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Analytic energy gradients with frozen molecular orbitals in coupled-cluster and many-body perturbation theory methods: Systematic study of the magnitude and trends of the effects of frozen molecular orbitals

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Analytic coupled-cluster (CC) and many-body perturbation theory (MBPT) energy gradient methods with restricted Hartree–Fock (RHF), unrestricted Hartree–Fock (UHF), restricted open-shell Hartree–Fock (ROHF), and quasi-RHF(QRHF) reference functions are extended to permit dropping core and excited orbitals. By using the canonical property of the semicanonical ROHF orbitals and the RHF orbitals from which the QRHF reference function is constructed, it is shown that a general procedure can be established not only for RHF and UHF, but also for ROHF and QRHF reference functions. The basic theory and implementation are reported. To provide a systematic study of the trends and magnitudes of the effects of dropped molecular orbitals (MOs) on the structures, harmonic frequencies, and ir intensities, we study HCN, C₂H₂, CO₂, HO₂, and C₂H₄ at increasing levels of correlation and basis sets. The effects of the dropped MOs with the largest basis sets are about 0.003 Å and 0.1° in structures and about 1% on harmonic frequencies and ir intensities. The magnitude and the direction of the drop-MO effect tend to be almost constant from MBPT(2) to CCSD(T) methods. The two isomers of S₃ are studied by the drop-MO-method, yielding very accurate results. © 1997 American Institute of Physics. [S0021-9606(97)00534-5]

I. INTRODUCTION

It is a well-established chemical principle that most atomic and molecular properties are largely determined by the valence electrons. A corollary of this is that most properties that do not depend explicitly on the core electrons are little affected by core correlation. This has practical computational consequences, since the cost of correlated calculations with the commonly used methods is proportional to n^2 or n^3 , where n is the number of active occupied molecular orbitals (MOs). Even for the ozone molecule O₃ to correlate all electrons is almost twice as costly as if the 1s electrons are not correlated. The effect for heavier elements is clearly much larger. In view of the anticipated unimportance of correlating core electrons, the savings in computational cost, and the fact that few basis sets have been designed to describe core correlation, most calculations choose not to correlate core electrons. In addition, the highest few virtual orbitals that basically correlate the core are often neglected.

Among many methods for calculating the correlation energy, coupled-cluster (CC) and many-body perturbation theory (MBPT) methods^{1,2} offer several advantages. If one wishes to drop MOs and calculate the correlation energy with such methods, no complications arise in the computational implementation, compared with the case where no MOs are dropped. MO integrals involving the dropped MOs are not generated in the integral transformation step, and the code to evaluate the CC/MBPT energy needs no information

about dropped MOs. The evaluation of analytical derivatives of the CC/MBPT energy, however, involves some additional implementational complications. Since analytical derivatives play a vital role in modern quantum chemistry, it is important to be able to evaluate them when some MOs are frozen.

In this paper, we report the evaluation of analytical derivatives of the CC/MBPT energy for several types of reference determinant when MOs are dropped. The reference determinants are restricted Hartree–Fock (RHF), unrestricted Hartree–Fock (UHF), restricted open-shell Hartree–Fock (ROHF), and quasi-(RHF) (QRHF). RHF is for closed-shell systems (as could be UHF and QRHF), although the others are mostly for open-shell systems. We present some basic aspects of the derivative formalism when some MOs are dropped. Several numerical examples are given and the effects of dropping MOs on calculated properties are illustrated. Analytical derivatives for the dropped MO case have been addressed in the past, but only for closed-shell (RHF) references. They have been implemented for the configuration interaction singles and doubles (CISD) method³ and for some CC methods,⁴ and applications have been reported for S₃,³ Cl₂O₂,⁴ and HCN/HNC,⁵ for example. Here we extend and implement the theory for CCSD(T)⁶ with any of the above references, and all its lower MBPT(2), MBPT(3), MBPT(4),⁷ CCD, and CCSD approximations.

While the primary reason for this work is the reduction in computational cost that comes from dropping MOs, there is increasing interest in calculating the correlation contribution of core electrons. Examples include effects of core correlation on bond lengths, vibrational frequency, and dissociation energies of simple molecules, like CH⁺,⁸ BH,⁹ and

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N_2 .^{10,11} According to a recent extensive study of N_2 ,¹¹ the effect of $1s$ electrons is about 0.005 \AA on r_e and 10 cm^{-1} on ω_e . Indirect estimates of core correlation effects in molecules with more degrees of freedom have been made by Martin¹² by using large valence basis sets and comparing with experiment. These studies show that core correlation effects on properties are small for first- and second-row elements, and provide direct estimates of core correlation effects. For heavier elements, of course, the separation between the nominal valence and core is very large, but the role of midvalence orbitals is greater, and there is sometimes less justification for neglecting them in the correlation treatment. With increasing interest in core correlation, basis sets which will describe it well are being designed.¹³ Although core correlation effects will be increasingly studied, because of their economy, dropped MO calculations will continue to be the choice for most large molecule applications.

II. THEORETICAL CONSIDERATIONS AND IMPLEMENTATIONS

The basic equations for the first derivative of the CC/MBPT energy^{14–16} are reconsidered here with special attention paid to the division into dropped occupied, active occupied, active virtual, and dropped virtual MOs. Throughout this work, the usual convention for indices is used for active MOs. Thus i, j denote active occupied MOs, a, b denote active virtual MOs, and p, q, r, s denote generic active MOs. Capital letters will be used to denote the dropped MOs: I, J for dropped occupied and A, B for dropped virtual MOs. For concise expressions, l, m, n will be used to refer to all occupied MOs, f, g, h to all virtual MOs, and u, v, w, x, y to all MOs. Greek letters are used to label atomic orbitals (AOs).

The first derivative of the CC/MBPT correlation energy is given by¹⁶

$$\frac{\partial E_{\text{CC/MBPT}}}{\partial \chi} = \sum_{p,q} D_{pq} \frac{\partial f_{pq}}{\partial \chi} + \sum_{p,q,r,s} \Gamma(pq,rs) \frac{\partial \langle pq || rs \rangle}{\partial \chi}, \quad (1)$$

where the one- and two-electron CC/MBPT-response density matrices, D_{pq} and $\Gamma(pq,rs)$, are functions of the amplitudes of the excitation and deexcitation operators, T and Λ , respectively. The forms of D and Γ depend on the correlation methods and are given in the literature for several CC/MBPT methods.^{4,16–21,6,22}

The steps which use most of the computer time in a CC/MBPT derivative calculation are the evaluation of the T and Λ amplitudes and, for methods which include a noniterative triple excitation contribution, the two-particle density. When some MOs are dropped, costs of these steps depend only on the number of active MOs and once appropriate integrals have been prepared, no knowledge of the dropped MOs is required. However, the derivatives in Eq. (1) lead to orbital response terms which depend on all MOs, whether or not any MOs are dropped. These lead to additional complexities in the implementation for the dropped MO case compared with the all MO case. To make

this explicit, we develop Eq. (1) further into a computationally more tractable form. First we make several definitions and establish notation.

The MOs ϕ_w are linear combinations of atomic orbitals (AOs) φ_μ

$$\phi_w = \sum_{\mu} c_{\mu w} \varphi_{\mu}. \quad (2)$$

The coupled-perturbed Hartree–Fock (CPHF) coefficients²³ U_{uw}^χ are defined by

$$\frac{\partial c_{\mu w}}{\partial \chi} = \sum_u U_{uw}^\chi c_{\mu u}. \quad (3)$$

It is to be noted that the response of each MO depends on all MOs. In particular, response of active MOs does not depend on just the active set.

The derivatives in Eq. (1) lead to two types of terms, one involving derivatives of AO integrals and one involving derivatives of MO coefficients (leading to CPHF coefficients). The following notation, introduced previously,¹⁹ is used to denote derivatives of AO integrals which are rotated into the MO basis:

$$S_{pq}^\chi = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{\partial S_{\mu\nu}}{\partial \chi} = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{\partial \langle \mu | \nu \rangle}{\partial \chi}, \quad (4)$$

$$h_{pq}^\chi = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{\partial h_{\mu\nu}}{\partial \chi} = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{\partial \langle \mu | h | \nu \rangle}{\partial \chi}, \quad (5)$$

$$\langle pq || rs \rangle^\chi = \sum_{\mu, \nu, \lambda, \sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \frac{\partial \langle \mu \nu || \lambda \sigma \rangle}{\partial \chi}. \quad (6)$$

For the part of the Fock matrix derivative which involves no MO coefficient derivatives, the notation

$$f_{pq}^{(\chi)} = h_{pq}^\chi + \sum_m \langle pm || qm \rangle^\chi \quad (7)$$

is used.

The derivatives of the Fock-matrix elements and two-electron integrals in Eq. (1) can be expressed in terms of rotated AO integral derivatives and CPHF coefficients as follows:

$$\begin{aligned} \frac{\partial f_{pq}}{\partial \chi} = & f_{pq}^{(\chi)} + \sum_u [f_{uq} U_{up}^\chi + f_{up} U_{uq}^\chi] \\ & + \sum_{l,u} (\langle pu || ql \rangle + \langle pl || qu \rangle) U_{ul}^\chi, \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{\partial \langle pq || rs \rangle}{\partial \chi} = & \langle pq || rs \rangle^\chi + \sum_u [U_{up}^\chi \langle uq || rs \rangle \\ & + U_{uq}^\chi \langle pu || rs \rangle + U_{ur}^\chi \langle pq || us \rangle \\ & + U_{us}^\chi \langle pq || ru \rangle]. \end{aligned} \quad (9)$$

As stated above, u refers to all orbitals, l refers to all occupied orbitals, while p, q, r, s represent only active orbitals.

After inserting the above expressions for the Fock-matrix and two-electron integral derivatives, Eq. (1) can be written

$$\frac{\partial E_{\text{CC/MBPT}}}{\partial \chi} = \sum_{p,q} D_{pq} f_{pq}^{(\chi)} + \sum_{p,q,r,s} \Gamma(pq,rs) \langle pq || rs \rangle^{\chi} - 2 \sum_{u,v} I'_{uv} U_{uv}^{\chi}, \quad (10)$$

where the one-particle intermediate I'_{uv} is given by

$$I'_{uv} = -\frac{1}{2} \left[\sum_q (D_{vq} + D_{qv}) f_{uq} \delta_{v,\text{active}} + \sum_{qrs} (\langle uq || rs \rangle \Gamma(vq,rs) + \langle qu || rs \rangle \Gamma(qv,rs) + \langle qr || us \rangle \Gamma(qr,vs) + \langle qr || su \rangle \Gamma(qr,sv)) \delta_{v,\text{active}} + \sum_{pq} (\langle pu || qv \rangle + \langle pv || qu \rangle) D_{pq} \delta_{v,\text{occ}} \right]. \quad (11)$$

I'_{uv} has been defined for all orbitals, but there are zero contributions (controlled by the Kronecker deltas) unless v is either an occupied orbital ($\delta_{v,\text{occ}}$) or an active orbital ($\delta_{v,\text{active}}$).

Inspection of Eq. (11) shows that the following additional two-electron integrals are required in order to calculate one-particle intermediates, even though these integrals are not required to solve the CC and Λ equations:

$$\langle pI || qJ \rangle, \quad \langle pI || qr \rangle, \quad \langle pA || qJ \rangle, \quad \langle pA || qr \rangle. \quad (12)$$

These additional two-electron integrals can be generated by a separate integral transformation. Other two-electron integrals involving dropped MOs need not be generated at all. If D_{pq} and $\Gamma(pq,rs)$ are expanded into D_{uw} and $\Gamma(uw,xy)$ by adding zeros in the proper positions, and two-electron MO integrals $\langle uv || wx \rangle$ are made by combining $\langle pq || rs \rangle$ and the integrals in Eq. (12), then the procedure for the implementation of Eq. (11) becomes the same as that for the all active MO case.

Because of the orthonormality of the MOs, the independent CPHF coefficients are those with $u > v$, while others are determined by the condition, $U_{uv}^{\chi} + S_{uv}^{\chi} + U_{vu}^{\chi} = 0$. The last term in Eq. (10) is rewritten as

$$-2 \sum_{u,v} I'_{uv} U_{uv}^{\chi} = 2 \sum_{u>v} X'_{uv} U_{uv}^{\chi} + \sum_{u,v} I''_{uv} S_{uv}^{\chi} \quad (13)$$

with $X'_{uv} = I'_{vu} - I'_{uv}$, $I''_{uv} = I'_{uv}$ for $u \leq v$, and $I''_{uv} = I'_{vu}$ for $u > v$.

If the correlation energy is invariant to certain classes of orbital mixing, certain CPHF coefficients can be simply obtained from the orthonormality condition. For example, for RHF and UHF references, if all MOs are active, the correlation energy is invariant to occupied–occupied and virtual–virtual mixing, and we may use the relations

$$U_{lm}^{\chi} = -\frac{1}{2} S_{lm}^{\chi}, \quad U_{fg}^{\chi} = -\frac{1}{2} S_{fg}^{\chi}. \quad (14)$$

The remaining CPHF coefficients may be determined by differentiating the Brillouin condition

$$\frac{\partial f_{fi}}{\partial \chi} = 0. \quad (15)$$

The CPHF coefficients, of course, need not be solved explicitly to obtain the first derivative, since the Z-vector method²⁴ can be used to eliminate them, but the Z-vector equations depend on the underlying CPHF equations.²⁵

When some MOs are dropped, the invariance relations are more complicated. For example, the energy is not invariant to mixing of inactive and active occupied (or virtual orbitals). One can still use $U_{vw}^{\chi} = -\frac{1}{2} S_{vw}^{\chi}$, for the U_{IJ}^{χ} , U_{ij}^{χ} , U_{ab}^{χ} , and U_{AB}^{χ} sets, while U_{il}^{χ} and U_{Aa}^{χ} are defined by requiring that the appropriate elements of the Fock matrix be zero and differentiating these canonical conditions

$$\frac{\partial f_{il}}{\partial \chi} = 0, \quad \frac{\partial f_{Aa}}{\partial \chi} = 0. \quad (16)$$

The ROHF orbitals do not satisfy the Brillouin condition, but equations for the CPHF coefficients between different classes of MOs (i.e., doubly occupied, singly occupied, or virtual) can be obtained by differentiating the ROHF variational conditions. When all MOs are active, the CPHF coefficients between members of the same class can be obtained by the orthonormality condition. When some MOs are dropped, Eq. (16) can be applied if one imposes a canonical condition on the α and β occupied and virtual orbitals. This semicanonical condition has been used to obtain analytical derivatives for the ROHF-CCSD(T) method.⁶ Exactly the same procedure can be used in this drop-MO gradient method with ROHF orbitals, except we have to handle additional terms implicitly given in Eq. (11). It is noted here that the drop-MO analytic derivative is possible only with semicanonical ROHF orbitals, otherwise the CPHF coefficient U_{il} and U_{Aa} (or the corresponding Z-vector equation) cannot be defined.

The open-shell Fock matrices of the QRHF orbitals²⁶ do not satisfy any particular conditions, but the Brillouin and canonical conditions are satisfied by the RHF Fock matrix of these orbitals. As explained in the first paper on analytical QRHF-CCSD derivatives,²⁰ the Brillouin condition and the canonical property of initial RHF orbitals can be used for the solution of the Z-vector equation not only for the occupied–virtual block, but also for the occupied–occupied and virtual–virtual parts. In the dropped MO space, however, the canonical property of the RHF orbitals has to be used not only for orbitals whose occupation number changes from RHF to QRHF, but also for all other orbitals. This means that instead of using the requirement

$$\frac{\partial f_{il}^{\text{RHF}}}{\partial \chi} = 0 \quad \text{and/or} \quad \frac{\partial f_{1g}^{\text{RHF}}}{\partial \chi} = 0 \quad (17)$$

for only the CPHF coefficients U_{il} and U_{1g} involving the open-shell orbital (which is denoted as 1, and has different occupation in RHF and QRHF), an equivalent requirement has to be applied for all CPHF coefficients

$$\frac{\partial f_{uv}^{\text{RHF}}}{\partial \chi} = 0, \quad u \neq v. \quad (18)$$

Instead of using Eq. (20) of Ref. 20 (or the equivalent equation for U_{A1}^{χ}), the following CPHF equations and the corresponding Z-vector equations have to be used when some MOs are dropped:

$$\sum_g \sum_m [\langle fg || lm \rangle + \langle fm || lg \rangle] U_{gm}^{\chi} + \delta_{fg} \delta_{lm} (\epsilon_f^{\text{RHF}} - \epsilon_l^{\text{RHF}}) U_{gm}^{\chi} = B_{fl}^{\chi}, \quad (19)$$

$$\sum_g \sum_m [\langle lg || nm \rangle + \langle lm || ng \rangle] U_{gm}^{\chi} + (\epsilon_l^{\text{RHF}} - \epsilon_n^{\text{RHF}}) U_{ln}^{\chi} = B_{ln}^{\chi}, \quad (20)$$

$$\sum_g \sum_m [\langle fg || hm \rangle + \langle fm || hg \rangle] U_{gm}^{\chi} + (\epsilon_f^{\text{RHF}} - \epsilon_h^{\text{RHF}}) U_{fh}^{\chi} = B_{fh}^{\chi}. \quad (21)$$

All orbital indices in Eqs. (19)–(21) refer to the RHF configuration. Once the intermediate I'_{uv} of Eq. (11) is constructed with u and v referring to the QRHF occupation, in order to make X' and I'' in Eq. (13), I'_{uv} has to be repartitioned according to the original RHF configuration, i.e., the occupied and virtual MOs have to be redefined in terms of the RHF configurations. The orthonormality of the RHF orbitals is used here, and the relation of Eq. (13) is still valid. The procedures to solve the contribution from the independent CPHF coefficient $\sum_{u>v} X'_{uv} U_{uv}^{\chi}$ include the contraction between α - or β -spin X' and the two-electron integral sets defined in terms of the RHF configuration. The procedures described in earlier work,²⁰ can be extended provided the QRHF configuration can be formed from an RHF configuration because one of the α - and β -spin two-electron integrals correspond to the two-electron integrals of the RHF configuration. The implementation and application of the drop-MO method with the QRHF reference function will be explored further in future work in connection with multireference CC/MBPT methods.

Considering all these different reference functions, the most general way to treat the first part of Eq. (13), $2\sum_{u>v} X'_{uv} U_{uv}^{\chi}$, is not to use any relations like Eq. (14), but to define all independent CPHF coefficients from canonical or semicanonical conditions. Otherwise, the contributions to I' of Eq. (11) and some part of the Z-vector equations have to be treated separately for dropped–active occupied, occupied–virtual, and active–dropped virtual blocks. Such separation has little advantage, conceptually or computationally. Although some computation time may be saved in the construction of I' and solution of the Z-vector equations, this saving is insignificant.

The procedure to solve the Z-vector equations with occupied–occupied and virtual–virtual CPHF coefficients requires the following additional steps for the orbital response contribution to the one-particle density matrix

$$D_{lm}^{\text{orb-resp}} = \frac{-X'_{lm}}{f_{ll} - f_{mm}}, \quad D_{fg}^{\text{orb-resp}} = \frac{-X'_{fg}}{f_{ff} - f_{gg}}, \quad (22)$$

$$X_{fl} = X'_{fl} + \frac{1}{2} \sum_{mn} D_{mn}^{\text{orb-resp}} A_{mnfl} + \frac{1}{2} \sum_{gh} D_{gh}^{\text{orb-resp}} A_{ghfl}, \quad (23)$$

where A_{ghfl} is defined in terms of two-electron MO integrals, and the contribution from Fock matrix elements is also needed in semicanonical ROHF orbitals.²² Potential singularities of Eq. (22) are treated as in previous work.²⁷ After eliminating CPHF coefficients by solving the Z-vector equations, which also give the orbital response contribution to the one-electron density $D_{fm}^{\text{orb-resp}}$, the final relaxed density $D'_{u,v}$ and intermediate $I_{u,v}$ are given by

$$D'_{uv} = D_{uv} + D_{uv}^{\text{orb-resp}}, \quad (24)$$

$$I_{lm} = I''_{lm} - f_{mm} D_{lm}^{\text{orb-resp}} - \sum_{uv} D_{uv}^{\text{orb-resp}} \langle ul || vm \rangle, \quad (25)$$

$$I_{fg} = I''_{fg} - f_{gg} D_{fg}^{\text{orb-resp}}, \quad (26)$$

$$I_{fm} = I''_{fm} - f_{mm} D_{fm}^{\text{orb-resp}}, \quad (27)$$

and the final expression for the energy derivative is

$$\begin{aligned} \frac{\partial E}{\partial \chi} = & \sum_{u,v} D'_{uv} f_{tu}^{\chi} + \sum_{p,q,r,s} \Gamma(pq,rs) \langle pq || rs \rangle^{\chi} \\ & + \sum_{u,v} I_{uv} S_{uv}^{\chi}. \end{aligned} \quad (28)$$

For QRHF references, the indices in Eqs. (22) and (23) refer to the RHF configuration. All contributions from $D^{\text{orb-resp}}$ in Eqs. (24)–(27) also have to be handled with RHF indices. Once the CPHF equation is solved and the additional contributions in Eqs. (24)–(27) are treated, all indices have to be returned to those of the QRHF configuration, which means all D_{uv} and I_{uv} in Eqs. (24)–(27) have to be repartitioned according to the QRHF configuration. This procedure, from Eqs. (22) to (28), is a general technique for drop-MO gradients for CC/MBPT methods with RHF, UHF, ROHF, and QRHF reference functions.

The final D and I intermediates have to be augmented with the contributions from the reference energy derivative. Because the two-particle densities, $\Gamma(pq,rs)$ in Eq. (28), depend only on active orbitals, the back transformation²⁸ of $\Gamma(pq,rs)$ into atomic indices is performed in the active MO space. After the back transformation of D , Γ , and I into atomic indices, the remaining steps are the same as for the full MO space.

The above equations have been implemented into the ACES II program.²⁹ The analytical energy gradient with dropped MOs was checked by comparing with the numerical gradient. First-order properties like dipole moments, quadrupole moments, electric field gradients, spin densities, etc. can be computed with dropped MOs without any further considerations.

III. THE EFFECTS OF CORE CORRELATION ON GEOMETRY AND VIBRATIONAL FREQUENCIES

In order to study the effect of core correlation rigorously, both the correlation method and the one-particle basis set have to be chosen carefully. The main point of this section, however, is to compare the results when all electrons and all MOs are included in the correlation calculation (this method will be referred to as the all-MO method) and the results when some core electrons and virtual MOs are not included in the correlation calculation (this method will be referred to as the drop-MO method). The comparison uses the MBPT(2), CCSD, and CCSD(T) methods with widely used basis sets like DZP, cc-pVTZ, and a modified one, TZ2PH (see below).

The DZP (double-zeta plus polarization) basis sets are $(4s1p)/[2s1p]$ (for H) and $(9s5p1d)/[4s2p1d]$ (for C, N, and O) with *sp* parts from Dunning³⁰ and polarization exponents from Redmon *et al.*³¹ Dunning's cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis sets³² are $(5s2p1d)/[3s2p1d]$ for H and $(10s5p2d1f)/[4s3p2d1f]$ for the C, N, and O. TZ2PH (triple-zeta valence with double first polarization and a higher second polarization function) sets comprise TZ2P sets augmented with a *d* function for H and an *f* function for C, N, and O. The *d* and *f* functions are from the cc-pVTZ set. The TZ2P basis sets are $(5s3p)/[3s2p]$ (for H) and $(10s6p3d)/[5s3p2d]$ (for C, N, and O). They come from Dunning's contractions³³ of Huzinaga's primitive sets³⁰ and correlation optimized polarization functions.²⁹ From results with other basis sets of TZ2PH quality, TZ(2*df*,2*pd*),³⁴ TZ2P + *f*,³⁵ and TZ2Pf,^{5,36} it is found that augmenting a TZ2P basis set with the *f* function from the cc-pVTZ basis sets gives slightly better results for π -type bending vibrations than other choices of *f* functions. Unless otherwise specified, spherical polarization functions are used in the cc-pVTZ and TZ2PH basis sets, while Cartesian polarization functions are used in the DZP basis sets.

The selection of dropped MOs is determined mainly by orbital energy. The MOs corresponding to 1*s* AOs of first row atoms and 1*s*,2*s*,2*p* AOs of second row atoms may be chosen as the dropped core MOs. Depending on the basis set, some virtual MOs with high orbital energies can be dropped without degrading the results. As noted by the referee, it is essential to make sure that the character of the dropped orbitals does not change as a function of geometry, otherwise potential energy surfaces will be discontinuous. In general, the dropped orbitals should be well separated energetically from the active orbitals. When N_c core orbitals from n_o occupied orbitals and N_v virtual orbitals from a total of n_v virtual orbitals are dropped, the calculation will be referred to as drop-MO($N_c/N_v//n_o/n_v$) or just drop-MO(N_c/N_v). The reduction in computation time can be estimated from the total numbers of occupied and virtual MOs (n_o, n_v) and the number of dropped MOs (N_c, N_v). The computation times roughly scale asymptotically as $M_o^2 M_v^4 N_{it}$ in CCSD and $M_o^3 M_v^4$ in CCSD(T) where M_o and M_v are, respectively, the numbers of active occupied and virtual MOs, and N_{it} is the

number of iterations needed to solve the *T* and Λ equations. In our experience, there is no significant difference in N_{it} for all-MO and drop-MO cases.

According to a recent study of the balance between theoretical method and the quality of basis set,³⁴ TZ2PH-type basis sets and the CCSD(T) method are a well-balanced pair, and their combination produces good agreement with experiment. One of the main objectives of this section is to study whether the drop-MO CCSD(T)/TZ2PH method is good enough for predictive calculations of molecular structure and vibrational properties. In order to study the general trends and magnitudes of the drop-MO effects, both all-MO method and drop-MO method are used with the same basis set. Results of calculations on HCN, C₂H₂, CO₂, and HO₂ are shown in Tables I–IV.

A. HCN

Description of the π -bending of HCN is a challenge for *ab initio* methods.^{36,37} The drop-MO method with a TZ2Pf basis set has been previously applied.⁵ There are a few differences between the TZ2Pf basis set and the TZ2PH basis set of this work. Two primitive *d* functions were used in the TZ2Pf set, while the two *d* functions of the TZ2PH set are a (2,1) contraction of three primitives. Cartesian *d* and *f* functions were used in the TZ2Pf set, but spherical functions are used in the TZ2PH set of this work. The number of dropped MOs is also different. Lee and Rendell used the drop-MO(2/2) method, while we drop two occupied and five virtual orbitals, i.e., the drop-MO(2/5) method. *ir* intensities are also calculated with the TZ2PH basis set. These differences have a very small effect on the results.

Data in Table I show the basic effects of dropped MOs on geometry and harmonic frequencies. The all-MO results are not given, but they can be obtained by adding the value of Δ to the drop-MO value. When a basis set does not contain *f* functions, the drop-MO effects are about 0.001 Å on bond length and about 5 cm^{−1} on the harmonic frequency. Though the results with 6-31G* and TZ2P basis sets are not included in Table I, our test calculations confirmed this fact. As expected, neglect of core correlation gives larger bond lengths and lower vibrational frequencies. It is noticeable that the value of Δ with a given basis set and method is smaller by an order of magnitude than the changes caused by different basis sets or by different methods. In this sense, drop-MO effects are negligible with these basis sets.

The drop-MO effects are more noticeable with the cc-pVTZ and TZ2PH sets. Since the cc-pVTZ set is only minimal for the core, inclusion of core correlation with this set is expected to increase the basis set superposition error (BSSE) significantly compared with the drop-MO calculation. The TZ2PH set is double-zeta for the core, so the BSSE effect is expected to be smaller. This explains, at least in part, why the values of Δ are larger for the cc-pVTZ set. The larger values of Δ are more of an indication of deficiencies in the all-MO cc-pVTZ calculations than in the drop-MO calculations.

Because of the unsymmetric nature of HCN compared with C₂H₂ (see below), drop-MO effects on harmonic fre-

TABLE I. The bond length (R in Å), harmonic frequencies (ω in cm^{-1}) and ir intensities (I_ν in km/mol) of HCN.^a

	Basis method	DZP		cc-pVTZ		TZ2PH	
		drop(2/2)	Δ^b	drop(2/1)	Δ^b	drop(2/5)	Δ^b
R_{CN}	MBPT(2)	1.1861	-0.0012	1.1665	-0.0032	1.1654	-0.0027
	CCSD	1.1719	-0.0010	1.1527	-0.0031	1.1517	-0.0025
	CCSD(T)	1.1779	-0.0010	1.1599	-0.0031	1.1589	-0.0025
R_{CH}	MBPT(2)	1.0703	-0.0009	1.0641	-0.0048	1.0641	-0.0021
	CCSD	1.0713	-0.0009	1.0646	-0.0051	1.0647	-0.0021
	CCSD(T)	1.0727	-0.0009	1.0666	-0.0052	1.0668	-0.0022
$\omega_1(\sigma^+)$	MBPT(2)	3499	4	3477	12	3485	-4
	CCSD	3488	5	3474	12	3480	-3
	CCSD(T)	3467	4	3445	13	3452	-3
$\omega_2(\pi)$	MBPT(2)	712	4	719	10	726	-1
	CCSD	721	5	742	11	750	0
	CCSD(T)	698	4	716	11	723	0
$\omega_3(\sigma^+)$	MBPT(2)	1991	6	2031	14	2035	9
	CCSD	2141	5	2177	15	2181	9
	CCSD(T)	2088	5	2115	13	2117	9
I_1	MBPT(2)	72.9	-0.2	71.7	-0.5	85.4	0.4
	CCSD	58.8	-0.2	62.2	-0.5	73.2	0.4
	CCSD(T)	56.7	-0.3	59.9	-0.6	71.4	0.4
I_2	MBPT(2)	89.4	0.2	72.5	0.6	74.6	-0.5
	CCSD	83.4	0.3	71.2	0.6	72.2	-0.7
	CCSD(T)	85.4	0.4	72.8	0.7	74.1	-0.7
I_3	MBPT(2)	0.4	0.0	0.4	0.1	0.3	-0.1
	CCSD	0.3	0.0	0.4	-0.1	0.5	0.0
	CCSD(T)	>0.1	0.0	>0.1	0.0	>0.1	0.0

^aExperimental values (Ref. 38) are $R_{\text{CN}} = 1.1532$, $R_{\text{CH}} = 1.0655$, $\omega_1 = 3440$, $\omega_2 = 727$, $\omega_3 = 2128$, $I_1 = 54.0$, $I_2 = 46.0$, and $I_3 = 0.14$.

^bThe drop-MO effect; $\Delta = (\text{all-MO result}) - (\text{drop-MO result})$.

quencies are relatively small even with cc-pVTZ sets. The effects on harmonic frequencies and ir intensities are less than 1% of the calculated and experimental values. The differences between the drop-MO results with the cc-pVTZ and TZ2PH basis sets are very small.

One important and useful trend of drop-MO effects can be seen from the results in Table I. Regardless of the correlation method, the magnitude and direction of the effects on bond length and vibrational frequency are almost constant for a given basis set.

B. C_2H_2

According to recent studies,^{40,41} CCSD(T) with basis sets having polarization functions like DZP, TZ2P, etc., is very successful for the calculations of geometries and vibrational frequencies of most molecules consisting of first and second row atoms. A CCSD study of C_2H_2 (Ref. 35) showed that the addition of f functions to carbon is important for the calculation of the π_g -type vibrational frequency. [We must also recognize that CCSD(T) is still an approximation to CCSDT.] Addition of an f function to the TZ2P basis set increases the π_g vibrational frequency by about 100 cm^{-1} . A CCSD(T)/DZP study of C_2H_2 showed that the inclusion of noniterative triple excitations reduces the π_g vibrational frequency by about 50 cm^{-1} .

Results of MBPT(2), CCSD, and CCSD(T) calculations on C_2H_2 with DZP, cc-pVTZ, and TZ2PH basis sets are shown in Table II. The changes in ir intensities are almost negligible. The results are very satisfactory from several

points of view. When DZP and TZ2PH basis sets are used, drop-MO effects are very small and almost negligible. Though the results with cc-pVTZ basis sets show slightly larger values of Δ , the values are about 0.004 Å for bond lengths and the effects on vibrational frequencies are less than 1% of experimental and calculated values, except for $\omega_4(\pi_g)$ in which the effect is about 2% of the calculated value. As noted above, the drop-MO effect is expected to be overestimated for the cc-pVTZ set. The CCSD values of ω_4 with the cc-pVTZ and TZ2PH basis sets are about 2% larger than the experimental value, 624 cm^{-1} . The CCSD(T) results for ω_4 , on the other hand, are about 4%–5% smaller than the experimental value. It appears that one more f function or even a g function is required for accurate results for this mode. Additional basis functions will probably make only a small change of geometry and other vibrational frequencies, but will give a better result for $\omega_4(\pi_g)$. As noticed for HCN, the values of Δ in Table II do not depend on the correlation method.

C. CO_2

Results for CO_2 are shown in Table III. The MBPT(4) gradient⁷ method is also employed for this molecule. It shows the same general trends and sizes of the drop-MO effect as other methods. The DZP drop-MO effects are negligible for CO_2 . The changes in results on going from the DZP to the TZ2PH basis set are not large. The TZ2PH basis set gives better bond lengths, harmonic frequencies, and ir intensities. Both spherical and Cartesian polarization func-

TABLE II. The bond length (R in Å), harmonic frequencies (ω in cm^{-1}) and ir intensities (I_v in km/mol) of C_2H_2 .^a

	Basis method	DZP		cc-pVTZ		TZ2PH	
		drop(2/2)	Δ	drop(2/1)	Δ	drop(2/2)	Δ
R_{CC}	MBPT(2)	1.2284	−0.0014	1.2113	−0.0039	1.2110	−0.0027
	CCSD	1.2211	−0.0013	1.2032	−0.0038	1.2028	−0.0024
	CCSD(T)	1.2265	−0.0013	1.2097	−0.0039	1.2093	−0.0025
R_{CH}	MBPT(2)	1.0683	−0.0005	1.0615	−0.0043	1.0613	−0.0027
	CCSD	1.0693	−0.0004	1.0620	−0.0047	1.0616	−0.0027
	CCSD(T)	1.0707	−0.0005	1.0636	−0.0048	1.0635	−0.0027
$\omega_1(\sigma_g^+)$	MBPT(2)	3547	4	3537	25	3545	−1
	CCSD	3535	2	3536	25	3540	0
	CCSD(T)	3514	4	3508	24	3515	0
$\omega_2(\sigma_g^+)$	MBPT(2)	1950	3	1977	16	1978	8
	CCSD	2016	3	2050	16	2051	7
	CCSD(T)	1976	3	1999	16	2003	7
$\Omega_3(\sigma_u^+)$	MBPT(2)	3464	0	3442	4	3455	−4
	CCSD	3443	−1	3430	2	3441	−4
	CCSD(T)	3425	1	3407	1	3421	−5
$\omega_4(\pi_g)$	MBPT(2)	542	4	593	6	608	5
	CCSD	557	6	621	12	635	5
	CCSD(T)	513	5	579	11	593	6
$\omega_5(\pi_u)$	MBPT(2)	730	1	756	3	758	−2
	CCSD	730	4	767	7	770	0
	CCSD(T)	709	1	747	7	749	−1
I_3	MBPT(2)	91	0	96	0	99	0
	CCSD	92	0	85	0	87	0
	CCSD(T)	91	0	83	0	85	0
I_5	MBPT(2)	191	0	179	−1	180	−1
	CCSD	148	0	182	−1	182	−1
	CCSD(T)	146	0	179	−1	179	−1

^aExperimental values (Ref. 42) are $R_{\text{CC}} = 1.2026$, $R_{\text{CH}} = 1.0622$, $\omega_1 = 3495$, $\omega_2 = 2008$, $\omega_3 = 3415$, $\omega_4 = 624$, $\omega_5 = 747$, $I_3 = 71$, and $I_5 = 175$.

tions are used in TZ2PH calculations on CO_2 . The additional s and p functions increase the BSSE, and so the Cartesian basis shows larger drop-MO effects, especially for the symmetric stretch. The Cartesian and spherical TZ2PH drop-MO calculations, however, give very similar results. Bond lengths, harmonic frequencies, and ir intensities of CO_2 calculated by the drop-MO method with the TZ2PH basis set are in good agreement with experiment. All-MO results with the spherical TZ2PH basis set are almost the same as with the TZ(2df,2pd) basis sets,³⁴ in spite of small differences in the polarization functions.

D. HO_2

The X^2A'' state of HO_2 is used to illustrate the drop-MO effects for an open-shell molecule. HO_2 has been studied by various methods and basis sets,^{6,21,43} and some aspects of the theoretical results are discussed there. Both UHF and ROHF reference state functions are used. The UHF and ROHF drop-MO effects, Δ in Table IV, show negligible differences. The magnitude of the drop-MO effect is very small for the DZP and TZ2PH basis sets. The calculated geometry is in very good agreement with experiment. The experimental frequencies are not harmonic, so a comparison with these is not possible. Overall, the drop-MO effects for this open-shell system show the same trends and sizes as for the closed-shell molecules studied.

IV. APPLICATION OF THE DROP-MO METHOD ON C_2H_4 AND TWO ISOMERS OF S_3

A. C_2H_4

There have been some theoretical studies on C_2H_4 with large basis sets and/or high level correlation methods.⁴⁶ The present calculations illustrate drop-MO analytical derivatives on a larger system than those in the previous section. Results are shown in Table V. The DZP drop-MO effects are negligible, and confirm the fact that the magnitude and the direction of the drop-MO effects on geometrical parameters and vibrational properties are almost constant from MBPT(2) to CCSD(T). All calculated properties, not only the geometry and harmonic frequencies but also the ir intensities, by the drop-MO CCSD(T) method with cc-pVTZ and TZ2PH basis sets show good agreement with the experimental values. The present drop-MO CCSD(T) results show slightly better agreement with experiment than the BLYP-density functional study with TZ2Pf basis sets.⁴⁷

Drop-MO CCSD(T) calculations can be performed with extended basis sets like cc-pVTZ or TZ2PH. If the direction and the magnitude of the drop-MO effect have to be estimated, economical MBPT(2) all-MO and drop-MO calculations could be performed to give a value of Δ . Both all-MO MBPT(2) and drop-MO MBPT(2) with cc-pVTZ and TZ2PH basis sets are used for the geometry optimization and the calculation of vibrational properties. Though the geom-

TABLE III. The bond length (R in Å), harmonic frequencies (ω in cm^{-1}) and ir intensities (I_v in km/mol) of CO_2 .^a

	Basis method	DZP		TZ2PH ^b		TZ2PH ^c	
		drop(3/3)	Δ	drop(3/5)	Δ	drop(3/3)	Δ
R_{CO}	MBPT(2)	1.1825	-0.0009	1.1679	-0.0035	1.1678	-0.0023
	MBPT(4)	1.1889	-0.0010	1.1741	-0.0038	1.1740	-0.0024
	CCSD	1.1732	-0.0009	1.1577	-0.0033	1.1576	-0.0022
	CCSD(T)	1.1792	-0.0009	1.1647	-0.0033	1.1646	-0.0022
$\omega_1(\sigma^+)$	MBPT(2)	1324	2	1335	18	1332	4
	MBPT(4)	1256	3	1273	20	1270	5
	CCSD	1376	3	1393	19	1390	4
	CCSD(T)	1338	3	1350	19	1347	5
$\omega_2(\pi)$	MBPT(2)	653	3	664	32	660	-1
	MBPT(4)	633	2	642	34	638	-1
	CCSD	679	3	694	34	689	-1
	CCSD(T)	659	2	669	34	664	-1
$\omega_3(\sigma^+)$	MBPT(2)	2450	6	2416	15	2418	3
	MBPT(4)	2364	7	2340	17	2340	4
	CCSD	2441	7	2427	18	2428	5
	CCSD(T)	2411	7	2389	17	2390	3
I_2	MBPT(2)	49.4	0.2	49.1	0.7	49.5	0.5
	MBPT(4)	47.1	0.2	46.3	0.8	46.7	0.5
	CCSD	70.5	0.2	69.6	0.7	69.9	0.6
	CCSD(T)	59.2	0.2	57.7	0.7	58.1	0.5
I_3	MBPT(2)	569	2	560	8	556	5
	MBPT(4)	422	3	435	11	431	7
	CCSD	767	2	741	8	736	5
	CCSD(T)	643	3	626	7	621	5

^aExperimental values (Ref. 39) are $R_{\text{CO}} = 1.160$, $\omega_1 = 1354$, $\omega_2 = 673$, $\omega_3 = 2397$, $I_2 = 48.0$, and $I_3 = 548$.^bCartesian polarization functions.^cSpherical polarization.

etry optimization by the all-MO CCSD(T) method is unnecessary, it is also performed here, and its results confirm that the drop-MO effect on a geometrical parameter is almost constant from MBPT(2) to CCSD(T). The same is expected for vibrational properties.

B. S_3 isomers

Two isomers of S_3 have been the subject of a number of theoretical and experimental studies.^{50,51} Theoretical studies have used semiempirical methods,⁵² the transition state method,⁵³ the local density approximation,^{54,55} all-MO methods,^{56–59} and a drop-MO method.^{3,60} The basis sets employed in the geometry optimizations by these methods are limited to DZP,^{3,58,59} TZ,^{56,57} TZP with effective core potential,⁶⁰ and TZP⁵⁴ and TZ2P + f ⁵⁵ with the density functional method.

In this study, both DZP and TZ2PH basis sets are used not only in energy calculations on the two isomers, but also for the geometry optimization and the calculation of vibrational properties. The DZP basis set used in this work is exactly the same as the (DZ+P) basis set used by Rice *et al.*³ The TZ2PH basis set of the present work is made by adding an f function from Dunning's cc-pVTZ basis set³² to the extended basis set employed by Rice *et al.*,³ who used this extended basis set only for single point energy calculations at DZ+P geometries. The technical description of the TZ2PH basis set for the sulfur atom is $(12s8p2d1f)/[7s5p2d1f]$ with $\alpha_d = 0.7$, 0.2 , and α_f

$= 0.557$. For both basis sets used here, the 15 core MOs (corresponding to $1s$, $2s$, and $2p$ sulfur AOs) and the 15 outermost virtual MOs were dropped.

Both all-MO and drop-MO methods were used with the DZP basis set. The magnitudes of the drop-MO effects with the DZP basis set are negligible again. One noticeable thing is that the magnitude of the drop-MO effect for the C_{2v} isomer changed a lot from MBPT(2) to CCSD(T). Since the MBPT(2) method is less adequate than the CCSD(T) method for describing the multireference character in the C_{2v} isomer, the drop-MO effects obtained by the MBPT(2) method might be less reliable. Bearing in mind this limitation, the magnitude of the drop-MO effect in the CCSD(T) calculations with the TZ2PH basis set will be estimated from the drop-MO effect calculated with MBPT(2) calculations. The magnitudes of the drop-MO effect with TZ2PH basis sets are expected to be around 0.003 Å and 0.1° on the structure and 1% in vibrational properties.

While Meyer⁵¹ identified the symmetric stretch $\nu_1 = 590 \text{ cm}^{-1}$, Hopkins *et al.*⁵⁰ have observed a 495 cm^{-1} ir signal, as well as Raman frequencies at 310, 490, 585, and 651 cm^{-1} . Recent experimental work⁶¹ identified three vibrational frequencies, $\omega_1 = 575$, $\omega_2 = 256$, $\omega_3 = 656 \text{ cm}^{-1}$. Agreement between the drop-MO CCSD(T)/TZ2PH results and the experimental values for C_{2v} isomer is so good that all other results by this method should be of predictive value. As expected, the present results for structure and vibrational properties of the C_{2v} isomer show better agreement with ex-

TABLE IV. The bond length (R in Å), bond angle (\angle in °), harmonic frequencies (ω in cm^{-1}), and ir intensities (I_ν in km/mol) of HO_2 .^a The two entries in each item mean results using by UHF and ROHF reference functions, respectively.

	Method	DZP		TZ2PH	
		drop(2/2)	Δ	drop(2/2)	Δ
R_{OO}	MBPT(2)	1.3218, 1.3209	− 0.0007, − 0.0009	1.3127, 1.3110	− 0.0009, − 0.0010
	CCSD	1.3369, 1.3379	− 0.0008, − 0.0008	1.3266, 1.3270	− 0.0008, − 0.0010
	CCSD(T)	1.3441, 1.3443	− 0.0007, − 0.0009	1.3363, 1.3366	− 0.0009, − 0.0011
R_{OH}	MBPT(2)	0.9746, 0.9744	− 0.0007, − 0.0007	0.9706, 0.9704	− 0.0007, − 0.0012
	CCSD	0.9735, 0.9734	− 0.0007, − 0.0007	0.9677, 0.9676	− 0.0007, − 0.0012
	CCSD(T)	0.9753, 0.9754	− 0.0007, − 0.0008	0.9709, 0.9708	− 0.0008, − 0.0011
$\angle \text{ HOO}$	MBPT(2)	104.5, 104.5	0.0, 0.0	104.7, 104.8	0.0, 0.0
	CCSD	104.3, 104.3	0.0, 0.0	104.6, 104.6	0.0, 0.0
	CCSD(T)	104.0, 104.0	0.0, 0.0	104.1, 104.1	0.0, 0.0
ω_1	MBPT(2)	3718, 3723	5, 4	3711, 3715	− 5, − 5
	CCSD	3720, 3721	5, 5	3741, 3743	− 5, − 5
	CCSD(T)	3689, 3688	5, 7	3691, 3693	− 6, − 4
ω_2	MBPT(2)	1445, 1447	2, 2	1457, 1459	2, 2
	CCSD	1446, 1446	2, 2	1466, 1466	2, 3
	CCSD(T)	1422, 1422	2, 2	1436, 1436	2, 1
ω_3	MBPT(2)	1225, 1178	1, 2	1230, 1190	4, 5
	CCSD	1142, 1142	1, 2	1168, 1168	5, 5
	CCSD(T)	1113, 1111	1, 1	1132, 1128	4, 4
I_1	MBPT(2)	35.9, 35.3	0.3, 0.3	52.4, 50.9	0.6, 0.6
	CCSD	22.7, 22.7	0.2, 0.2	38.4, 38.3	0.5, 0.5
	CCSD(T)	19.2, 19.1	0.2, 0.3	33.7, 33.6	0.5, 1.1
I_2	MBPT(2)	33.4, 35.7	0.2, 0.1	30.9, 33.0	0.0, 0.1
	CCSD	41.3, 41.3	0.1, 0.1	42.8, 42.9	0.1, 0.1
	CCSD(T)	40.0, 40.1	0.1, 0.1	41.3, 41.4	0.1, − 0.4
I_3	MBPT(2)	101.7, 105.5	0.2, 0.1	97.2, 104.3	0.0, 0.3
	CCSD	33.1, 32.5	− 0.1, − 0.1	34.1, 33.7	0.2, 0.3
	CCSD(T)	31.0, 30.9	− 0.1, − 0.2	30.9, 30.7	0.1, − 0.1

^aExperimental values (Ref. 44) are $R_{\text{OO}} = 1.3305$, $R_{\text{OH}} = 0.9707$, $\angle_{\text{HOO}} = 104.3$, $\omega_1 = 3436$, $\omega_2 = 1392$, $\omega_3 = 1098$.TABLE V. The results by CCSD(T) method for bond length (R in Å), bond angle (\angle in °), harmonic frequencies (ω in cm^{-1}), and ir intensities (I_ν in km/mol) of C_2H_4 .

	DZP		cc-pVTZ		TZ2PH		Expt ^a
	drop(2/2)	Δ^b	drop(2/0)	Δ^b	drop(2/2)	Δ^b	
R_{CC}	1.3532	− 0.0014	1.3373	− 0.0040	1.3369	− 0.0031	1.339
R_{CH}	1.0872	− 0.0009	1.0831	− 0.0042	1.0825	− 0.0023	1.087
\angle_{HCH}	117.2	0.0	117.1	0.1	117.0	0.0	117.4
$\omega_1(a_g)$	3210	5	3158	22	3175	− 2	3139
$\omega_2(a_g)$	1682	3	1671	11	1671	2	1655
$\omega_3(a_g)$	1371	1	1369	9	1372	3	1371
$\omega_4(a_u)$	1026	1	1047	3	1048	4	1047
$\omega_5(b_{1g})$	3287	6	3220	2	3244	− 9	3212
$\omega_6(b_{1g})$	1250	1	1242	2	1252	4	1245
$\omega_7(b_{1u})$	928	1	966	10	968	0	968
$\omega_8(b_{2g})$	781	2	941	10	951	3	959
$\omega_9(b_{2u})$	3314	6	3247	4	3264	− 8	3234
$\omega_{10}(b_{2u})$	819	0	823	5	826	4	843
$\omega_{11}(b_{3u})$	3187	5	3140	18	3156	− 4	3138
$\omega_{12}(b_{3u})$	1496	2	1479	8	1482	4	1473
$I_7(b_{1u})$	95.4	0.3	89.0	0.6	94.7	0.2	84.4
$I_9(b_{2u})$	33.1	− 0.4	20.7	− 0.9	8.7	− 0.2	26.0
$I_{10}(b_{2u})$	0.6	0.0	> 0.1	0.0	0.3	0.0	0.0
$I_{11}(b_{3u})$	17.2	− 0.2	14.0	0.3	8.3	− 0.1	14.3
$I_{12}(b_{3u})$	6.2	0.2	7.8	0.6	9.9	0.4	10.4

^aExperimental values for structure (Ref. 45), harmonic frequencies (Ref. 48), and ir intensities (Ref. 49).^bThe drop-MO effects by the MBPT(2) method.

TABLE VI. The results by the CCSD(T) method for the bond length (R in Å), bond angle (\angle in °), harmonic frequencies (ω in cm^{-1})^a, and ir intensities (I_ν in km/mol) of S_3 isomers. The positive number of the energy difference (ΔE_e) between two isomers means that the C_{2v} isomer is more stable.

Isomers	DZP		TZ2PH	
	drop (15/15)	Δ^b	drop(15/15)	Δ^b
D_{3h}				
R_{S-S}	2.1250	-0.0010	2.1043	-0.0012
$\omega_1(a'_1)$	596	1	600	0
$\omega_2(e')$	449	1	454	0
I_2	1.09	-0.03	0.84	0.00
C_{2v}				
R_{S-S}	1.9695	-0.0001	1.9451	-0.0012
\angle_{S-S-S}	116.66	0.00	117.03	0.01
$\omega_1(a_1)$	561	1	579	0
$\omega_2(a_1)$	246	0	253	0
$\omega_3(b_2)$	645	1	670	0
I_1	0.10	-0.01	0.63	0.00
I_2	1.38	-0.03	0.75	-0.02
I_3	49.94	0.16	76.39	0.16
ΔE_e				
(kcal/mol)	6.66		4.99	

^aExperimental vibrational frequencies (Ref. 61) of the C_{2v} isomer are $\omega_1 = 575$, $\omega_2 = 256$, $\omega_3 = 656 \text{ cm}^{-1}$.

^bThe drop-MO effect by MBPT(2) method.

periment than recent results⁵⁴ by the density functional method with the TZ2P + f basis set. Based on the present results, the observed ir frequency at 495 cm^{-1} and the Raman frequency at 490 cm^{-1} can be assigned as the $\omega_2(e')$ mode of the D_{3h} isomer, while the $\omega_1(a'_1)$ mode is responsible for the Raman frequency at 585 cm^{-1} . Except for the b_2 vibrational mode of the C_{2v} isomer, all vibrational modes have very low ir intensity.

On going from the DZP to the TZ2PH basis set, the bond lengths of both isomers decrease by about 0.02 Å and the isomer energy difference is lowered by about 2 kcal/mol . The present TZ2PH bond lengths, bond angles, and the isomer energy difference are similar to the MRCISD results.⁵⁷ Because of the large multireference character of the C_{2v} isomer, the energy difference is expected to increase by a few kcal/mol in a higher-level correlation method with a multireference function and a more extensive basis set. The results in Table VI, however, are expected to be good enough to have predictive value. The calculated vibrational frequencies are expected to be correct within a few percent and the bond length and angle within 0.003 Å and 1° , respectively.

V. CONCLUSIONS

The orbital response part of the analytic energy derivative is scrutinized with special attention paid to the complications of dropped MOs. An efficient procedure of implementing these considerations is explained for cases with RHF, UHF, ROHF, and QRHF reference functions. To determine general trends and the order of magnitudes of drop-MO effects on structure and vibrational properties of a

molecule, systematic studies are performed for HCN, C_2H_2 , CO_2 , and HO_2 with MBPT(2), CCSD, and CCSD(T) methods and DZP, cc-pVTZ and TZ2PH basis sets.

When DZP basis sets are used, the magnitude of the drop-MO effects is negligible regardless of the basis sets and the molecule. Once a basis set includes an f function, the drop-MO effects tend to increase. The results of the drop-MO calculations with cc-pVTZ basis sets are almost identical to the drop-MO results with TZ2PH basis sets. The CCSD(T)/TZ2PH drop-MO effects are about 0.003 Å and 0.1° on geometry and $\sim 1\%$ for vibrational properties. It is shown that the drop-MO method is efficient and reliable for predictive work.

The drop-MO effects obtained by the MBPT(2) method are usually good estimates of CCSD or CCSD(T) values with the same basis sets. Exceptions are likely to be systems with significant multireference character, such as $C_{2v}S_3$.

Results on C_2H_4 and S_3 are quite encouraging for wider applications of the present drop-MO method to larger systems with CC/MBPT methods and extended basis sets. ACES II now has this capability.

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