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The article by Thorne Lay and Hiroo Kanamori, published in the July 2012 issue of *Physics Today*, is an interesting read. It discusses the energy released by the 2011 Tohoku earthquake and compares it to the energy released by nuclear weapons. The authors conclude that the earthquake released approximately five times as much energy as the atomic bomb dropped on Nagasaki in 1945. This is a significant finding, as it highlights the immense power of natural events compared to human-made nuclear weapons. The article also discusses the potential for future earthquakes and the importance of seismic monitoring and early warning systems. It is a well-written and informative piece that provides a clear and concise overview of the topic.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck team. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarvill, 14 July 2012 19:59

Quadratically convergent algorithm for orbital optimization in the orbital-optimized coupled-cluster doubles method and in orbital-optimized second-order Møller-Plesset perturbation theory

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Using a Lagrangian-based approach, we present a more elegant derivation of the equations necessary for the variational optimization of the molecular orbitals (MOs) for the coupled-cluster doubles (CCD) method and second-order Møller-Plesset perturbation theory (MP2). These orbital-optimized theories are referred to as OO-CCD and OO-MP2 (or simply “OD” and “OMP2” for short), respectively. We also present an improved algorithm for orbital optimization in these methods. Explicit equations for response density matrices, the MO gradient, and the MO Hessian are reported both in spin-orbital and closed-shell spin-adapted forms. The Newton-Raphson algorithm is used for the optimization procedure using the MO gradient and Hessian. Further, orbital stability analyses are also carried out at correlated levels. The OD and OMP2 approaches are compared with the standard MP2, CCD, CCSD, and CCSD(T) methods. All these methods are applied to H₂O, three diatomics, and the O₄⁺ molecule. Results demonstrate that the CCSD and OD methods give nearly identical results for H₂O and diatomics; however, in symmetry-breaking problems as exemplified by O₄⁺, the OD method provides better results for vibrational frequencies. The OD method has further advantages over CCSD: its analytic gradients are easier to compute since there is no need to solve the coupled-perturbed equations for the orbital response, the computation of one-electron properties are easier because there is no response contribution to the particle density matrices, the variational optimized orbitals can be readily extended to allow inactive orbitals, it avoids spurious second-order poles in its response function, and its transition dipole moments are gauge invariant. The OMP2 has these same advantages over canonical MP2, making it promising for excited state properties via linear response theory. The quadratically convergent orbital-optimization procedure converges quickly for OMP2, and provides molecular properties that are somewhat different than those of MP2 for most of the test cases considered (although they are similar for H₂O). Bond lengths are somewhat longer, and vibrational frequencies somewhat smaller, for OMP2 compared to MP2. In the difficult case of O₄⁺, results for several vibrational frequencies are significantly improved in going from MP2 to OMP2.
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I. INTRODUCTION

The Brueckner orbitals are defined to be a set of orbitals for which the single-excitation coefficients are zero in the full configuration interaction (CI) wave function. In 1953, these orbitals were introduced by Brueckner¹ in a self-consistent method for the study of nuclear matter. In 1958, Nesbet² first introduced Brueckner orbitals into quantum chemistry. Over the last two decades, several studies showed that *ab initio* methods may become more complete when based on Brueckner orbitals rather than usual Hartree-Fock orbitals.^{3–14}

In a 1981 study, Chiles and Dykstra⁶ utilized Brueckner orbitals in coupled-cluster (CC) theory for the first time. They used coupled-cluster singles and doubles method

(CCSD) and rotated the molecular orbitals (MOs) with single excitation amplitudes in an iterative manner until they became zero. Chiles and Dykstra referred this algorithm as CCD ($\hat{T}_1 = 0$), and later this method was renamed to Brueckner coupled-cluster doubles (BCCD),^{4–7} or even more simply Brueckner doubles (BD).³ Further, the Brueckner doubles and triples (BDT) (Ref. 8) and Brueckner doubles with perturbative triples [BD(T)] (Refs. 3 and 10) methods also were implemented by several research groups.

In 1991 studies, Kobayashi *et al.* presented analytic gradients with respect to nuclear coordinates for the BD (Ref. 11) and BD(T) (Ref. 12) methods. In subsequent studies, Kobayashi *et al.* reported molecular properties such as equilibrium geometries, dipole moments, vibrational frequencies, and infrared (IR) intensities for several small molecules.^{18–20} These studies demonstrated that the differences in the

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total energies and physical properties between BD and CCSD or BD(T) and CCSD(T) are generally small. However, in some cases such as spin or spatial symmetry breaking problems^{21,22} Brueckner CC methods have certain advantages over standard CC methods.^{3–5,13} For open-shell systems, spin-restricted Brueckner orbitals have been investigated by Crawford *et al.*²³

As discussed by Sherrill *et al.*,¹³ an alternative way to obtain approximate Brueckner orbitals is to exclude single excitation determinants from the wave function and find the orbitals that minimize the energy. This procedure yields what may be called “variational Brueckner double orbitals.” It has been postulated that the variational Brueckner orbitals and projective Brueckner orbitals are the same in the Full CI limit,¹³ even if for truncated wave functions this equality does not exist. However, as shown by Köhn and Olsen,²⁴ this equivalence is not precisely obtained in the Full CI limit, with differences of tens of microhartrees in total energies for projective Brueckner orbitals and optimized orbitals for small molecules. Nevertheless, for truncated cluster operators, there remain some advantages to variationally optimized orbitals, especially if one stops at low orders instead of attempting to converge to the full CI limit. Once the orbitals are optimized, the wave function will obey the Hellmann-Feynman theorem for orbital rotation parameters. Therefore, there is no need for orbital response terms in the evaluation of analytic gradients. In other words, it is unnecessary to solve the first order coupled-perturbed coupled-cluster doubles equations. Further, computation of one-electron properties is easier because there are no response contributions to the particle density matrices. Another advantage is that the variational optimized orbitals can be readily extended to allow inactive orbitals. Thus, frozen occupied and frozen virtual approximations can be incorporated to the CCD wave function.^{13,25–27} Additionally, orbital-optimized coupled-cluster avoids spurious second-order poles in its response function, and its transition dipole moments are gauge invariant.^{28,29}

Variational orbitals for the CCD wave function were first considered by Purvis and Bartlett.¹⁵ In a 1983 study, Purvis *et al.*³⁰ investigated the C_{2v} insertion pathway for BeH_2 and concluded that variational orbitals could be useful in CC studies of reactions where the dominant CI coefficients change along the reaction path. In a 1987 study, Scuseria and Schaefer⁹ optimized MOs for the CCD and CCSD wave functions. They rotated the orbitals until the orbital Z-vector³¹ became zero. This idea is based on the fact that the variationally optimized orbitals make no orbital response contribution to the CC gradient at convergence.³² Scuseria and Schaefer observed that, for the CCD method, optimized orbitals were obtained without any difficulty in their test cases. However, for the CCSD method they observed an erratic behavior of the Z-vector and they concluded that the problem was related to the presence of $e^{\hat{T}_1}$ in the CCSD model which already describes orbital relaxation effects. Scuseria and Schaefer further noted that the CCD energies obtained from the optimized orbitals were very close to the CCSD energies from the Hartree-Fock orbitals for their test cases. The difference in convergence properties of CCD and CCSD orbital optimization procedures was also discussed by Jankowski *et al.*³³

In 1998, Sherrill *et al.*¹³ presented energies and analytic gradients for a CCD model using variationally optimized orbitals. Givens rotations were used for the unitary transformation of MOs,³⁴ and they computed amplitude response via the Z-vector approach of Handy and Schaefer,³¹ which was first applied to CC theory by Adamowicz *et al.*³⁵ The orbital optimization equations are

$$\frac{\partial E}{\partial \mathbf{U}} \frac{\partial \mathbf{U}}{\partial \theta} = 0, \quad (1)$$

$$\mathbf{C} = \mathbf{C}^{(0)}\mathbf{U}(\theta), \quad (2)$$

where \mathbf{C} is the MO coefficient matrix, $\mathbf{U}(\theta)$ is a unitary transformation matrix expressed as products of Givens rotations,³⁴ and θ is the rotation angle between a pair of MOs. Sherrill *et al.* obtained new θ by scaling the current orbital rotation angles by a crude approximation to the diagonal elements of the orbital Hessian. They used a steepest-descent algorithm and accelerated convergence by employing Pulay’s direct inversion of the iterative subspace (DIIS) method.³⁶

In this study, we will present a quadratically convergent algorithm for optimization of the MOs for the CCD method. First and second derivatives of the coupled-cluster doubles Λ -functional^{37,38} (CCD- Λ) with respect to orbital rotation parameters are presented. A Newton-Raphson algorithm is used for optimization via the MO gradient and Hessian. Further, MO stability analyses are carried out using the MO Hessian at correlated levels (note that, by considering only the orbital-orbital portion of the Hessian, we neglect any orbital/amplitude coupling). Differences between our approach and the previous approach,¹³ can be summarized as follows:

- (1) we minimize the CCD- Λ functional with respect to orbital rotation parameters, while Ref. 13 considered amplitude derivative contributions via the Z-vector approach;
- (2) we use the exact MO Hessian, while Ref. 13 used an approximate diagonal MO Hessian;
- (3) in order to achieve quadratic convergence we use a full Newton-Raphson step, while Ref. 13 employed the DIIS technique;
- (4) we used an exponential transformation, while Ref. 13 used Givens rotations for rotating the orbitals.

Although in this initial work we focus on ground electronic states, orbital optimization of correlated wavefunctions can also be very useful for excited state studies. Equation-of-motion coupled-cluster (EOM-CC) wavefunctions for doublet states are improved when using an OD reference, and similarly, orbital optimization can improve open-shell CIS(D) computations.³⁹

We also consider orbital optimization in second-order Møller-Plesset perturbation theory (OMP2). Like OD compared to CCD, OMP2 has a number of theoretical advantages over standard MP2. OMP2 allows the computation of response properties (such as excitation energies, transition moments, and frequency-dependent polarizabilities) to be computed, which is not the case for canonical MP2.

Thus, response computations based on OMP2 may become an attractive alternative to methods such as second-order approximate coupled cluster singles and doubles model (CC2) (Ref. 40) and second-order polarization propagator approach (SOPPA).⁴¹ Again, we have minimized the MP2 Λ -functional^{38,42} (MP2- Λ) with respect to orbital rotation parameters. The main difference of our new approach for MP2 from the earlier OO-MP2 approaches is that in previous studies^{43–46} the Hylleraas functional (J_2) was minimized with respect to orbital rotations

$$J_2 = \langle \Psi^{(1)} | \hat{H}_0 - E^{(0)} | \Psi^{(1)} \rangle - 2 \langle \Psi^{(1)} | \hat{V} - E^{(1)} | \Psi^{(1)} \rangle, \quad (3)$$

where J_2 is the Hylleraas functional, $\Psi^{(1)}$ is the first order correction to wave function, \hat{H}_0 is the unperturbed Hamiltonian, $E^{(0)}$ and $E^{(1)}$ are zeroth and first order energy corrections, and \hat{V} is the perturbation operator.

The Hylleraas functional J_2 provides an upper limit for the second-order energy, hence the minimization of J_2 yields a variational approach for finding the first-order wavefunction and second-order energy.⁴⁷ The stationary points of the the Hylleraas functional J_2 coincide with the stationary points of the MP2- Λ functional.⁴⁸ More generally, it is possible to construct a Hylleraas functional J_{2n} , the minimum of which corresponds to the wavefunction $\Psi^{(n)}$ and the energy $E^{(2n)}$. However, this method does not provide a variational approach for the energy corrections of odd order. For example, for both second- and third-order energy corrections one only needs to the first-order wavefunction $\Psi^{(1)}$. By minimizing J_2 one can find the $\Psi^{(1)}$ that minimizes $E^{(2)}$ but not $E^{(3)}$. In other words, the Hylleraas functional J_2 is an upper bound for $E^{(2)}$, but it is not an upper bound for $E^{(3)}$. Hence, the complete minimization for MP3 is not possible with that approach. Thus, the Hylleraas functional based approaches are not straightforward to apply higher orders of perturbation. However, our method is quite general and can be easily extended to higher orders of many-body perturbation theory. We will pursue such extensions in the near future.

We apply our algorithms to the H_2O , C_2 , N_2 , F_2 , and O_4^+ molecules and compare results for total energies and selected molecular properties with those from the standard MP2, CCD, CCSD, and CCSD(T) methods. Our C++ codes for OD and OMP2 are written by present authors for this research and interfaced with a preliminary version of PSI4 package.⁴⁹ Our new CCD lambda (CCD- Λ) and response density matrices codes are tested against the ACES II program.⁵⁰ In order to validate the MO rotation formalism we wrote a separate quadratically convergent self-consistent field (QC-SCF) program and tested against the standard SCF code of PSI3 program, CSCF.⁵¹ The overall OD code is tested against QCHEM OD code.⁵² We have also reproduced the results of Sherrill *et al.*¹³ and Krylov *et al.*²⁵ for optimized doubles (OD) and valence optimized doubles (VOD) using the DZP basis set. Further, we have verified our MO Hessian code comparing eigenvalues with previously published results at the SCF level.^{53,54}

II. THEORETICAL APPROACH

A. Quadratically convergent orbital-optimized coupled-cluster doubles method (OD)

1. The CCD- Λ energy functional and amplitude equations

In this section, for the MO indexing we will use conventional notation: i, j, k, l, m, n for occupied orbitals; a, b, c, d, e, f for virtual orbitals; and p, q, r, s, t, u, v, w for general spin orbitals. The Hamiltonian operator can be written using second-quantization formalism^{55–57} as

$$\hat{H} = \sum_{p,q} h_{pq} \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}, \quad (4)$$

where h_{pq} is the one-electron Hamiltonian matrix element, $\langle pq || rs \rangle$ is the antisymmetrized two-electron integral, and \hat{p}^\dagger and \hat{q} are creation and annihilation operators.

The coupled-cluster doubles (CCD) energy and amplitude equations can be summarized as follows:^{56,58}

$$E_{ccd} = \langle 0 | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} | 0 \rangle, \quad (5)$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} | 0 \rangle = 0, \quad (6)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} t_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}, \quad (7)$$

$$E_{ccd} = E_{scf} + \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} t_{ij}^{ab} \langle ij || ab \rangle, \quad (8)$$

where $e^{\hat{T}_2}$ is the usual cluster double excitation operator, $|0\rangle$ is the reference determinant, t_{ij}^{ab} is the CCD t_2 -amplitude, $\langle \Phi_{ij}^{ab} |$ is doubly excited Slater determinant, E_{ccd} is the CCD energy and E_{scf} is the reference, self-consistent field (SCF), energy.

In order to obtain a variational energy functional (\tilde{E}_{ccd}) it is convenient to introduce the following functional (CCD- Λ).³⁸

$$\tilde{E}_{ccd} = \langle 0 | (1 + \hat{\Lambda}_2) e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} | 0 \rangle, \quad (9)$$

$$\hat{\Lambda}_2 = \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} \lambda_{ab}^{ij} \hat{i}^\dagger \hat{j}^\dagger \hat{b} \hat{a}, \quad (10)$$

where $\hat{\Lambda}_2$ is the double de-excitation operator and λ_{ij}^{ab} is a particular de-excitation amplitude.

The standard CCD t_2 -amplitude equation is obtained by requiring that \tilde{E}_{ccd} be stationary with respect to λ_2 -amplitudes, while the stationary requirement with respect to t_2 -amplitudes leads to the λ_2 -amplitude equation^{59–61}

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} | 0 \rangle = 0, \quad (11)$$

$$\langle 0 | (1 + \hat{\Lambda}_2) [e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} - E_{ccd}] | \Phi_{ij}^{ab} \rangle = 0. \quad (12)$$

2. The parametrization of OD wave function

The orbital variations may be expressed by means of an exponential unitary operator^{48,62–65}

$$|\tilde{\Psi}\rangle = e^{\hat{K}}|\Psi\rangle = e^{\hat{K}}e^{\hat{T}_2}|0\rangle, \quad (13)$$

where \hat{K} is the orbital rotation operator

$$\hat{K} = \sum_{p,q} K_{pq} \hat{E}_{pq} = \sum_{p>q} \kappa_{pq} \hat{E}_{pq}^-, \quad (14)$$

$$\hat{E}_{pq} = \hat{p}^\dagger \hat{q}, \quad (15)$$

$$\hat{E}_{pq}^- = \hat{E}_{pq} - \hat{E}_{qp}, \quad (16)$$

$$\mathbf{K} = \text{Skew}(\kappa). \quad (17)$$

The effect of the orbital rotations on the MO coefficients can be written as

$$\mathbf{C}(\kappa) = \mathbf{C}^{(0)} e^{\mathbf{K}}, \quad (18)$$

where $\mathbf{C}^{(0)}$ is the initial MO coefficient matrix and $\mathbf{C}(\kappa)$ is the new MO coefficient matrix as a function of κ . Now, let us define a variational energy functional (Lagrangian) as a function of κ ,

$$\tilde{E}(\kappa) = \langle 0|(1 + \hat{\Lambda}_2)e^{-\hat{T}_2}e^{-\hat{K}}\hat{H}e^{\hat{K}}e^{\hat{T}_2}|0\rangle, \quad (19)$$

and first and second derivatives of the energy with respect to the κ parameter at $\kappa = 0$

$$w_{pq} = \left. \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \right|_{\kappa=0}, \quad (20)$$

$$A_{pq,rs} = \left. \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\kappa=0}, \quad (21)$$

$$w_{pq} = \langle 0|(1 + \hat{\Lambda}_2)e^{-\hat{T}_2}[\hat{H}, \hat{E}_{pq}^-]e^{\hat{T}_2}|0\rangle, \quad (22)$$

$$A_{pq,rs} = \frac{1}{2} \langle 0|(1 + \hat{\Lambda}_2)e^{-\hat{T}_2} \times \{ [[\hat{H}, \hat{E}_{pq}^-], \hat{E}_{rs}^-] + [[\hat{H}, \hat{E}_{rs}^-], \hat{E}_{pq}^-] \} e^{\hat{T}_2}|0\rangle. \quad (23)$$

Then the energy can be expanded up to second-order as follows:

$$\tilde{E}^{(2)}(\kappa) = \tilde{E}^{(0)} + \kappa^\dagger \mathbf{w} + \frac{1}{2} \kappa^\dagger \mathbf{A} \kappa, \quad (24)$$

where \mathbf{w} is the MO gradient vector, κ is the MO rotation vector, and \mathbf{A} is the MO Hessian matrix. Therefore, minimizing the energy with respect to κ yields

$$\kappa = -\mathbf{A}^{-1} \mathbf{w}. \quad (25)$$

This final equation corresponds to the usual Newton-Raphson (NR) step.

3. Response (relaxed) density matrices

We will present both the MO gradient and Hessian expressions with respect to orbital rotation parameters in terms of response (relaxed) density matrices.^{13,38,59–61,66} Therefore, it is appropriate to first introduce response density matrices for the CCD- Λ functional. However, it should be noted that in some articles the definition of the response density matrices might be slightly different from ours. We have defined response density matrices as follows:

$$\gamma_{pq} = \frac{1}{2} \hat{P}_+(pq) \langle 0|(1 + \hat{\Lambda}_2) e^{-\hat{T}_2} \hat{p}^\dagger \hat{q} e^{\hat{T}_2}|0\rangle, \quad (26)$$

$$\Gamma_{pqrs} = \frac{1}{8} \hat{P}_+(pq, rs) \langle 0|(1 + \hat{\Lambda}_2) e^{-\hat{T}_2} \hat{p}^\dagger \hat{q}^\dagger \hat{r} \hat{s} e^{\hat{T}_2}|0\rangle, \quad (27)$$

where $\hat{P}_\pm(pq)$ is defined as

$$\hat{P}_\pm(pq) = 1 \pm \hat{P}(pq), \quad (28)$$

with $\hat{P}(pq)$ acts to permute the indices p and q . Using these definitions the one- and two-particle density matrices (PDMs) have the same permutational symmetries as the one-electron and antisymmetrized two-electron integrals, respectively. Furthermore, we can decompose the PDMs into reference and correlation contributions as follows:

$$\gamma_{pq} = \gamma_{pq}^{ref} + \gamma_{pq}^{corr}, \quad (29)$$

$$\begin{aligned} \Gamma_{pqrs} &= \Gamma_{pqrs}^{ref} + \Gamma_{pqrs}^{corr} \\ &+ \frac{1}{4} \delta_{pr}^{occ} \gamma_{qs}^{corr} + \frac{1}{4} \delta_{qs}^{occ} \gamma_{pr}^{corr} \\ &- \frac{1}{4} \delta_{ps}^{occ} \gamma_{qr}^{corr} - \frac{1}{4} \delta_{qr}^{occ} \gamma_{ps}^{corr}, \end{aligned} \quad (30)$$

where γ_{pq}^{ref} and Γ_{pqrs}^{ref} are the reference (SCF) contributions to PDMs, while γ_{pq}^{corr} and Γ_{pqrs}^{corr} are the correlation contributions. δ_{pr}^{occ} denotes Kronecker delta and superscript *occ* means that the orbital p must be an occupied orbital. The reference PDMs are given as follows:

$$\gamma_{pq}^{ref} = \delta_{pq}^{occ}, \quad (31)$$

$$\Gamma_{pqrs}^{ref} = \frac{1}{4} (\delta_{pr}^{occ} \delta_{qs}^{occ} - \delta_{ps}^{occ} \delta_{qr}^{occ}), \quad (32)$$

The energy of the CCD- Λ functional can be expressed in terms of PDMs as follows:

$$\tilde{E}_{ccd} = \sum_{p,q} \gamma_{pq} h_{pq} + \sum_{p,q,r,s} \Gamma_{pqrs} \langle pq||rs\rangle, \quad (33)$$

$$\Delta \tilde{E}_{ccd} = \sum_{p,q} \gamma_{pq}^{corr} f_{pq} + \sum_{p,q,r,s} \Gamma_{pqrs}^{corr} \langle pq||rs\rangle, \quad (34)$$

where $\Delta\tilde{E}_{ccd}$ is the correlation energy for the CCD- Λ functional and f_{pq} is the matrix element of the Fock operator. Correlation contributions for unique non-zero blocks of response one- and two-particle density matrices and some useful intermediates are presented in Appendix A.

4. Generalized-Fock and orbital (MO) gradient

Before writing the explicit equation for the MO gradient let us first define a generalized-Fock matrix (MO Lagrangian) as

$$F_{tu} = \sum_p h_{tp} \gamma_{pu} + 2 \sum_{p,q,r} \langle pq || rt \rangle \Gamma_{pqr}, \quad (35)$$

where F_{tu} is a generalized-Fock matrix element. Then, the MO gradient can be written in terms of the elements of the generalized-Fock as follows:

$$w_{tu} = 2(F_{tu} - F_{ut}). \quad (36)$$

The MO gradient is defined by the asymmetry of the generalized-Fock matrix and at convergence the generalized-Fock matrix will be symmetric.

5. Orbital (MO) Hessian

We can express the MO Hessian in terms of the generalized-Fock and response density matrices as follows:

$$\begin{aligned} A_{tu,vw} = & \delta_{uv}(F_{tw} + F_{wt}) + \delta_{tw}(F_{vu} + F_{uv}) \\ & - \delta_{tv}(F_{uw} + F_{wu}) - \delta_{uw}(F_{vt} + F_{tv}) \\ & + 2h_{tv}\gamma_{wu} - 2h_{uw}\gamma_{vt} - 2h_{tw}\gamma_{vu} + 2h_{uw}\gamma_{vt} \\ & + 4 \sum_{p,q} \langle pq || vt \rangle \Gamma_{pqwu} - 4 \sum_{p,q} \langle pq || vu \rangle \Gamma_{pqwt} \\ & - 4 \sum_{p,q} \langle pq || wt \rangle \Gamma_{pqvu} + 4 \sum_{p,q} \langle pq || wu \rangle \Gamma_{pqvt} \\ & + 8 \sum_{p,q} \langle pv || qt \rangle \Gamma_{pqwu} - 8 \sum_{p,q} \langle pv || qu \rangle \Gamma_{pqwt} \\ & - 8 \sum_{p,q} \langle pv || qt \rangle \Gamma_{pqvu} + 8 \sum_{p,q} \langle pv || qu \rangle \Gamma_{pqvt}. \end{aligned} \quad (37)$$

Intentionally, we keep our equations quite general in Eq. (37);⁶⁷ however, we need only to consider Hessian block(s) corresponding to non-redundant rotations (see below). One can show that for the CCD wave function with all orbitals active, only occupied-virtual (O-V) rotations are non-redundant.⁴⁸ More generally, there may be inactive occupied (INO) and virtual (INV) orbitals (with frozen occupied and virtual approximations). In such a case, active occupied-inactive occupied (ACO-INO) and active virtual-inactive virtual (ACV-INV) rotations also should be considered in addition to all occupied-all virtual (O-V) rotations.¹³

Another important point is that, once the MO gradient vector is constructed, it can be seen that some rotations al-

ready have zero gradients due to symmetry constraints. Further, some rotations may have numerically very small gradients, which can be disregarded if the corresponding MO gradients are lower than a predefined cutoff value such as 10^{-10} . Therefore, there is no need to construct Hessian or κ vector elements for those rotations. The Hessian and κ vector are only required for the independent-pairs (IDP) for which gradients are computationally non-zero. Hence, the number of computationally significant IDPs may be smaller than the number of non-redundant pairs (NRPs). We observed that the number of IDPs is significantly smaller than the number of total O-V type rotations (NRPs) in the case where all orbitals are active for test cases considered in this research. Constructing the MO Hessian explicitly only for the computationally significant independent-pairs, one can achieve both lower storage and quadratic convergence.

The computational cost for construction of the full MO Hessian scales as n^6 , hence, one may consider solving Eq. (25) using iterative procedures with one index transformed quantities which scales as n^5 .⁴⁸ However, constructing the MO Hessian only for computationally significant IDPs one can decrease the scaling to $n_{idp}^2 \cdot n^2$, which is $\sim n^4 - n^5$ for test cases considered in this research. Moreover, as OD and OMP2 iterations proceed, the number of numerically significant non-zero IDPs decreases, and after several iterations we observed that the number of IDPs is significantly reduced. Thus, it appears that our current algorithm is even more efficient than one-index transformation procedure. Further, in case of all orbitals active, one only needs to construct *VOVO* block of the MO Hessian, in case of frozen-core approximation one additionally needs *VOOO* and *Oooo* blocks. Hence, for the most cases where the CC methods are applicable one can store the MO Hessian in core memory since it has only two virtual index. Nevertheless, for large molecules, in order to avoid explicit construction and inversion of the MO Hessian matrix we also implemented the preconditioned conjugate gradient algorithm⁶⁸ for iterative solution of Eq. (25).

6. Updating MO coefficients

In each iteration, we need to update the MO-coefficients and transform one- and two-electron integrals from atomic orbital (AO) basis to MO basis

$$\mathbf{C} = \mathbf{C}^{(0)}\mathbf{U} = \mathbf{C}^{(0)}e^{\mathbf{K}}, \quad (38)$$

$$C_{\mu p} = \sum_r C_{\mu r}^{(0)} U_{rp}, \quad (39)$$

where $\mathbf{C}^{(0)}$ is the old MO-coefficients matrix, \mathbf{C} is the new MO-coefficients matrix, and \mathbf{U} is the MO-rotation matrix. In order to use Eq. (38) we can expand the exponential term up to the second order

$$\mathbf{U} = e^{\mathbf{K}} = \mathbf{1} + \mathbf{K} + \frac{1}{2}\mathbf{K}^2, \quad (40)$$

$$U_{pq} = \delta_{pq} + K_{pq} + \frac{1}{2} \sum_r K_{pr} K_{rq}, \quad (41)$$

However, this approximate \mathbf{U} matrix will not be unitary. Therefore, at each step we orthogonalize the \mathbf{U} matrix with a modified Gram-Schmidt procedure.⁶⁸

7. MO optimization procedure

Our quadratically convergent orbital-optimized CCD wave function is defined by a set of orbital rotation parameters κ , and double excitation, and de-excitation amplitudes \mathbf{t}_2 and λ_2 . In order to optimize the orbitals we need to construct the MO gradient via the generalized-Fock matrix and the MO Hessian. For computational efficiency, we optimize \mathbf{t}_2 , λ_2 , and κ simultaneously, similar to the process of Sherrill *et al.*¹³ We can summarize the MO optimization procedures as follows:

- (1) Perform the SCF procedure and store necessary parameters.
- (2) Transform the AO integrals to the MO space.
- (3) Make initial guess to \mathbf{t}_2 and λ_2 amplitudes using the standard MP2 amplitudes.
- (4) Form the initial one and two PDMs (OPDM and TPDM).
- (5) Form the initial generalized-Fock matrix.
- (6) Select the numerically significant independent pairs and form the gradient vector for these IDPs.
- (7) Form the MO Hessian matrix for the independent pairs.
- (8) Solve the simultaneous equation, Eq. (25), for the κ vector.⁶⁹
- (9) Form the \mathbf{U} matrix by Eq. (41).
- (10) Orthogonalize the \mathbf{U} matrix.
- (11) Update the MO coefficient matrix by Eq. (39).
- (12) Transform the atomic orbital (AO) integrals to the MO space.
- (13) Solve the \mathbf{t}_2 -amplitude equation to obtain new \mathbf{t}_2 amplitudes.
- (14) Solve the λ_2 -amplitude equation to obtain new λ_2 amplitudes.
- (15) Form the new OPDM and TPDM.
- (16) Form the new generalized-Fock matrix.
- (17) Select the numerically significant independent pairs and form the gradient vector for these IDPs.
- (18) Check the convergence for the energy, root-mean-square (rms) MO gradient, maximum MO gradient, rms κ vector, maximum κ vector, rms \mathbf{t}_2 , and rms λ_2 .
- (19) If convergence criteria are not satisfied for the seven parameters in Step 18 go back to Step 7.

B. The closed-shell (RHF reference) spin adapted equations

In this section, we present the spin-adapted equations for the closed-shell (RHF reference) case. The closed-shell spin-adapted equations for the PDMs, generalized-Fock matrix, and MO Hessian are presented. One can find closed-shell spin adapted equations for t_2 amplitudes in the papers of Scuseria *et al.*^{16,17} and for λ_2 amplitudes (as Z-vector) in the paper of Scheiner *et al.*⁶⁶

1. Spin-adapted equations for response density matrices

The spin integration for PDMs has been carried out diagrammatically following the prescription of Bartlett and Musial.⁷⁰ For the closed-shell case, we have defined the spin-adapted PDMs as follows:

$$\gamma_{PQ} = 2\gamma_{p_a q_a}, \quad (42)$$

$$\Gamma_{PQRS} = 2(\Gamma_{p_a q_a r_a s_a} + \Gamma_{p_a q_b r_a s_b}), \quad (43)$$

where uppercase indices indicate the spatial orbitals. For the one-particle density matrix (OPDM) we will use the same definition as in Eq. (26). However, the two-particle density matrix (TPDM) given in Eq. (27) loses some permutational symmetry properties with spin-adaptation. Therefore, in order to achieve the same (8-fold) permutational symmetry as the two-electron integrals in the spin-adapted formalism we have re-symmetrized TPDM. Our new definition can be written as

$$\tilde{\Gamma}_{PQRS} = \frac{1}{2}(\Gamma_{PQRS} + \Gamma_{PSRQ}). \quad (44)$$

Hereafter, we will drop the tilde notation and all two-particle density matrix expressions refer to the fully symmetrized TPDM, Eq. (44). Reference contributions for non-zero blocks of the PDMs are

$$\gamma_{IJ}^{ref} = 2\delta_{IJ}, \quad (45)$$

$$\Gamma_{IJKL}^{ref} = \delta_{IK}\delta_{JL} - \frac{1}{4}\delta_{IL}\delta_{JK} - \frac{1}{4}\delta_{IJ}\delta_{KL}. \quad (46)$$

Spin-adapted equations for unique non-zero blocks of one-particle density matrix are

$$\gamma_{PQ} = \gamma_{PQ}^{ref} + \gamma_{PQ}^{corr}, \quad (47)$$

$$\gamma_{IJ}^{corr} = -(\mathcal{G}_{IJ} + \mathcal{G}_{JI}), \quad (48)$$

$$\gamma_{AB}^{corr} = -(\mathcal{G}_{AB} + \mathcal{G}_{BA}), \quad (49)$$

while spin-adapted equations for unique non-zero blocks of two-particle density matrix are

$$\begin{aligned} \Gamma_{PQRS} &= \Gamma_{PQRS}^{ref} + \Gamma_{PQRS}^{corr} \\ &+ \frac{1}{2}\delta_{PR}^{occ}\gamma_{QS}^{corr} + \frac{1}{2}\delta_{QS}^{occ}\gamma_{PR}^{corr} \\ &- \frac{1}{8}\delta_{PS}^{occ}\gamma_{QR}^{corr} - \frac{1}{8}\delta_{QR}^{occ}\gamma_{PS}^{corr} \\ &- \frac{1}{8}\delta_{PQ}^{occ}\gamma_{RS}^{corr} - \frac{1}{8}\delta_{RS}^{occ}\gamma_{PQ}^{corr}, \end{aligned} \quad (50)$$

$$\Gamma_{IJKL}^{corr} = \frac{1}{8}(V_{IJKL} + V_{KLIJ} + V_{ILKJ} + V_{KJIL}), \quad (51)$$

$$\Gamma_{ABCD}^{corr} = \frac{1}{8}(V_{ABCD} + V_{CDAB} + V_{ADCB} + V_{CBAD}), \quad (52)$$

$$\Gamma_{IAJB}^{corr} = -\frac{1}{4}(V'_{IAJB} + V'_{JBIA} + V'_{IBJA} + V'_{JAIB}), \quad (53)$$

$$\begin{aligned} \Gamma_{IJAB}^{corr} = & \frac{1}{8}(2t_{IJ}^{AB} - t_{JI}^{AB}) + \frac{1}{8}(2\lambda_{AB}^{IJ} - \lambda_{BA}^{IJ}) \\ & + \frac{1}{8} \sum_M^{occ} \sum_E^{vir} (2t_{IM}^{AE} - t_{MI}^{AE}) V''_{JEMB} \\ & + \frac{1}{8} \sum_M^{occ} \sum_E^{vir} (2t_{JM}^{BE} - t_{MJ}^{BE}) V''_{IEMA} \\ & - \frac{1}{8} \sum_M^{occ} \sum_E^{vir} t_{JM}^{AE} V''_{IEMB} - \frac{1}{8} \sum_M^{occ} \sum_E^{vir} t_{IM}^{BE} V''_{JEMA} \\ & + \frac{1}{8} \sum_M^{occ} \sum_E^{vir} t_{MJ}^{AE} V'_{IEMB} + \frac{1}{8} \sum_M^{occ} \sum_E^{vir} t_{MI}^{BE} V'_{JEMA} \\ & - \frac{1}{8} \sum_M^{occ} (2t_{MJ}^{AB} - t_{JM}^{AB}) \mathcal{G}_{IM} \\ & - \frac{1}{8} \sum_M^{occ} (2t_{IM}^{AB} - t_{MI}^{AB}) \mathcal{G}_{JM} \\ & + \frac{1}{8} \sum_E^{vir} (2t_{IJ}^{EB} - t_{JI}^{EB}) \mathcal{G}_{EA} \\ & + \frac{1}{8} \sum_E^{vir} (2t_{JI}^{EA} - t_{IJ}^{EA}) \mathcal{G}_{EB} \\ & + \frac{1}{4}(V''_{JAIB} + V''_{IBJA}) + \frac{1}{8} \sum_{M,N}^{occ} t_{MN}^{AB} V_{IJMN}. \end{aligned} \quad (54)$$

The intermediates \mathcal{G} , V , V' , and V'' are provided in Appendix B.

2. Spin-adapted equations for the generalized-Fock and MO gradient

For the closed-shell, case we have defined the spin-adapted generalized-Fock and MO gradient as follows:

$$F_{PQ} = 2F_{p_\alpha q_\alpha}, \quad (55)$$

$$w_{PQ} = 2w_{p_\alpha q_\alpha}. \quad (56)$$

Spin-adapted equations for the generalized-Fock and MO gradient are

$$F_{TU} = \sum_P h_{TP} \gamma_{PU} + 4 \sum_{P,Q,R} \langle PQ|RT \rangle \Gamma_{PQRU}, \quad (57)$$

$$w_{TU} = 2(F_{TU} - F_{UT}), \quad (58)$$

where h_{TP} and $\langle PQ|RT \rangle$ are spin-free core Hamiltonian matrix element and two-electron integrals ($h_{TP} = h_{t_\alpha p_\alpha}$ and $\langle PQ|RT \rangle = \langle p_\alpha q_\alpha | r_\alpha t_\alpha \rangle$).

3. Spin-adapted equations for the MO Hessian

For the closed-shell case, we have defined the spin-adapted MO Hessian as follows:

$$A_{TU,VW} = 2(A_{t_\alpha u_\alpha, v_\alpha w_\alpha} + A_{t_\alpha u_\alpha, v_\beta w_\beta}). \quad (59)$$

The explicit spin-adapted equation for the MO Hessian is

$$\begin{aligned} A_{TU,VW} = & \delta_{UV}(F_{TW} + F_{WT}) + \delta_{TW}(F_{VU} + F_{UV}) \\ & - \delta_{TV}(F_{UW} + F_{WU}) - \delta_{UW}(F_{VT} + F_{TV}) \\ & + 2h_{TV} \gamma_{WU} - 2h_{UV} \gamma_{WT} \\ & - 2h_{TW} \gamma_{VU} + 2h_{UW} \gamma_{VT} \\ & + 16 \sum_{P,Q} \langle PQ|VT \rangle \Gamma_{PQWU} \\ & - 16 \sum_{P,Q} \langle PQ|VU \rangle \Gamma_{PQWT} \\ & - 16 \sum_{P,Q} \langle PQ|WT \rangle \Gamma_{PQVU} \\ & + 16 \sum_{P,Q} \langle PQ|WU \rangle \Gamma_{PQVT} \\ & + 8 \sum_{P,Q} \langle PV|QT \rangle \Gamma_{PWQU} \\ & - 8 \sum_{P,Q} \langle PV|QU \rangle \Gamma_{PWQT} \\ & - 8 \sum_{P,Q} \langle PW|QT \rangle \Gamma_{PVQU} \\ & + 8 \sum_{P,Q} \langle PW|QU \rangle \Gamma_{PVQT}. \end{aligned} \quad (60)$$

Now, Eq. (25) can be rewritten as

$$w_{PQ} + \sum_{RS} A_{PQ,RS} \kappa_{RS} = 0. \quad (61)$$

We have kept the equations for the MO hessian, Eq. (60), and the generalized-Fock matrix, Eq. (57), quite general. However, for computational efficiency we have decomposed these equations in terms of unique non-zero blocks of the PDMs. Further, we have constructed only necessary block(s) of the MO Hessian.

C. Quadratically convergent orbital-optimized second-order Møller-Plesset perturbation theory (OMP2)

Because the MP2 method may be regarded as an approximate CCD method, we may use a similar approach for orbital optimization, although the detailed equations will of course differ. The MP2 energy and amplitude equations can be summarized as follows:

$$\Delta E^{(2)} = \langle 0 | (\hat{W}_N \hat{T}_2^{(1)})_c | 0 \rangle, \quad (62)$$

$$\langle \Phi_{ij}^{ab} | (\hat{f}_N \hat{T}_2^{(1)} + \hat{W}_N)_c | 0 \rangle = 0, \quad (63)$$

$$\hat{f}_N = \sum_{p,q} f_{pq} \{ \hat{p}^\dagger \hat{q} \}, \quad (64)$$

$$\hat{W}_N = \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \}, \quad (65)$$

where \hat{f}_N and \hat{W}_N are one- and two-electron components of the normal ordered Hamiltonian operator and subscript c means only connected diagrams are included. The MP2 amplitude equation can be written more explicitly as follows:^{42,71,72}

$$t_{ij}^{ab(1)} D_{ij}^{ab} = \langle ij || ab \rangle - \hat{P}_-(ij) \sum_{m \neq j}^{occ} t_{im}^{ab(1)} f_{mj} + \hat{P}_-(ab) \sum_{e \neq b}^{vir} t_{ij}^{ae(1)} f_{be}, \quad (66)$$

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb}. \quad (67)$$

The $\{t_{ij}^{ab(1)}\}$ are the first-order amplitudes (expansion coefficients for first-order correction to the wave function). In the regular RHF based MP2 method the last two terms of Eq. (66) may be set to zero because of the use of the canonical orbitals. However, since during the OMP2 iterations the Fock matrix will not be diagonal anymore, we add these off-diagonal Fock contributions to the amplitude equation. Alternatively, one may semicanonicalize the active Fock matrix at each iteration to get rid of those off-diagonal Fock contributions.

The MP2- Λ correlation energy functional can be defined as⁷³

$$\Delta \tilde{E}^{(2)} = \langle 0 | \{ \hat{W}_N \hat{T}_2^{(1)} \}_c | 0 \rangle + \langle 0 | [\hat{\Lambda}_2^{(1)} \{ \hat{f}_N \hat{T}_2^{(1)} + \hat{W}_N \}_c]_c | 0 \rangle, \quad (68)$$

$$\hat{\Lambda}_2^{(1)} = \hat{T}_2^{\dagger(1)}. \quad (69)$$

Correlation contributions for the unique non-zero blocks of PDMs are

$$\gamma_{ij}^{corr(2)} = -\frac{1}{2} (\mathcal{G}_{ij}^{(2)} + \mathcal{G}_{ji}^{(2)}), \quad (70)$$

$$\gamma_{ab}^{corr(2)} = -\frac{1}{2} (\mathcal{G}_{ab}^{(2)} + \mathcal{G}_{ba}^{(2)}), \quad (71)$$

$$\Gamma_{ijab}^{corr(1)} = \frac{1}{4} t_{ij}^{ab(1)}. \quad (72)$$

Second-order OPDM equations are similar to those for the CCD case. We can obtain the second-order $\mathcal{G}_{ij}^{(2)}$ and $\mathcal{G}_{ab}^{(2)}$ intermediates by replacing both t_2 - and λ_2 -amplitudes in Eq. (A4) and Eq. (A5) with first-order t_2 -amplitudes. In the

usual canonical SCF case, diagonal parts of \hat{f}_N appear in zeroth-order and \hat{W}_N in first-order of perturbative energy corrections.^{71,74} Therefore, to obtain an overall second-order energy correction, (OO) and (VV) blocks of OPDM appear in second-order and the TPDM appears in first-order. Thus, we can write the correlation energy of the MP2- Λ functional in terms of PDMs as follows:

$$\Delta \tilde{E}^{(2)} = \sum_{p,q} \gamma_{pq}^{corr(2)} f_{pq} + \sum_{p,q,r,s} \Gamma_{pqrs}^{corr(1)} \langle pq || rs \rangle. \quad (73)$$

We did not consider single excitations, although the Fock matrix will not be diagonal during OMP2 iterations, by analogy to the OD method.

III. RESULTS AND DISCUSSION

Results from the OD and OMP2 methods have been obtained for H₂O, three diatomics (N₂, F₂, and C₂), and O₄⁺ for comparison with those from the standard MP2, CCD, CCSD, and CCSD(T) methods. The geometry and harmonic vibrational frequencies of the H₂O molecule were determined using numerical differentiation of the total energies. For diatomic molecules, bond distances, vibrational frequencies, and spectroscopic constants (B_e , D_e , and α_e) are obtained using the DIATOMIC (Ref. 75) program. For each method five single point energies, uniformly distributed about the equilibrium bond length (± 0.005 Å, ± 0.010 Å), are provided to the DIATOMIC program. The CCSD, CCSD(T), and MP2 energies are obtained from PSI3 program,⁵¹ while the CCD, OD, and OMP2 energies are obtained from our new codes. Pople's 6-311G(d) and 6-311G(d,p) basis sets,⁷⁶⁻⁷⁸ Dunning's correlation-consistent polarized core-valence double- and triple- ζ basis sets (cc-pCVDZ and cc-pCVTZ),^{79,80} and Huzinaga-Dunning DZP and TZ2P basis sets⁸¹⁻⁸⁴ were used without the frozen core approximation for correlated procedures. For single point energy computations, 10^{-10} was used as a convergence criterion for the total energies.

Table I presents comparison of total number of iterations for quadratically convergent (QC) and DIIS algorithms in the OD method. Total number of iterations are very similar for both algorithms. However, it should be noted that our new algorithm is more reliable. It is well-known that in problematic cases, such as the molecules which have flat orbital spaces, DIIS may fail to converge or may locate a undesired stationary point when initial guess orbitals are not enough close to the optimized orbitals.⁸⁵ Especially in case of active space approximations, such as the valence active space, the initial MO Hessian may include negative eigenvalue(s). In such a case the DIIS algorithm may converge to a saddle-point rather than a minimum. However, our algorithm along with the augmented Hessian method guarantees convergence to a minimum if there is any.⁶⁹

A. H₂O

Table II presents the total energies, equilibrium O-H bond distances (r_{OH}), H-O-H bond angles (θ_{HOH}), and harmonic vibrational frequencies ($\omega_1, \omega_2, \omega_3$) for the H₂O (\tilde{X}^1A_1) molecule with the six correlated methods. The

TABLE I. Comparison of total number of iterations for quadratically convergent (QC) and DIIS algorithms in the OD method.

Molecule	Basis set	QC ^a	DIIS ^b
H ₂ O	DZP	9	10
	cc-pCVDZ	8	8
	6-311G(d,p)	8	9
	TZ2P	9	10
	cc-pCVTZ	8	9
N ₂	DZP	11	10
	cc-pCVDZ	11	11
	6-311G(d)	11	10
	TZ2P	11	10
	cc-pCVTZ	10	10
F ₂	DZP	14	11
	cc-pCVDZ	13	11
	6-311G(d)	13	11
	TZ2P	13	11
	cc-pCVTZ	12	11

^aPresent algorithm.^bThe algorithm presented in Ref. 13.

total energies of CCSD and OD remain nearly identical due to the very similar equilibrium geometries. The energy difference between OD and CCSD is roughly 0.1–0.2 millihartree. The OD and OMP2 methods provide total energies that are 1–2 millihartrees lower than those of CCD and MP2. In general as the basis set size increases the energy difference between orbital-optimized and unoptimized methods increases slightly.

The computed O–H bond distance and H–O–H bond angle are in reasonable agreement with the experimental values⁸⁶ of $r_{OH} = 0.9580$ Å and $\theta_{HOH} = 104.5^\circ$ especially with triple- ζ quality basis sets. The equilibrium O–H bond distance and H–O–H bond angle of the OD method are almost the same with the CCSD, and slightly longer (by 0.0007–0.0009 Å), than those for the CCD. Similarly, the OMP2 method provides roughly 0.001–0.002 Å longer bond lengths than MP2.

The predicted harmonic vibrational frequencies are in satisfactory agreement with the experimental harmonic values⁸⁷ of 3832 (ω_1), 1648 (ω_2), and 3943 (ω_1) cm⁻¹. The OD method provides almost identical harmonic vibrational frequencies with the CCSD method ($\Delta\omega \leq 2$ cm⁻¹), while yielding significantly lower frequencies than CCD. The MP2 and OMP2 methods provide slightly different frequencies; the difference between predicted ω_2 values is less than 4 cm⁻¹, while ω_1 and ω_3 values differ by as much as 33 cm⁻¹. Another salient feature appearing in Table II is that the orbital optimized methods yield slightly lower vibrational frequencies than corresponding unoptimized methods, since orbital optimization leads to longer bond distances.

B. N₂

Table III presents the total energies, equilibrium bond distances (r_e), harmonic (ω_e) and fundamental (anharmonic) (ν_e) vibrational frequencies, rotational constants (B_e), centrifugal distortion constants (D_e), and vibration-rotation coupling constants (α_e) for the N₂ molecule ($X^1\Sigma_g^+$) with the

six correlated methods. The OD and CCSD total energies are again close to each other. However, the energy differences, 1–2 millihartrees, are 10 times higher than in the H₂O molecule, 0.1–0.2 millihartrees. Further, the OMP2 method provides energies 5–8 millihartrees lower than MP2, while the OD method provides energies lower than CCD by 3–4 millihartrees. Thus for the N₂ molecule, the MP2 method is more sensitive to the orbitals than CCD, and the Hartree-Fock (HF) orbitals are far from being optimal choice for the MP2 method. Since the MP2 energies are already close to the CCSD energies, by optimizing the orbitals the OMP2 energies fall below the CCSD energies by 3–8 millihartrees. However, the OMP2 energies are still higher than those for CCSD(T) by 7–12 millihartrees.

All the predicted bond distances are in satisfactory agreement with the experimental value⁸⁸ of 1.0977 Å. The OD method provides slightly shorter bond lengths than the CCSD method, whereas OMP2 provides longer bond lengths than MP2. The difference between OD and CCSD is $\Delta r_e = 0.0005$ – 0.0007 Å, while it is $\Delta r_e = 0.0068$ – 0.0074 Å between MP2 and OMP2. Further, the MP2, OMP2, and CCSD(T) methods predict longer bond distances than experiment with all basis sets considered in this research. The OMP2 method in particular overestimates bond distances with the double- ζ basis sets. Thus, our results indicate that in order to obtain an accurate bond distance for the N₂ molecule using the OMP2 method one needs to use large basis sets (at least triple- ζ quality basis sets).

For the harmonic vibrational frequency of the N₂ molecule, the MP2 and OMP2 methods provide significantly lower frequencies than other methods ($\Delta\omega_e \sim 250$ and ~ 350 cm⁻¹, respectively), since these methods yield longer bond distances. The predictions of other methods are in reasonable agreement with the experiment.⁸⁸ A similar feature is also observed for the fundamental frequencies. For spectroscopic constants, again the OD and CCSD methods yield very close results. Centrifugal distortion and vibration-rotation coupling constants are virtually the same for these methods. However, rotational constants differ by as much as 0.026 cm⁻¹ because of the slightly different bond distances. The MP2 and OMP2 methods again provide significantly different results compared to the other four methods. The rotational constant is underestimated with these methods due to the overestimated bond distances. Another prominent feature of Table III is that the CCSD(T) method gives better results for spectroscopic constants than other five methods comparing to experiment.

C. F₂

Table IV presents total energies and spectroscopic constants for the F₂ ($X^1\Sigma_g^+$) molecule with the six correlated methods. The OMP2 method provides lower total energies than the CCSD method by 3–7 millihartrees with triple- ζ basis sets. However, OMP2 energies are still higher than those of CCSD(T) by 10–14 millihartrees.

Except in the cc-pCVTZ basis, both OMP2 and CCSD(T) methods significantly overestimate the bond length. However, with the cc-pCVTZ basis these methods provide better results

TABLE II. Predicted total energies (in hartrees), geometries, and harmonic vibrational frequencies (in cm^{-1}) for the $\text{H}_2\text{O} (\tilde{X}^1A_1)$ molecule (bond distances in \AA) with the six correlated methods.

Basis set	Method	E_{tot}	r_{OH}	θ_{HOH}	ω_1	ω_2	ω_3
DZP	MP2	-76.257 742	0.9654	103.7°	3888	1660	4022
DZP	OMP2	-76.258 893	0.9664	103.5°	3866	1658	4002
DZP	CCD	-76.265 953	0.9641	104.0°	3905	1681	4024
DZP	OD	-76.266 717	0.9648	103.9°	3891	1679	4009
DZP	CCSD	-76.266 874	0.9649	103.9°	3889	1679	4008
DZP	CCSD(T)	-76.270 156	0.9659	103.7°	3871	1673	3991
cc-pCVDZ	MP2	-76.268 761	0.9643	101.9°	3853	1679	3973
cc-pCVDZ	OMP2	-76.269 754	0.9654	101.7°	3830	1676	3951
cc-pCVDZ	CCD	-76.278 364	0.9633	102.3°	3869	1701	3973
cc-pCVDZ	OD	-76.279 047	0.9640	102.2°	3852	1699	3956
cc-pCVDZ	CCSD	-76.279 154	0.9641	102.2°	3849	1698	3954
cc-pCVDZ	CCSD(T)	-76.282 505	0.9656	101.9°	3824	1692	3931
6-311G(d,p)	MP2	-76.282 896	0.9572	102.5°	3910	1667	4017
6-311G(d,p)	OMP2	-76.284 394	0.9585	102.3°	3884	1664	3993
6-311G(d,p)	CCD	-76.289 441	0.9558	102.9°	3929	1692	4022
6-311G(d,p)	OD	-76.290 368	0.9565	102.8°	3912	1690	4006
6-311G(d,p)	CCSD	-76.290 546	0.9567	102.8°	3910	1689	4003
6-311G(d,p)	CCSD(T)	-76.295 380	0.9583	102.5°	3882	1682	3976
TZ2P	MP2	-76.316 483	0.9579	104.4°	3861	1663	3982
TZ2P	OMP2	-76.318 850	0.9597	104.2°	3828	1659	3951
TZ2P	CCD	-76.321 029	0.9548	104.8°	3901	1693	4006
TZ2P	OD	-76.322 271	0.9557	104.7°	3886	1691	3990
TZ2P	CCSD	-76.322 568	0.9558	104.7°	3883	1690	3987
TZ2P	CCSD(T)	-76.329 386	0.9582	104.4°	3845	1679	3951
cc-pCVTZ	MP2	-76.374 875	0.9580	103.6°	3857	1651	3976
cc-pCVTZ	OMP2	-76.376 927	0.9596	103.4°	3828	1648	3947
cc-pCVTZ	CCD	-76.380 225	0.9551	104.1°	3895	1679	3997
cc-pCVTZ	OD	-76.381 317	0.9559	104.0°	3881	1678	3983
cc-pCVTZ	CCSD	-76.381 555	0.9560	104.0°	3879	1678	3980
cc-pCVTZ	CCSD(T)	-76.389 797	0.9584	103.7°	3841	1668	3945
Experiment ^{a,b}			0.9580	104.5°	3832	1648	3943

^aGeometrical parameters from Hoy *et al.* (Ref. 86).^bHarmonic vibrational frequencies from Wathelet *et al.* (Ref. 87).

than the other methods. These results again suggest that one should use the OMP2 method with large basis sets (at least triple- ζ quality basis sets) in order to obtain reliable bond distances. Further, since OMP2 and CCSD(T) methods overestimate the bond length, they also give lower vibrational frequencies compared to other methods.

The OMP2 and CCSD(T) methods underestimate the rotational constant due to overestimated bond distance except for the cc-pCVTZ basis. The difference between the OD and CCSD methods is $\Delta B_e \leq 0.0015 \text{ cm}^{-1}$, while for OMP2 and MP2 it is $\Delta B_e \leq 0.0318 \text{ cm}^{-1}$. For centrifugal distortion constant results, all methods are in reasonable agreement with the experimental value⁸⁸ of $3.3 \times 10^{-6} \text{ cm}^{-1}$. However, all methods underestimate the vibration-rotation coupling constant. MP2 and CCD methods provide smaller constants than other methods.

D. C_2

Table V presents the total energies and spectroscopic constants for the C_2 molecule ($X^1\Sigma_g^+$) with the six correlated methods. The most remarkable feature of Table V is

that the OMP2 total energies are even lower than those for CCSD(T) except for the cc-pCVTZ basis. Since MP2 energies are already lower than those for CCSD, by optimizing orbitals the OMP2 energies fall below the CCSD(T) by 2–3 milihartrees.

For the CCSD method \mathcal{T}_1 -diagnostics^{89–91} are 0.03, which are higher than the reference value of 0.02. Further, the percentage of reference determinants in the OD and OMP2 wavefunctions are approximately 89% and 88%, respectively. These results indicate a slight multireference character for the C_2 molecule. It is well-known that the C_2 molecule has low-lying excited states which strongly interact with the ground state.⁹² Hence, low total energies of OMP2 may be attributed to multireference character of the C_2 molecule, since the perturbation theory assumes that the exact wavefunction is dominated by a single determinant. Another interesting point is that with each basis set, the energy of the LUMO is negative. Further analyses with natural orbitals (NO) show that occupation numbers are 0.2424 and 0.2562 for the LUMO at OD/cc-pCVTZ and OMP2/cc-pCVTZ levels, respectively. The NO analysis show that the occupied character of the LUMO is more than for a regular virtual orbital.

TABLE III. Predicted total energies (in hartrees), geometries (bond distances in angstroms), harmonic and anharmonic vibrational frequencies (in cm^{-1}), and spectroscopic constants (B_e and α_e in cm^{-1} , D_e in $10^6 \times \text{cm}^{-1}$) for the N_2 ($X^1\Sigma_g^+$) molecule with the six correlated methods.

Basis set	Method	E_{tot}	r_e	ω_e	ν_e	B_e	D_e	α_e
DZP	MP2	-109.295 106	1.1391	2114	2087	1.8557	5.7	0.0192
DZP	OMP2	-109.300 981	1.1462	2023	1992	1.8325	6.0	0.0213
DZP	CCD	-109.293 854	1.1182	2379	2358	1.9257	5.0	0.0148
DZP	OD	-109.296 234	1.1197	2364	2343	1.9205	5.1	0.0149
DZP	CCSD	-109.296 825	1.1202	2357	2336	1.9187	5.1	0.0150
DZP	CCSD(T)	-109.308 760	1.1261	2293	2272	1.8985	5.2	0.0156
6-311G(d)	MP2	-109.334 062	1.1190	2186	2152	1.9227	6.0	0.0202
6-311G(d)	OMP2	-109.341 354	1.1264	2090	2051	1.8978	6.3	0.0226
6-311G(d)	CCD	-109.329 849	1.1001	2440	2415	1.9896	5.3	0.0153
6-311G(d)	OD	-109.332 872	1.1016	2424	2399	1.9840	5.3	0.0155
6-311G(d)	CCSD	-109.333 657	1.1022	2417	2391	1.9819	5.3	0.0156
6-311G(d)	CCSD(T)	-109.348 671	1.1086	2345	2319	1.9589	5.5	0.0165
cc-pCVDZ	MP2	-109.339 919	1.1284	2177	2144	1.8910	5.7	0.0202
cc-pCVDZ	OMP2	-109.346 254	1.1354	2085	2048	1.8678	6.0	0.0223
cc-pCVDZ	CCD	-109.339 972	1.1091	2435	2410	1.9573	5.1	0.0155
cc-pCVDZ	OD	-109.342 610	1.1106	2419	2394	1.9520	5.1	0.0156
cc-pCVDZ	CCSD	-109.343 280	1.1112	2412	2388	1.9500	5.1	0.0156
cc-pCVDZ	CCSD(T)	-109.356 337	1.1174	2342	2318	1.9284	5.2	0.0164
TZ2P	MP2	-109.365 161	1.1116	2191	2154	1.9484	6.2	0.0214
TZ2P	OMP2	-109.372 729	1.1189	2094	2052	1.9231	6.5	0.0239
TZ2P	CCD	-109.360 970	1.0930	2441	2413	2.0152	5.5	0.0165
TZ2P	OD	-109.364 083	1.0945	2425	2397	2.0098	5.5	0.0166
TZ2P	CCSD	-109.364 856	1.0951	2418	2390	1.9993	5.5	0.0167
TZ2P	CCSD(T)	-109.382 036	1.1020	2340	2310	1.9826	5.7	0.0177
cc-pCVTZ	MP2	-109.462 530	1.1101	2208	2174	1.9539	6.1	0.0205
cc-pCVTZ	OMP2	-109.470 338	1.1175	2109	2068	1.9279	6.4	0.0231
cc-pCVTZ	CCD	-109.458 559	1.0913	2459	2433	2.0218	5.5	0.0158
cc-pCVTZ	OD	-109.461 852	1.0928	2442	2415	2.0160	5.5	0.0160
cc-pCVTZ	CCSD	-109.462 698	1.0935	2434	2409	2.0137	5.5	0.0161
cc-pCVTZ	CCSD(T)	-109.482 426	1.1006	2355	2329	1.9876	5.7	0.0170
Experiment			1.0977	2359	2330	1.998	5.8	0.0173 ^a

^aHuber and Herzberg (Ref. 88).

Since the standard MP2 method already overestimates the bond distance, by optimizing the MOs the OMP2 method provides even longer bond distances. However, as the basis set size increases the OMP2 method gives a more reasonable bond distance. As observed for N_2 and F_2 , one should use the OMP2 method with large basis sets (larger basis sets than triple- ζ quality basis sets) in order to obtain a reliable bond distance. The predicted harmonic vibrational frequencies are in reasonable agreement with the experimental harmonic value⁸⁸ of 1828 cm^{-1} except for the OMP2 method which provides values around 1650 cm^{-1} . The low vibrational frequencies of the OMP2 method are arising from the overestimated bond distances. The difference between predicted frequencies with the OD and CCSD methods is $\Delta\omega_e \leq 13 \text{ cm}^{-1}$, while it is $\Delta\omega_e \leq 219 \text{ cm}^{-1}$ with OMP2 and MP2. A similar situation is also observed for the fundamental frequencies. For spectroscopic constants of the C_2 molecule results of all methods except for OMP2 are in general agreement with experiment.⁸⁸ The OMP2 method significantly underestimates the rotational constant due to the overestimated bond distances. However, for the vibration-rotation coupling constant the OMP2 method provides lower errors than other

methods compared to experiment, differing by 0.0013 cm^{-1} or less from experiment.

E. O_4^+

The O_4^+ molecule is an important species in atmospheric ion chemistry.⁹³ In a 1994 study, Lindh and Barnes⁹⁴ demonstrated that the standard wavefunctions, even including the complete active space SCF (CASSCF) method, suffer from an artifactual symmetry breaking problem. In symmetry breaking problems, wavefunctions fail to show the full point group symmetry of molecules.^{5,22,48,95-97} Spatial symmetry problems in reference (SCF) wavefunctions arise when the MO Hessian has a negative eigenvalue corresponding to a rotation which mixes the orbitals of different irreducible representations. The energy is a stationary point with respect to symmetry breaking rotations due to the symmetry constraints; however, that stationary point is not necessarily a minimum. If the energy is a saddle-point with respect to symmetry breaking rotations, it is possible to find a lower energy symmetry broken solution. Such instabilities indicate

TABLE IV. Predicted total energies (in hartrees), geometries (bond distances in angstroms), harmonic and anharmonic vibrational frequencies (in cm^{-1}), and spectroscopic constants (B_e and α_e in cm^{-1} , D_e in $10^6 \times \text{cm}^{-1}$) for the F_2 ($X^1\Sigma_g^+$) molecule with the six correlated methods.

Basis set	Method	E_{tot}	r_e	ω_e	ν_e	B_e	D_e	α_e
DZP	MP2	-199.117 578	1.4201	981	964	0.8799	2.8	0.0103
DZP	OMP2	-199.126 283	1.4408	895	877	0.8548	3.1	0.0119
DZP	CCD	-199.120 671	1.4119	996	978	0.8902	2.8	0.0105
DZP	OD	-199.125 518	1.4216	954	934	0.8782	3.0	0.0114
DZP	CCSD	-199.126 294	1.4222	952	933	0.8774	3.0	0.0113
DZP	CCSD(T)	-199.136 045	1.4390	876	854	0.8571	3.3	0.0134
cc-pCVDZ	MP2	-199.162 247	1.4235	934	919	0.8758	3.1	0.0101
cc-pCVDZ	OMP2	-199.169 248	1.4451	855	840	0.8498	3.4	0.0114
cc-pCVDZ	CCD	-199.167 847	1.4184	934	918	0.8821	3.1	0.0105
cc-pCVDZ	OD	-199.171 734	1.4297	892	875	0.8681	3.3	0.0112
cc-pCVDZ	CCSD	-199.172 177	1.4306	890	875	0.8672	3.3	0.0111
cc-pCVDZ	CCSD(T)	-199.182 523	1.4566	788	771	0.8364	3.8	0.0136
6-311G(d)	MP2	-199.193 333	1.4113	919	901	0.8910	3.4	0.0120
6-311G(d)	OMP2	-199.201 674	1.4366	820	803	0.8599	3.8	0.0138
6-311G(d)	CCD	-199.193 741	1.4012	937	918	0.9038	3.4	0.0124
6-311G(d)	OD	-199.197 992	1.4124	890	871	0.8896	3.6	0.0134
6-311G(d)	CCSD	-199.198 637	1.4136	887	869	0.8881	3.6	0.0133
6-311G(d)	CCSD(T)	-199.211 691	1.4416	773	753	0.8540	4.2	0.0163
TZ2P	MP2	-199.260 980	1.4193	965	949	0.8810	2.9	0.0098
TZ2P	OMP2	-199.272 254	1.4456	864	845	0.8492	3.3	0.0119
TZ2P	CCD	-199.259 546	1.4051	1002	985	0.8989	2.9	0.0097
TZ2P	OD	-199.264 615	1.4138	967	949	0.8878	3.0	0.0104
TZ2P	CCSD	-199.265 566	1.4150	964	946	0.8863	3.0	0.0104
TZ2P	CCSD(T)	-199.281 999	1.4394	867	846	0.8565	3.3	0.0127
cc-pCVTZ	MP2	-199.395 434	1.3956	1021	1002	0.9112	2.9	0.0099
cc-pCVTZ	OMP2	-199.404 787	1.4159	934	912	0.8851	3.2	0.0119
cc-pCVTZ	CCD	-199.394 799	1.3833	1065	1055	0.9275	2.8	0.0123
cc-pCVTZ	OD	-199.399 068	1.3904	1024	1003	0.9179	3.0	0.0103
cc-pCVTZ	CCSD	-199.399 845	1.3915	1021	1001	0.9165	3.0	0.0104
cc-pCVTZ	CCSD(T)	-199.419 094	1.4133	925	901	0.8885	3.3	0.0129
Experiment			1.4119	917	894	0.890	3.3	0.0138 ^a

^aHuber and Herzberg (Ref. 88).

the presence of different electronic states with close energies. Symmetry breaking problems manifest themselves when second- and higher-order molecular properties, such as vibrational frequencies, are computed.⁴⁸ Symmetry breaking in the wavefunction leads to anomalous behavior in force constants, hence yielding spurious vibrational frequencies.^{97,98}

Sherrill *et al.*¹³ investigated the performance of the OD method for the O_4^+ molecular ion. They showed that the OD method yields reliable vibrational frequencies as opposed to the standard CCSD method and discussed the symmetry-breaking problem in O_4^+ in detail. Hence, we will not repeat that discussion. However, we are interested to compare the performance of the MP2 and OMP2 methods for this challenging system. Table VI presents total energies, geometries, and harmonic vibrational frequencies, for rectangular O_4^+ ($^4B_{1g}$) using the 6-31G(d) basis set. R_{oo} denotes the bond length in each O_2 subunit, while R_{cc} denotes the distance between the two parallel O_2 units. For the UHF MP2 and UHF CCD methods, geometry optimizations and frequency computations were carried out via analytic derivatives with the CFOUR program,⁹⁹ while UHF OMP2 com-

putations were performed with our new codes via numerical derivatives.

Comparing to other methods both the OMP2 and MP2 methods, especially OMP2, yield a longer bond length for R_{oo} , while yielding a shorter distance for R_{cc} . The OMP2 method yields a longer bond length by 0.057–0.172 Å for R_{oo} , while it yields a shorter distance for R_{cc} by 0.015–0.061 Å than other methods. The MP2 method yield an anomalous vibrational frequency of 3540 cm^{-1} for ω_6 (b_{3u}), which differs by a remarkable 2200 cm^{-1} from the experimental value of 1320 cm^{-1} .¹⁰⁰ The OMP2 method gives an underestimated vibrational frequency of 769 cm^{-1} for ω_6 , which differs by 550 cm^{-1} from experiment. The low vibrational frequency of 769 cm^{-1} may be arising from the longer R_{oo} value comparing to other methods. Although ω_6 of OMP2 is not in a good agreement with experiment, it is still much better than MP2. Further, the MP2 method gives a spuriously high vibrational frequency for ω_5 (b_{2u}) due to the symmetry breaking. The OMP2 method yields a frequency of 144 cm^{-1} , which is in agreement with the OD and BD methods. For ω_2 (a_g) and ω_4 (a_u) OMP2 predictions differ by only 1 and

TABLE V. Predicted total energies (in hartrees), geometries (bond distances in Å), harmonic and anharmonic vibrational frequencies (in cm^{-1}), and spectroscopic constants (B_e and α_e in cm^{-1} , D_e in $10^6 \times \text{cm}^{-1}$) for the C_2 ($X^1\Sigma_g^+$) molecule with the six correlated methods.

Basis set	Method	E_{tot}	r_e	ω_e	ν_e	B_e	D_e	α_e
DZP	MP2	-75.731 842	1.2743	1868	1849	1.7302	5.9	0.0148
DZP	OMP2	-75.761 930	1.3039	1667	1652	1.6526	6.5	0.0163
DZP	CCD	-75.720 144	1.2583	1891	1869	1.7746	6.3	0.0161
DZP	OD	-75.730 383	1.2597	1879	1857	1.7706	6.3	0.0161
DZP	CCSD	-75.732 709	1.2620	1867	1845	1.7640	6.3	0.0161
DZP	CCSD(T)	-75.759 633	1.2659	1832	1810	1.7532	6.4	0.0164
6-311G(d)	MP2	-75.754 754	1.2648	1875	1852	1.7564	6.2	0.0153
6-311G(d)	OMP2	-75.786 698	1.2958	1666	1649	1.6734	6.7	0.0170
6-311G(d)	CCD	-75.739 929	1.2500	1891	1866	1.7982	6.5	0.0164
6-311G(d)	OD	-75.750 440	1.2514	1881	1858	1.7940	6.5	0.0162
6-311G(d)	CCSD	-75.752 939	1.2539	1868	1846	1.7871	6.5	0.0162
6-311G(d)	CCSD(T)	-75.783 748	1.2572	1835	1812	1.7775	6.7	0.0165
TZ2P	MP2	-75.769 799	1.2562	1877	1854	1.7805	6.4	0.0162
TZ2P	OMP2	-75.802 562	1.2877	1658	1636	1.6945	7.1	0.0188
TZ2P	CCD	-75.752 812	1.2400	1894	1866	1.8272	6.8	0.0182
TZ2P	OD	-75.763 671	1.2411	1888	1861	1.8239	6.8	0.0179
TZ2P	CCSD	-75.766 240	1.2437	1875	1847	1.8166	6.8	0.0180
TZ2P	CCSD(T)	-75.799 501	1.2470	1842	1815	1.8068	7.0	0.0183
cc-pCVDZ	MP2	-75.772 750	1.2742	1873	1853	1.7305	5.9	0.0148
cc-pCVDZ	OMP2	-75.803 878	1.3042	1674	1658	1.6518	6.4	0.0163
cc-pCVDZ	CCD	-75.762 485	1.2602	1882	1857	1.7691	6.3	0.0164
cc-pCVDZ	OD	-75.772 692	1.2615	1874	1851	1.7654	6.3	0.0161
cc-pCVDZ	CCSD	-75.775 156	1.2639	1861	1839	1.7587	6.3	0.0161
cc-pCVDZ	CCSD(T)	-75.803 987	1.2680	1828	1806	1.7474	6.4	0.0163
cc-pCVTZ	MP2	-75.853 955	1.2555	1889	1867	1.7823	6.3	0.0156
cc-pCVTZ	OMP2	-75.886 572	1.2862	1678	1658	1.6985	7.0	0.0179
cc-pCVTZ	CCD	-75.835 725	1.2393	1912	1887	1.8293	6.7	0.0171
cc-pCVTZ	OD	-75.845 917	1.2406	1904	1879	1.8255	6.7	0.0169
cc-pCVTZ	CCSD	-75.848 549	1.2429	1892	1867	1.8187	6.7	0.0169
cc-pCVTZ	CCSD(T)	-75.883 828	1.2465	1856	1831	1.8083	6.9	0.0173
Experiment			1.2425	1855	1828	1.820	6.9	0.0176 ^a

^aHuber and Herzberg (Ref. 88).

TABLE VI. Predicted total energies (in hartrees), geometries (bond distances in Å), and harmonic vibrational frequencies (in cm^{-1}), for rectangular O_4^+ ($^4B_{1g}$) using the 6-31G(d) basis set.

Method	E_{tot}	R_{oo}	R_{cc}	ω_1 (a_g)	ω_2 (a_g)	ω_3 (b_{1g})	ω_4 (a_u)	ω_5 (b_{2u})	ω_6 (b_{3u})
UHF ^b	-298.761 605	1.1176	2.4058	2242	255	396	196	542i	3223
ROHF ^b	-298.739 290	1.1152	2.4073	2256	258	417	199	83	3612
UHF CCD ^a	-299.475 770	1.1704	2.3801	1835	269	^e	203	822	3940
UHF CCSD ^b	-299.484 239	1.1737	2.3792	1808	269	341	178	154	1726
ROHF CCSD ^b	-299.482 497	1.1730	2.3793	1813	269	372	179	66i	2036
BD ^b	-299.482 212	1.1723	2.3794	1821	269	342	179	82	1194
OD ^b	-299.482 683	1.1728	2.3793	1816	269	372	179	84	1193
UHF CCSD(T) ^c	-299.512 786	1.1846	2.3751	1713	271	372	175	97	1922
BD(T) ^c	-299.512 778	1.1846	2.3751	1713	270				1322
UHF MP2 ^a	-299.518 903	1.2304	2.3612	1254	264	609	196	^e	3540
UHF OMP2 ^a	-299.545 981	1.2870	2.3462	708	268	332	171	144	769
Experiment ^d									1320

^aThis paper.

^bSherrill *et al.* (Ref. 13).

^cBarnes and Lindh (Ref. 4).

^dJacox and Thompson (Ref. 100).

^eSpurious vibrational frequency due to symmetry breaking in the reference wave function.

2 cm⁻¹ from those of the OD and BD methods, while for ω_3 (b_{1g}) the OMP2 result differs by 40 and 10 cm⁻¹ from those of OD and BD, respectively. For ω_3 , the MP2 prediction of 609 cm⁻¹ differs by 237 and 267 cm⁻¹ from those of OD and BD. For ω_1 , both OMP2 and MP2 methods yield lower vibrational frequencies by 1108 and 562 cm⁻¹ than OD, respectively, while they yield lower frequencies by 1113 and 567 cm⁻¹ than BD. Overall, then, both MP2 and OMP2 provide significantly different vibrational frequencies than the presumably more reliable OD and BD frequencies. Although OMP2 underestimates ω_1 more severely than MP2 does, it provides significantly improved predictions for ω_3 , ω_5 , and ω_6 .

IV. CONCLUSIONS

We have presented a quadratically convergent algorithm for variational optimization of the molecular orbitals for the CCD and MP2 methods. We have reported explicit spin-orbital and closed-shell spin-adapted equations for the response density matrices, generalized-Fock matrix (thus the MO gradient), and the MO Hessian explicitly. We have compared our OD and OMP2 approaches with the standard MP2, CCD, CCSD, and CCSD(T) methods.

For variational optimization of the molecular orbitals for OMP2 method, we have considered MP2 as an approximate CCD and we have used the same algorithm. Hence, we have constructed MP2- Λ functional and minimized it with respect to orbital-rotation parameters. Comparing to earlier attempts to obtain variationally optimized MOs for MP2,⁴³⁻⁴⁶ we have minimized MP2- Λ functional instead of the Hylleraas functional. It should be pointed out that our method is more general than the Hylleraas functional based approaches and can be easily extended to higher orders of many-body perturbation theory.

When we compare the scaling of each method, CCD and CCSD scale as n^6 , while MP2 scales n^5 (due to integral transformation). However, scaling of OD is $3n^6$ (t_2 -amplitude n^6 , λ_2 -amplitude n^6 , response PDMs n^6 , generalized-Fock n^5 , and MO hessian $\sim n^4 - n^5$), whereas scaling of OMP2 is n^5 . Thus, for large molecules, a single point OD computation will be approximately 3-times more expensive than a CCSD computation. Similarly, the OMP2 method will be several times more expensive than the standard MP2 method. However, it should be noted that the OMP2 method generally converges in fewer iterations (6–8 iterations) than CCD, CCSD, and OD. For a geometry optimization procedure the computational times for CCSD and OD, or MP2 and OMP2, will be comparable.

For the molecules considered in this research we observed that the CCSD and OD methods give very close results. However, the OMP2 and MP2 methods provide the significantly different total energies. The OMP2 method yields 1–2 milihartrees lower energies than MP2 for the H₂O molecule. For diatomics (N₂, F₂, and C₂) the energy differences between the OMP2 and MP2 methods are larger, 6–33 milihartrees. Further, for diatomics we have observed that OMP2 provides lower energies than CCSD. For the C₂ molecule, perhaps due to its small HOMO-LUMO gap, the OMP2 method yields

even lower energies than CCSD(T). For each molecule considered in this research, the MO stability analyses have been carried out at OMP2/cc-pCVTZ and OD/cc-pCVTZ levels. The results of the MO stability analyses show that the OD and OMP2 methods properly converge to minima in orbital rotation space.

For geometrical parameters, the OMP2 method generally yields longer bond lengths than the MP2 and CCSD methods by 0.0207–0.0433 Å. For the H₂O and F₂ molecules the OMP2 method provides reasonable results for bond distances and frequencies, even better than CCSD, when compared to experiment. However, for the N₂ and C₂ molecules the OMP2 method overestimates bond lengths and underestimates vibrational frequencies. For the test cases considered, if the standard MP2 total energy is higher than that of CCD, then OMP2 yields reasonable predictions for bond distances and vibrational frequencies. In such cases, OMP2 predictions for bond lengths and frequencies are close to those from CCSD(T). However, if the MP2 total energy is lower than the CCD energy, then OMP2 considerably overestimates bond lengths and underestimates vibrational frequencies. Finally, the OMP2 method provides better vibrational frequencies than MP2 method in case of symmetry breaking problems (for O₄⁺).

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APPENDIX A: SPIN-ORBITAL EQUATIONS FOR CORRELATION PDMS

$$V_{ijmn} = \frac{1}{2} \sum_e^{vir} \sum_f^{vir} t_{ij}^{ef} \lambda_{ef}^{mn}, \quad (\text{A1})$$

$$V_{abcd} = \frac{1}{2} \sum_m^{occ} \sum_n^{occ} t_{mn}^{cd} \lambda_{ab}^{mn}, \quad (\text{A2})$$

$$V_{iajb} = \frac{1}{2} \sum_m^{occ} \sum_e^{vir} t_{im}^{be} \lambda_{ae}^{jm}, \quad (\text{A3})$$

$$\mathcal{G}_{ea} = -\frac{1}{2} \sum_m^{occ} \sum_n^{occ} \sum_f^{vir} t_{mn}^{af} \lambda_{ef}^{mn} = -\sum_f^{vir} V_{efaf}, \quad (\text{A4})$$

$$\mathcal{G}_{im} = \frac{1}{2} \sum_n^{occ} \sum_e^{vir} \sum_f^{vir} t_{in}^{ef} \lambda_{ef}^{mn} = \sum_n^{occ} V_{inmn}, \quad (\text{A5})$$

$$\gamma_{ij}^{corr} = -\frac{1}{2} (\mathcal{G}_{ij} + \mathcal{G}_{ji}), \quad (\text{A6})$$

$$\mathcal{V}_{ab}^{corr} = -\frac{1}{2} (\mathcal{G}_{ab} + \mathcal{G}_{ba}), \quad (\text{A7})$$

$$\Gamma_{ijkl}^{corr} = \frac{1}{8} (V_{ijkl} + V_{klij}), \quad (\text{A8})$$

$$\Gamma_{abcd}^{corr} = \frac{1}{8} (V_{abcd} + V_{cdab}), \quad (\text{A9})$$

$$\Gamma_{iajb}^{corr} = -\frac{1}{4} (V_{iajb} + V_{jbia}), \quad (\text{A10})$$

$$\begin{aligned} \Gamma_{ijab}^{corr} &= \frac{1}{8} t_{ij}^{ab} + \frac{1}{8} \lambda_{ab}^{ij} \\ &- \frac{1}{8} \hat{P}_-(ij) \hat{P}_-(ab) \sum_m^{occ} \sum_e^{vir} t_{mi}^{ae} V_{jemb} \\ &- \frac{1}{8} \hat{P}_-(ij) \sum_m^{occ} t_{mj}^{ab} \mathcal{G}_{im} \\ &+ \frac{1}{8} \hat{P}_-(ab) \sum_e^{vir} t_{ij}^{eb} \mathcal{G}_{ea} \\ &+ \frac{1}{16} \sum_{m,n}^{occ} t_{mn}^{ab} V_{ijmn}. \end{aligned} \quad (\text{A11})$$

APPENDIX B: THE CLOSED-SHELL SPIN-ADAPTED EQUATIONS FOR PDM INTERMEDIATES

$$V_{IJMN} = 2V_{i_\alpha j_\beta m_\alpha n_\beta} - V_{i_\alpha j_\beta n_\alpha m_\beta}, \quad (\text{B1})$$

$$V_{IJMN} = \sum_{E,F}^{vir} t_{IJ}^{EF} (2\lambda_{EF}^{MN} - \lambda_{FE}^{MN}), \quad (\text{B2})$$

$$t_{IJ}^{AB} = t_{i_\alpha j_\beta}^{a_\alpha b_\beta}, \quad (\text{B3})$$

$$\lambda_{AB}^{IJ} = \lambda_{a_\alpha b_\beta}^{i_\alpha j_\beta}, \quad (\text{B4})$$

$$V_{ABCD} = 2V_{a_\alpha b_\beta c_\alpha d_\beta} - V_{a_\alpha b_\beta d_\alpha c_\beta}, \quad (\text{B5})$$

$$V_{ABCD} = \sum_{M,N}^{occ} t_{MN}^{CD} (2\lambda_{AB}^{MN} - \lambda_{BA}^{MN}), \quad (\text{B6})$$

$$(\text{B7})$$

$$V_{i_\alpha a_\beta j_\alpha b_\beta} = \frac{1}{2} \sum_M^{occ} \sum_E^{vir} t_{MI}^{BE} \lambda_{EA}^{JM}, \quad (\text{B8})$$

$$\begin{aligned} V_{i_\alpha a_\beta j_\beta b_\alpha} &= \sum_M^{occ} \sum_E^{vir} t_{IM}^{BE} \lambda_{AE}^{JM} \\ &- \frac{1}{2} \sum_M^{occ} \sum_E^{vir} t_{MI}^{BE} \lambda_{AE}^{JM} \\ &- \frac{1}{2} \sum_M^{occ} \sum_E^{vir} t_{IM}^{BE} \lambda_{EA}^{JM}, \end{aligned} \quad (\text{B9})$$

$$V'_{IAJB} = 2V_{i_\alpha a_\beta j_\alpha b_\beta} + V_{i_\alpha a_\beta j_\beta b_\alpha}, \quad (\text{B10})$$

$$V''_{IAJB} = 2V_{i_\alpha a_\beta j_\beta b_\alpha} + V_{i_\alpha a_\beta j_\alpha b_\beta}, \quad (\text{B11})$$

$$\mathcal{G}_{EA} = -\sum_F^{vir} V_{EFAF}, \quad (\text{B12})$$

$$\mathcal{G}_{IM} = \sum_N^{occ} V_{INMN}. \quad (\text{B13})$$

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