (R)		11.85		12.93	11.63	
1 ¹ B _{2u} (R)		10.43		11.60	10.36	
2 ¹ B _{2u} (R)		11.91		13.10	11.86	
3 ¹ B _{2u} (R)		12.30		13.54	12.28	
4 ¹ B _{2u} (R)		12.34		13.90	12.30	
1 ¹ B _{3u} (R)	7.31	7.35	7.13	8.15	7.03	7.11
2 ¹ B _{3u} (R)	8.86	8.91	8.63	9.70	8.62	8.62
3 ¹ B _{3u} (R)	9.18	9.22	8.93	9.99	8.92	
4 ¹ B _{3u} (R)		9.40	9.11	10.14	9.10	8.90

^a5d functions used. Hartree–Fock energy is $-78.055\,980$ hartree.^bReference 73.^cOO-CCD total energy is $-78.412\,618$ hartree.^dReference 77.^eVOO-CCD total energy is $-78.197\,893$ hartree.^fOrbitals are optimized for the ground state.^gOrbital relaxation is approximately described by semi-internal double excitations.TABLE VIII. Excitation and total energies for BeO, $r_{\text{BeO}}=1.3308$ Å.^a

State	CCSD	OO-CCD	VOO-CCD ^b	CIS	MRCI ^{c,d}	Expt. ^{c,e}
2 ¹ Σ ⁺ (V)	2.77	2.63	2.56	4.55	2.47	2.64
3 ¹ Σ ⁺ (R)	7.28	7.16	7.21	8.17		
1 ¹ Σ ⁻ (V)	5.76	5.64	5.41	10.38	5.25	
2 ¹ Σ ⁻ (R)	8.04	7.98	8.02	10.54		
1 ¹ Δ (V)	5.74	5.65	5.49	5.98	5.28	
2 ¹ Δ (R)	8.08	7.94	7.99	8.73		
1 ¹ Π (V)	1.44	1.32	1.29	2.46	0.91	1.17
2 ¹ Π (V)	6.92	6.80	6.55	7.85		
3 ¹ Π (R)	7.25	7.15	7.22	7.97		
4 ¹ Π (R)	7.38	7.28	7.30	8.09		
X ¹ Σ ⁺	-89.746 098	-89.744 594	-89.607 431			

^aNuclear repulsion energy is $12.724\,430$ hartree, Hartree–Fock energy is $-89.449\,806$ hartree.^bOrbital relaxation is approximately described by semi-internal double excitations.^cBottom-to-bottom excitation energies (T_e).^dReference 83.^eReference 81.

TABLE IX. Excitation and total energies for CH^+ , $r_{\text{CH}}=2.137\ 130$ bohr.^a

State	FCI ^b	CCSD ^c	OO-CCD	MCLR ^b	CASSCF ^d	VOO-CCD ^d	CASSCF ^e	VOO-CCD ^f
$^1\Sigma^+ (2e)$	8.549	9.11	9.12	11.75	13.90	13.66		8.91
$^1\Sigma^+ (1e)$	13.525	13.58	13.59	14.37	22.65	14.78		13.72
$^1\Sigma^+ (1e)$	17.217		17.33	18.06	25.53	18.42		17.44
$^1\Pi (1e)$	3.230	3.26	3.26	3.20	6.60	3.82	3.20	2.93
$^1\Pi (1e)$	14.127		14.44	14.70	17.68	15.59		14.17
$^1\Delta (2e)$	6.964	7.89	7.91	9.59	11.56	11.39	7.47	7.31
$^1\Delta (2e)^g$	16.833		17.70	20.77	22.69	22.06		17.16
$X\ ^1\Sigma^+$	-38.019 638		-38.017 698	-37.968 158	-37.968 158	-37.968 087	-37.968 158	-37.968 087

^aNuclear repulsion energy is 2.807 504 hartree, Hartree-Fock energy is -37.902 768 hartree.

^bReference 84.

^cReference 52.

^dOrbitals are optimized for the ground state.

^eIndividually optimized orbitals.

^fOrbital relaxation is approximately described by semi-internal double excitations.

^gThis state has significant contributions from triple excitations.

from the $1\sigma^2 2\sigma^2 1\pi^2$ configuration. The molecule possesses low-lying excited states with dominant contributions from two-electron excitations.

The present calculations were carried out with a basis set employed by Olsen *et al.*⁸⁴ The basis was comprised of the standard Dunning⁸⁵ double- ζ plus polarization (DZP) basis set augmented by diffuse s and p functions on carbon and one diffuse s function on hydrogen. The contraction scheme is $(10s6p1d)/[5s3p1d]$ for carbon and $(5s1p)/[3s1p]$ for hydrogen. We performed calculations at three geometries: (i) at $r_{\text{CH}}=r_e=2.137\ 13$ bohr as in Refs. 84 and 52; (ii) at $r_{\text{CH}}=1.5\cdot r_e$; and (iii) at $r_{\text{CH}}=2\cdot r_e$. For this small molecule, we can compare our results with FCI calculations (FCI results at $r_{\text{CH}}=r_e$ are from Ref. 84; FCI calculations at $1.5\cdot r_e$ and $2\cdot r_e$ have been performed in this work). For $r_{\text{CH}}=r_e$, CCSD (Ref. 52) and multiconfigurational linear response (MCLR) (Ref. 84) results are also available. In addition, we have performed FCI and VOO-CCD calculations of the entire PES's. The results are summarized in Tables IX–XIII.

The first $^1\Sigma^+$ state and two $^1\Delta$ states are doubly excited states. Moreover, analysis of the FCI wave function shows that at larger C–H distances the second $^1\Delta$ state becomes a

triply excited state — the leading determinant in FCI wave function corresponds to the excitation of three electrons from the reference configuration.

Comparison of the CCSD and OO-CCD excitation energies demonstrates an excellent agreement between the two models (differences do not exceed 0.01 eV). As expected, both models are very accurate for the singly excited states at equilibrium, and exhibit larger errors (about 1 eV) for doubly excited states. As the C–H bond is broken, OO-CCD becomes a worse approximation for the ground electronic state (just as for CCSD); this tends to add to the intrinsic error of the excited state procedure. Hence, errors in excitation energies grow with increasing C–H bond length, leading to distorted potential energy curves.

At the equilibrium geometry, VOO-CCD results can be compared with (i) linear response from the full valence space CASSCF (MCLR results from Ref. 84); (ii) full valence space CASSCF excitation energies with orbitals being optimized for ground state; and (iii) full valence space CASSCF calculations with orbitals optimized individually for each state. CASSCF, VOO-CCD, and MCLR (Ref. 84) calculations have been performed with four electrons in five (three σ and two π) orbitals. The errors for these models are visu-

TABLE X. Excitation energies for CH^+ , $r_{\text{CH}}=3.205\ 695$ bohr.^a

State	FCI	OO-CCD	CASSCF ^b	VOO-CCD ^b	CASSCF ^c	VOO-CCD ^d
$^1\Sigma^+$	6.954	7.70	11.34	10.20		7.47
$^1\Sigma^+$	9.344	9.53	12.88	12.31		9.48
$^1\Sigma^+$	13.988		17.15	15.10		14.27
$^1\Pi$	1.718	1.81	3.72	2.20	1.72	1.38
$^1\Pi$	8.202	8.78	10.74	10.17		8.40
$^1\Delta$	5.847	7.05	10.43	10.52	5.73	6.53
$^1\Delta^e$	13.949	15.99	18.70	19.34		15.60
$X\ ^1\Sigma^+$	-37.954 264	-37.951 360	-37.906 523	-37.906 273	-37.906 523	-37.906 273

^aNuclear repulsion energy is 1.871 669 hartree, Hartree-Fock energy is -37.818 452 hartree.

^bOrbitals are optimized for the ground state.

^cIndividually optimized orbitals.

^dOrbital relaxation is approximately described by semi-internal double excitations.

^eThis state has a dominant triply excited character.

TABLE XI. Excitation energies for CH^+ , $r_{\text{CH}}=4.274\ 26$ bohr.^a

State	FCI	OO-CCD	CASSCF ^b	VOO-CCD ^b	CASSCF ^c	VOO-CCD ^d
$1^1\Sigma^+$	5.353	5.84	8.15	7.11		5.67
$1^1\Sigma^+$	6.681	7.38	10.86	10.81		7.25
$1^1\Sigma^+$	11.005		12.48	12.30		11.34
$1^1\Pi$	0.566	0.75	1.36	0.93	0.57	0.27
$1^1\Pi$	5.363	5.96	6.62	6.54		5.65
$1^1\Delta$	4.964	6.34	9.17	9.36	4.87	5.91
$1^1\Delta^e$	10.901	14.71	13.64	17.12		14.37
$X\ 1^1\Sigma^+$	-37.900 984	-37.896 031	-37.854 182	-37.853 807	-37.854 182	-37.853 807

^aNuclear repulsion energy is 1.403 752 hartree, Hartree-Fock energy is -37.734 283 hartree.

^bOrbitals are optimized for the ground state.

^cIndividually optimized orbitals.

^dOrbital relaxation is approximately described by semi-internal double excitations.

^eThis state has a dominant triply excited character.

alized in Fig. 3. The errors for the CASSCF model with orbitals optimized for the ground state are largest, since this model completely disregards orbital relaxation. The errors of VOO-CCD with internal doubles are (i) considerably smaller; and (ii) the trend in error behavior is very similar to that of the CASSCF model. The errors of MCLR are smaller than VOO-CCD errors, since MCLR wave function is a FCI wave function in the active space, and the error behavior is again parallel to the errors of VOO-CCD. This suggests that both models suffer from the insufficient description of orbital relaxation. Errors are larger for doubly excited states, since orbital relaxation is more important when two electrons are promoted to the higher orbitals. VOO-CCD model with internal and semi-internal doubles gives errors within -0.3 to 0.36 eV for all states. For two states for which CASSCF energies with individually optimized orbitals are available, the VOO-CCD and CASSCF errors are very close.

Similar error behavior was observed at the other two geometries. Errors of CASSCF with orbitals optimized for the ground state and VOO-CCD with internal doubles become smaller as the C-H distance increases, which means that orbital relaxation for excited states becomes less important. The reason is that the ground and excited states become more similar when the overlap between fragments decreases, especially for states which dissociate to the same limit as the

ground state, e.g., first $1^1\Pi$ state. In other words, at equilibrium geometry the energy gap (and differences in electronic density) between bonding and antibonding orbitals is the greatest.

The VOO-CCD model fails to describe second $1^1\Delta$ state at large distances, because this state becomes predominantly triple excitation in character. For all other states, the errors for VOO-CCD remain small. The largest error has been observed for the first $1^1\Delta$ state, and it does not exceed 1 eV.

To explore the usefulness VOO-CCD with semi-internal doubles for excited states geometry optimization, we have performed calculations of the CH^+ PES's along the bond-breaking coordinate. Tables XII and XIII give total energies for FCI and VOO-CCD models, respectively, and Fig. 4 shows corresponding PES's. Though VOO-CCD lacks dynamical correlation, the overall shapes of PES's are reproduced quite satisfactorily. For the bound states, i.e., $1^1\Pi$, $2^1\Sigma$, and $1^1\Delta$ states, the VOO-CCD and FCI curves are essentially parallel around excited state minima. Moreover, except for the $1^1\Delta$ and $3^1\Sigma$ states which exhibit increasing error along the dissociation coordinate, PES's for other states follow FCI curves closely in a whole range of nuclear distortions.

To summarize: (i) the primary cause of the poor performance of the VOO-CCD model with internal doubles is an

TABLE XII. FCI total energies for CH^+ .

R_{CH} (bohr)	$X\ 1^1\Sigma$	$2^1\Sigma$	$3^1\Sigma$	$1^1\Delta$	$1^1\Pi$	$2^1\Pi$
2.0	-38.016 276	-37.695 051	-37.501 551	-37.755 295	-37.892 359	-37.469 402
2.137 13	-38.019 639	-37.705 464	-37.522 625	-37.763 712	-37.900 955	-37.500 483
2.2	-38.019 088	-37.708 250	-37.530 831	-37.765 573	-37.903 073	-37.513 247
2.4	-38.011 599	-37.711 638	-37.552 925	-37.765 966	-37.905 002	-37.550 525
2.6	-37.998 972	-37.710 066	-37.570 786	-37.761 283	-37.902 816	-37.583 555
2.8	-37.984 226	-37.706 379	-37.585 746	-37.754 329	-37.899 035	-37.611 519
3.0	-37.969 114	-37.702 274	-37.598 745	-37.746 761	-37.894 957	-37.634 244
3.205 695	-37.954 264	-37.698 693	-37.610 860	-37.739 367	-37.891 116	-37.652 833
3.4	-37.941 434	-37.696 498	-37.621 531	-37.733 275	-37.888 066	-37.666 821
3.6	-37.929 699	-37.695 761	-37.631 691	-37.728 138	-37.885 541	-37.678 424
3.8	-37.919 505	-37.696 672	-37.640 657	-37.724 160	-37.883 543	-37.687 839
4.0	-37.910 783	-37.699 117	-37.648 048	-37.721 220	-37.881 939	-37.695 535
4.274 26	-37.900 984	-37.704 251	-37.655 469	-37.718 560	-37.880 166	-37.703 878
4.5	-37.894 563	-37.709 094	-37.659 628	-37.717 267	-37.878 953	-37.709 194
5.0	-37.884 615	-37.716 185	-37.665 115	-37.716 185	-37.876 817	-37.717 176

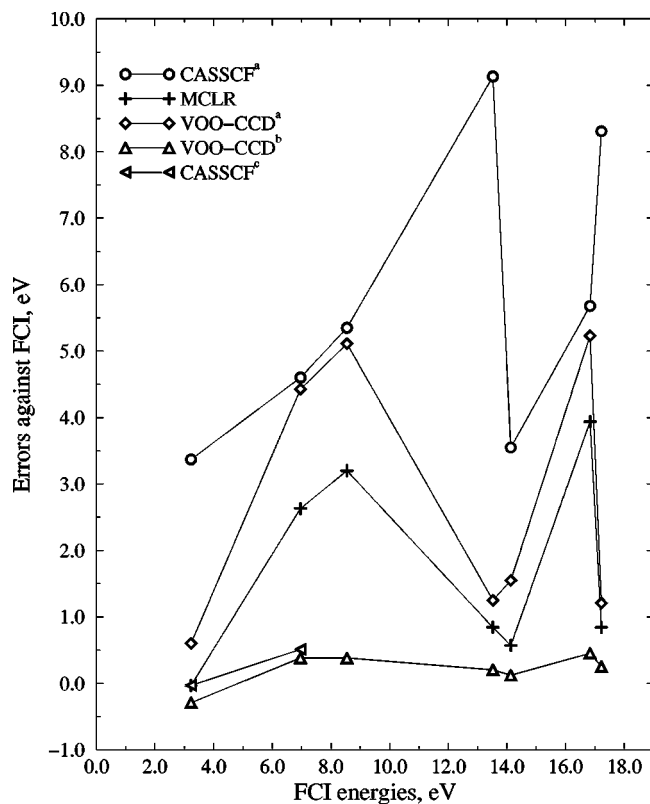


FIG. 3. Errors against FCI as functions of FCI excitation energies for CH^+ molecule. a, orbitals are optimized for the ground state. b, orbital relaxation is approximately described. c, individually optimized orbitals.

insufficient description of orbital relaxation (except for the states which involve excitation of more than two electrons); (ii) VOO-CCD with internal and semi-internal doubles describes PES's in case of a single bond-breaking for doubly and singly excited states with errors not exceeding 1 eV for CH^+ ; and (iii) with approximate treatment of orbital relaxation (semi-internal doubles), VOO-CCD model may be useful for excited state geometry optimization for both singly and doubly excited states.

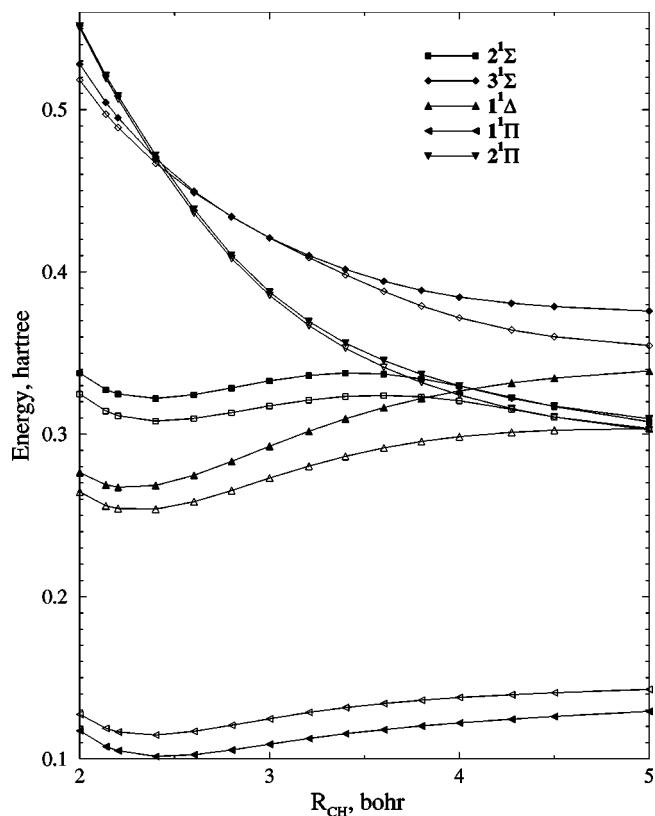


FIG. 4. PES's calculated by FCI (empty symbols) and VOO-CCD (filled symbols) model with semi-internal doubles. Curves are shifted such that equilibrium ground state energy equals zero. Note that around excited states minima ($1^1\Pi$, $2^1\Sigma$, $1^1\Delta$ states) VOO-CCD model reproduces the shapes of FCI PES's very well.

G. BH

BH is isoelectronic with CH^+ , and the effect of non-dynamical correlation is slightly larger, e.g., the weight of the $1\sigma^2 2\sigma^2 1\pi^2$ configuration in the VOO-CCD wave function at equilibrium geometry is 0.14 for CH^+ , and is 0.17 for BH. The calculation of excited states of BH by OO-CCD and

TABLE XIII. VOO-CCD^a total energies for CH^+ .

R_{CH} (bohr)	$X^1\Sigma$	$2^1\Sigma$	$3^1\Sigma$	$1^1\Delta$	$1^1\Pi$	$2^1\Pi$
2.0	-37.963 981	-37.630 4	-37.440 2	-37.691 7	-37.850 7	-37.416 7
2.137 13	-37.968 087	-37.640 7	-37.463 9	-37.699 4	-37.860 5	-37.447 4
2.2	-37.967 867	-37.643 3	-37.473 2	-37.700 9	-37.863 2	-37.459 8
2.4	-37.961 352	-37.646 1	-37.498 4	-37.699 8	-37.866 6	-37.496 4
2.6	-37.949 543	-37.643 9	-37.518 4	-37.693 6	-37.865 6	-37.529 5
2.8	-37.935 436	-37.639 7	-37.534 3	-37.684 9	-37.862 7	-37.557 8
3.0	-37.920 793	-37.635 3	-37.547 2	-37.675 6	-37.859 2	-37.580 6
3.205 695	-37.906 273	-37.631 9	-37.558 1	-37.666 4	-37.855 6	-37.598 7
3.4	-37.893 646	-37.630 5	-37.566 7	-37.658 6	-37.852 7	-37.612 0
3.6	-37.882 052	-37.631 1	-37.574 0	-37.651 8	-37.850 1	-37.622 8
3.8	-37.871 973	-37.634 0	-37.579 6	-37.646 1	-37.847 9	-37.631 4
4.0	-37.863 375	-37.638 4	-37.583 7	-37.641 5	-37.846 0	-37.638 4
4.274 26	-37.853 807	-37.645 5	-37.587 5	-37.636 6	-37.843 7	-37.646 0
4.5	-37.847 643	-37.651 2	-37.589 6	-37.633 6	-37.842 1	-37.651 0
5.0	-37.838 387	-37.660 5	-37.592 3	-37.629 2	-37.838 9	-37.658 6

^aOrbital relaxation is approximately described by semi-internal double excitations.

TABLE XIV. Vertical excitation energies (eV) for BH^a (aug-ccpVDZ basis set).

State	FCI ^b	CCSD ^b	OO-CCD ^c	VOO-CCD ^{d,e}	CASSCF ^{e,f}	VOO-CCD ^{d,g}	CASSCF ^{f,h}	Expt.
<i>B</i> ¹ Σ ⁺ (1 <i>e</i>)	6.378	6.42	6.42	7.18	11.64	6.170		6.49
<i>C</i> ¹ Σ ⁺ (2 <i>e</i>)	6.996	7.39	7.39	8.20	18.03	7.486		6.86
<i>E</i> ¹ Σ ⁺ (1 <i>e</i>)	7.559	7.75	7.76	8.90	18.93	7.952		7.67
<i>A</i> ¹ Π (1 <i>e</i>)	2.944	2.97	2.96	3.61	6.13	2.77	2.99	2.87
<i>D</i> ¹ Π (1 <i>e</i>)	7.466	7.50	7.52	8.22	13.51	7.75		
<i>G</i> ¹ Π (1 <i>e</i>)	8.256	8.28	8.28	8.97		8.58		
<i>C</i> ¹ Δ (2 <i>e</i>)	5.880	6.675	6.674	8.58	9.60	6.225		5.717

^a $r_e = 1.2324$ Å. Nuclear repulsion energy is 2.146 936 hartree. Hartree–Fock energy is $-25.126 475$ hartree.

^bReference 86.

^cOO-CCD energy is $-25.217 640$ hartree.

^dVOO-CCD energy is $-25.180 147$ hartree.

^eOrbitals are optimized for the ground state.

^fCASSCF energy is $-25.180 202$ hartree.

^gOrbital relaxation is approximately described by semi-internal double excitations.

^hIndividually optimized orbitals.

VOO-CCD methods has been performed with an aug-ccpVDZ basis set and at the geometry from Ref. 86. Results are given in Table XIV.

The difference between OO-CCD and CCSD models is within 0.01 eV, and both models reproduce FCI results for singly excited states very closely. VOO-CCD with internal doubles and CASSCF with orbitals optimized for the ground state behave similarly, as in previous cases. Approximate treatment of orbital relaxation by inclusion of semi-internal doubles improves results greatly; the errors are within -0.21 to 0.49 eV, for both singly and doubly excited states.

H. CH₂

Methylene in its 1^1A_1 state has a significant diradical character. The lowest excited state of the same symmetry is doubly excited state. The electronic structure of these two states is described by a combination of two configurations: $1a_1^2 2a_1^2 1b_2^2 3a_1^2$ and the doubly excited $1a_1^2 2a_1^2 1b_2^2 1b_1^2$ configuration, with a larger contribution from the first configuration in the 1^1A_1 state. Here we discuss excitation energy for the $1^1A_1 \rightarrow 2^1A_1$ transition. We performed calculations at (i) equilibrium geometry ($r_{\text{CH}} = 2.11$ bohr, $\alpha_{\text{HCH}} = 102.4^\circ$); (ii) at $\alpha = 170^\circ$; and (iii) with elongated C–H bonds ($r_{\text{CH}} = 1.5 \cdot r_e$); as in Ref. 87. The present calculations were carried out with a basis set employed in Refs. 88 and 87. The basis was comprised of the slightly modified standard Dunning⁸⁵ double- ζ plus polarization (DZP) basis set. The contraction scheme is $(9s5p)/[4s2p]$ for carbon and $(4s/2s)$ for hydrogen. FCI and CASSCF results are from Ref. 87, CCSD results are from Ref. 52.

Total FCI⁸⁷ SCF,⁸⁷ CASSCF,⁸⁷ OO-CCD, and VOO-CCD energies are given in Table XV. VOO-CCD energies are very close to CASSCF energies at all three geometries, which means that VOO-CCD does approximate ground state CASSCF very well for the range of geometrical distortions considered.

Table XVI summarizes results for the excitation energies. CCSD and OO-CCD results are very similar; both methods fail to describe this doubly excited state. For VOO-CCD model with internal doubles errors are very large and not uniform. In this small basis set, CASSCF with orbitals optimized for the ground state gives almost the same errors, which shows that VOO-CCD and CASSCF orbitals are very similar, and that orbital relaxation which is not properly described by VOO-CCD with orbitals optimized for the ground state and internal doubles cause large errors. In the previous cases, CASSCF errors are larger than those of VOO-CCD for singly and doubly excited states, and smaller for the states which acquire triple excited character. For methylene, the CASSCF errors are smaller than those of VOO-CCD as the two C–H bonds are simultaneously stretched (at $1.5 \cdot r_e$), since the VOO-CCD description of the ground state becomes poorer (simultaneous breaking of two strongly interacting bonds is beyond the scope of the VOO-CCD model). The approximate treatment of relaxation improves VOO-CCD results for the equilibrium and $\alpha = 170^\circ$ geometries (errors are 0.44 eV and -0.16 eV, respectively). As expected, at $1.5 \cdot r_e$ better treatment of orbital relaxation does not improve results significantly, since in this case the poor performance of VOO-CCD is not solely due to the relaxation, but to the absence of triple and quadruple excitations.

TABLE XV. Total energies for the 1^1A_1 state of methylene, DZP basis.

	FCI ^a	SCF ^a	CASSCF ^a	OO-CCD	VOO-CCD
r_e	$-39.027 183$	$-38.886 297$	$-38.945 529$	$-39.023 739$	$-38.945 349$
$\alpha = 170^\circ$	$-38.979 277$	$-38.829 519$	$-38.886 014$	$-38.966 678$	$-38.885 791$
$1.5r_e$	$-38.899 243$	$-38.720 110$	$-38.831 433$	$-38.892 292$	$-38.830 813$

^aReference 87.

TABLE XVI. Excitation energies for the $1^1A_1 \rightarrow 2^1A_1$ transition in methylene, DZP basis.

	FCI ^a	CCSD ^b	OO-CCD	CASSCF ^c	VOO-CCD ^c	CASSCF ^{a,d}	VOO-CCD ^e
r_e	4.60	6.00	6.00	9.43	9.36	4.85	5.04
$\alpha = 170^\circ$	1.07	1.68	1.68	1.09	1.06	1.03	0.90
$1.5r_e$	4.45	7.12	7.19	7.32	6.71	4.76	6.49

^aReference 87.^bReference 52.^cOrbitals are optimized for the ground state.^dIndividually optimized orbitals.^eOrbital relaxation is approximately described by semi-internal double excitations.

I. Rectangular O_4^+

Rectangular O_4^+ radical in its $^4B_{1g}$ exhibits symmetry breaking which affects even the usually orbital insensitive CCSD wave function. For example, CCSD predicts anomalously high frequency for b_{3u} stretch. On the other hand, OO-CCD model, which does not depend on symmetry-broken Hartree–Fock orbitals, treats this problem correctly.¹ We were interested in comparing OO-CCD predictions for excited states against those of the EOM-CCSD.

Table XVII shows vertical excitation energies for the three lowest excited states of the rectangular O_4^+ calculated in the 6-31G* basis set. The differences between two models are surprisingly small. The reason is that at the symmetric D_{2h} structure we are not allowed to see the symmetry breaking, i.e., symmetry-adapted orbitals have been used in EOM-CCSD calculations. EOM-CCSD wave functions could be affected by symmetry breaking at some distortions of lower symmetry, e.g., we expect that excited state frequencies would exhibit substantial differences, as it happens for the ground state.

IV. CONCLUSIONS

An excited state theory for the OO-CCD and VOO-CCD models has been presented, and its performance has been studied for several single-reference molecules (H_2O , CH_2O , C_2H_4O , C_2H_4 , BeO), as well as for molecules with more significant nondynamical correlation in the ground state (CH^+ , BH , CH_2), and for rectangular O_4^+ . We have found that:

- (1) The EOM OO-CCD model describes excited states with the same accuracy as EOM CCSD. The differences in excitation energies calculated by two models are very tiny, and usually do not exceed 0.01 eV.
- (2) The excited state VOO-CCD model with internal double excitations and with orbitals optimized for the ground state (single excitations are allowed in the whole space)

TABLE XVII. Vertical excitation energies for the $^4B_{1g}$ state of rectangular O_4^+ , 6-31G(*) basis set.^a

State	CCSD ^b	OO-CCD
$1A_u$	0.767	0.765
$1B_{3g}$	1.124	1.123
$1B_{2u}$	1.714	1.709

^aBasis set and geometry from Ref. 1.^bReference 90.

performs very similarly to the linear response CASSCF model. Both models suffer from insufficient description of orbital relaxation effects. The comparison of this VOO-CCD model with the model CASSCF calculations with orbitals optimized for the ground state demonstrated a similarity in error behavior and confirms this conclusion.

- (3) The approximate treatment of orbital relaxation by including semi-internal doubles improves results consistently. The overall errors of this corrected VOO-CCD model do not exceed 1 eV for singly and doubly excited states and along single bond breaking coordinates. Therefore, it can be considered as an inexpensive and simple alternative to multireference calculations, especially for excited state geometry optimization. It is essentially a CIS quality (semiquantitative) model for both singly and doubly excited state surfaces along single bond-breaking coordinates.
- (4) Errors of VOO-CCD with semi-internal doubles do not increase the molecule and/or basis set grows in size,

TABLE XVIII. Intermediates used in Eqs. (A1)–(A7). To avoid storage of large 6-index quantities, intermediates which have to be updated at each iteration of diagonalization procedure were introduced.

$$\begin{aligned}
 F_{ij} &= f_{ij} + \frac{1}{2} \sum_{kbc} a_{ik}^{bc} \langle jk || bc \rangle \\
 F_{ab} &= f_{ab} - \frac{1}{2} \sum_{jkc} a_{jk}^{ac} \langle jk || bc \rangle \\
 F_{ia} &= f_{ia} + \sum_{kbf} a_{kb}^{af} - \frac{1}{2} \sum_{klc} a_{kl}^{ac} \langle kl || ic \rangle - \frac{1}{2} \sum_{kcd} a_{ik}^{cd} \langle ka || cd \rangle \\
 I_{iajb}^{1} &= \langle ia || jb \rangle - \sum_{kc} a_{ik}^{bc} \langle jk || ac \rangle \\
 I_{ijkb}^{2} &= -\langle ij || kb \rangle + \sum_c a_{ij}^{bc} f_{kc} - \frac{1}{2} \sum_{cd} a_{ij}^{cd} \langle kb || cd \rangle \\
 &\quad + \sum_{lc} (a_{il}^{bc} \langle jc || kl \rangle - a_{jl}^{bc} \langle ic || kl \rangle) \\
 I_{jcab}^{3} &= -\langle jc || ab \rangle + \sum_k a_{jk}^{ab} f_{kc} - \frac{1}{2} \sum_{kl} a_{kl}^{ab} \langle jc || kl \rangle \\
 &\quad + \sum_{kd} (a_{jk}^{ad} \langle kb || cd \rangle - a_{jk}^{bd} \langle ka || cd \rangle) \\
 I_{ijkl}^{4} &= \frac{1}{2} \langle ij || kl \rangle + \frac{1}{4} \sum_{cd} a_{ij}^{cd} \langle kl || cd \rangle \\
 I_{abcd}^{5} &= \frac{1}{2} \langle ab || cd \rangle + \frac{1}{4} \sum_{kl} a_{kl}^{ab} \langle kl || cd \rangle \\
 T_{ij}^{1} &= \sum_{kc} r_k^c \langle ic || jk \rangle \\
 T_{ab}^{2} &= -\sum_{kc} r_k^c \langle ka || cb \rangle \\
 T_{ij}^{3} &= \frac{1}{2} \sum_{kcd} a_{ik}^{cd} \langle jk || cd \rangle \\
 T_{ab}^{4} &= \frac{1}{2} \sum_{klc} a_{kl}^{ac} \langle kl || bc \rangle \\
 T_{ij}^{5} &= \frac{1}{2} \sum_{kab} a_{ik}^{ab} a_{jk}^{ab} \\
 T_{ab}^{6} &= \frac{1}{2} \sum_{ijc} a_{ij}^{ac} a_{ij}^{bc}
 \end{aligned}$$

$$\begin{aligned}
 A_{iaia} &= F_{aa} - F_{ii} - I_{iaia}^1 \\
 D_{ijab,ijab} &= -F_{ii} - F_{jj} + F_{aa} + F_{bb} - (I_{ibib}^1 + I_{jbjb}^1 + I_{iaia}^1 + I_{jaja}^1) + I_{ijij}^4 + I_{abab}^5 \\
 &\quad - \frac{1}{2} \sum_l (\langle jl || ab \rangle a_{jl}^{ab} + \langle il || ab \rangle a_{il}^{ab}) - \frac{1}{2} \sum_d (\langle ij || bd \rangle a_{ij}^{bd} \\
 &\quad + \langle ij || ad \rangle a_{ij}^{ad})
 \end{aligned}$$

which means that any imbalance introduced by the inclusion of semi-internal double excitations has only minor numerical effects.

- (5) Explicit treatment of orbital relaxation by individual or state-average orbital optimization of excited states is expected to bring VOO-CCD model towards the accuracy of CASSCF with orbital optimization. We expect to explore this in future work.
- (6) VOO-CCD with semi-internal doubles still fails (i) for excited states which have a considerable contributions from triply excited configurations; and (ii) when more than one bond is broken. In order to treat these situations, higher excitations should be included in the model.

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APPENDIX

Programmable expressions for right and left σ from Eqs. (40)–(42) are

$$(AR_1)_i^a = \sum_b r_i^b F_{ab} - \sum_j r_j^a F_{ij} - \sum_{jb} r_j^b l_{ibja}^1, \quad (A1)$$

$$(XR_2)_i^a = \sum_{jb} r_{ij}^{ab} f_{jb} - \frac{1}{2} \left(\sum_{jkb} r_{jk}^{ab} \langle ib || jk \rangle + \sum_{jbc} r_{ij}^{bc} \langle ja || bc \rangle \right) \quad (A2)$$

$$(YR_1)_{ij}^{ab} = r_i^a F_{jb} - r_j^a F_{ib} + r_j^b F_{ia} - r_i^b F_{ja} \sum_k (r_k^a l_{ijkb}^2 - r_k^b l_{ijka}^2) + \sum_c (r_i^c l_{jcab}^3 - r_j^c l_{icab}^3) \\ + \sum_l (T_{il}^1 a_{jl}^{ab} - T_{jl}^1 a_{il}^{ab}) + \sum_d (T_{ad}^2 a_{ij}^{bd} - T_{bd}^2 a_{ij}^{ad}), \quad (A3)$$

$$(BR_2)_{ij}^{ab} = \sum_k (r_{jk}^{ab} F_{ik} - r_{ik}^{ab} F_{jk}) + \sum_c (r_{ij}^{ac} F_{bc} - r_{ij}^{bc} F_{ac}) + \sum_{kc} (r_{jk}^{ac} l_{ickb}^1 - r_{ik}^{ac} l_{jckb}^1 + r_{ik}^{bc} l_{jcka}^1 - r_{jk}^{bc} l_{icka}^1) \\ + \sum_{kl} r_{kl}^{ab} l_{ijkl}^4 + \sum_{cd} r_{ij}^{cd} l_{abcd}^5 + \sum_l (T_{il}^3 a_{jl}^{ab} - T_{jl}^3 a_{il}^{ab}) + \sum_d (T_{ad}^4 a_{ij}^{bd} - T_{bd}^4 a_{ij}^{ad})$$

$$(L_1A)_i^a = \sum_b l_i^b F_{ba} - \sum_j l_j^a F_{ji} - \sum_{jb} l_j^b l_{jaib}^1, \quad (A4)$$

$$(L_2Y)_i^a = \frac{1}{2} \sum_{jkb} l_{jk}^{ab} l_{jkib}^2 + \frac{1}{2} \sum_{jbc} l_{ij}^{bc} l_{jabc}^3 + \sum_{lk} T_{lk}^5 \langle ik || la \rangle + \sum_{dc} T_{dc}^6 \langle id || ac \rangle + \sum_{jb} l_{ij}^{ab} F_{jb}, \quad (A5)$$

$$(L_1X)_{ij}^{ab} = l_i^a f_{jb} - l_j^a f_{ib} + l_j^b f_{ia} - l_i^b f_{ja} \\ + \sum_k (l_k^b \langle ij || ka \rangle - l_k^a \langle ij || kb \rangle) + \sum_c (l_j^c \langle ic || ab \rangle - l_i^c \langle jc || ab \rangle), \quad (A6)$$

$$(L_2B)_{ij}^{ab} = \sum_k (l_{jk}^{ab} F_{ki} - l_{ik}^{ab} F_{kj}) + \sum_c (l_{ij}^{ac} F_{cb} - l_{ij}^{bc} F_{ca}) + \sum_{kl} l_{kl}^{ab} l_{kl ij}^4 + \sum_{cd} l_{ij}^{cd} l_{cd ab}^5 \\ + \sum_{kc} (-l_{ik}^{ac} l_{kbc}^1 + l_{jk}^{ac} l_{kbic}^1 + l_{ik}^{bc} l_{kajc}^1 - l_{jk}^{bc} l_{kaic}^1) + \sum_l (T_{il}^5 \langle jl || ab \rangle - T_{jl}^5 \langle il || ab \rangle) \\ + \sum_d (T_{ad}^6 \langle ij || bd \rangle - T_{bd}^6 \langle ij || ad \rangle). \quad (A7)$$

Intermediates used in Eqs. (A1)–(A7) are similar to transformed integrals from Ref. 19, and are summarized in Table XVIII. Table XVIII also contains expressions for the diagonal elements of the transformed Hamiltonian needed for the iterative diagonalization procedure. Most of the intermediates from Table XVIII are contractions of integrals with amplitudes T_2 , and thus are the same for all states and are calculated once. However, in order to avoid storage of large 6-index quantities, intermediates which have to be updated for each state and at each iteration of diagonalization procedure were introduced (those are $T_{ij}^1, T_{ab}^2, T_{ij}^3, T_{ab}^4, T_{ij}^5, T_{ab}^6$).

The equations and intermediates for VOO-CCD model with internal and semi-internal doubles are easily retrieved from Eqs. (A1)–(A7) and Table XVIII by zeroing corresponding blocks of doubly excited amplitudes and σ -vectors, e.g., VOO-CCD model with semi-internal doubles is described by the Eqs. (A1)–(A7) where R_2 , L_2 , $(BR_2)_{ij}^{ab}$, and $(L_2B)_{ij}^{ab}$ tensors have zero blocks if (i) both occupied indexes are core ones; or/and (ii) both virtual indexes are restricted virtual indexes. One can easily identify which blocks of intermediates from Table XVIII are zero by analyzing contractions of corresponding integrals with T_2 amplitudes which are zero unless all four indexes are from the active space. The coding of these equations have been performed using our C++ tensor library⁸⁹ which supports multidimensional tensors with an arbitrary type of zero-block structure.

We have found, that an approximate expression for the diagonal elements in the doubles block can be used in iterative diagonalization; no difference in convergence rate or excitation energies has been found when an approximate expression (neglecting four last terms) was used.

We have found that iterative diagonalization can become unstable in some cases, and that convergence is improved if, prior to excited state calculations, orbitals are canonicalized by a diagonalization of Fock matrix in four distinct subspaces.

Equations (A1)–(A7) contain some disconnected terms. All these terms are contraction of the effective Fock matrix F_{ia} , which is exactly zero for the B-CCD wave functions. Since OO-CCD orbitals are very close to B-CCD ones, these elements are small. For all test cases presented here, these terms does not change (V)OO-CCD transition energies by more than 0.01–0.04 eV. Therefore, we neglected all terms containing F_{ia} in the final version of the program.

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- ⁷¹Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
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