

# Gradients for the partitioned equation-of-motion coupled-cluster method

Steven R. Gwaltney and Rodney J. Bartlett

*Quantum Theory Project, University of Florida, Gainesville, Florida 32611-8435*

(Received 25 November 1997; accepted 25 September 1998)

Gradients for the partitioned equation-of-motion coupled-cluster method based on a second-order many-body perturbation theory ground state have been derived. The accuracy of this new method has been compared to the accuracy of other single reference methods for excited states, namely configuration interaction limited to single excitations (CIS), CIS with a perturbative doubles correction, and equation-of-motion coupled-cluster theory based on a coupled-cluster singles and doubles ground state. These have been compared based on calculations of low lying singlet excited states of H<sub>2</sub>, BH, BF, C<sub>2</sub>, CO, and N<sub>2</sub>, as well as the lowest singlet excited states of ammonia, formaldehyde, acetaldehyde, and acetone. Also, a question about the assignments of the vibrational spectrum for the first excited state of acetone is resolved. © 1999 American Institute of Physics. [S0021-9606(99)01901-7]

## I. INTRODUCTION

The equation-of-motion coupled-cluster method with single and double excitations for excitation energies (EOM-CCSD),<sup>1-3</sup> also known as the coupled-cluster linear response,<sup>4-6</sup> provides an accurate method for calculating the energy and properties of many excited states of molecules. With the development of gradients for EOM-CCSD<sup>7-9</sup> it became possible to study the excited state potential energy surfaces, just as the development of coupled-cluster gradients for ground state methods<sup>10-13</sup> made routine the study of ground state potential energy surfaces. More recently, Stanton and Gauss have developed second derivatives for EOM-CCSD<sup>14</sup> and gradients for ionization potential EOM-CCSD (IP-EOM-CCSD).<sup>15</sup> The key to all coupled-cluster gradients has been the recognition of how the interchange theorem of Dalgarno and Stewart,<sup>16</sup> initially used by Adamowicz *et al.*<sup>10</sup> and Bartlett<sup>11</sup> for coupled-cluster gradients and sometimes known in quantum chemistry as the *Z*-vector method,<sup>17</sup> could be used to avoid computing the response of the ground state *T* amplitudes to each perturbation.

In EOM-CC theory the excited states are represented as right-hand ( $\mathcal{R}$ ) and left-hand ( $\mathcal{L}$ ) eigenvectors of a similarity transformed Hamiltonian  $\bar{H}$ . In pure CC methods (e.g., CCSD or CCSDT),  $\bar{H}$  can be written as

$$\bar{H} = e^{-T} H e^T, \quad (1)$$

where *T* comes from the solution of the ground state coupled-cluster equations.

One of the primary problems with the EOM-CCSD method is its cost. An EOM-CCSD gradient calculation involves four iterative steps which scale as  $n_{\text{occ}}^2 N_{\text{virt}}^4$ , where  $n_{\text{occ}}$  stands for the number of orbitals occupied in the reference determinant, and  $N_{\text{virt}}$  stands for the number of orbitals unoccupied in the reference determinant. These iterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  steps are calculating the ground state *T* amplitudes, calculating  $\mathcal{R}$ , calculating  $\mathcal{L}$ , and inverting  $\bar{H}$ .

In the philosophy of replacing ground-state cluster amplitudes with second-order perturbation approaches,<sup>18,19</sup>

Stanton and Gauss<sup>20</sup> developed an EOM-CC method based on an  $\bar{H}$  that was expanded through second order. For calculations based on a Hartree-Fock reference, expanding  $\bar{H}$  through second order and replacing the CCSD amplitudes with the second-order many-body perturbation theory [MBPT(2)] amplitudes in the EOM-CC equations are functionally equivalent. This truncation of  $\bar{H}$  reduced the cost of calculating the *T* amplitudes to a noniterative  $n_{\text{occ}}(n_{\text{occ}} + N_{\text{virt}})^4$  step and reduced the cost of inverting  $\bar{H}$  to  $n_{\text{occ}}^2 N_{\text{virt}}^2$ .<sup>20</sup> However, the iterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  steps for calculating  $\mathcal{R}$  and  $\mathcal{L}$  still remained. Since this did not significantly reduce the cost, the method was not very useful in practice.

In order to further reduce the cost and to create a more practical method geared toward providing a robust second-order-like treatment of excited states, in analogy with the robust MBPT[2] for ground states,<sup>21</sup> we proposed partitioning away the doubles-doubles block of  $\bar{H}$ . It is in the doubles-doubles block of  $\bar{H}$  that all of the iterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  steps in calculating  $\mathcal{R}$  and  $\mathcal{L}$  arise. In practice this means replacing  $\bar{H}$  in the doubles-doubles block with the zeroth-order Hamiltonian  $H_0$ , which is diagonal in the Hartree-Fock case. Thus, the iterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  steps involved in calculating  $\mathcal{R}$  and  $\mathcal{L}$  are replaced with iterative  $n_{\text{occ}}^2 N_{\text{virt}}^3$  steps. The overall effect is that the cost is significantly reduced, with little loss in accuracy for vertical excitation energies.<sup>21</sup>

Now, however, the noniterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  step involved in calculating  $\bar{H}$  elements can also become significant. The point at which the cost of calculating the one  $n_{\text{occ}}^2 N_{\text{virt}}^4$  step in  $\bar{H}$  becomes dominant over the cost of calculating the three iterative  $n_{\text{occ}}^2 N_{\text{virt}}^3$  steps in the excited state can be estimated. The two will have approximately equal cost when the number of virtual orbitals is three times the number of iterations. Since it typically takes around 15 iterations to solve for each  $\mathcal{R}$  and each  $\mathcal{L}$ , this would imply that the cost of calculating  $\bar{H}$  would become significant when the number of virtual orbitals is more than about 90 per excited state being calculated. In practice, some of the terms not included in this

estimate also contribute significantly to the cost, increasing the break-even point substantially. Also, when calculating vertical excitation energies, multiple excited states can be calculated while forming  $\bar{H}$  only once.

## II. THEORY

### A. EOM-CC gradients

Before we begin with an overview of EOM-CC theory and EOM-CC gradients, it will be helpful to define some more notation. Given a set of spin orbitals and a reference determinant  $|0\rangle$ , the labels  $i, j, k, \dots$  represent spin orbitals occupied in  $|0\rangle$ , the labels  $a, b, c, \dots$  represent spin orbitals unoccupied in  $|0\rangle$ , and the labels  $p, q, r, \dots$  represent spin orbitals whose occupation is not specified. The reference determinant is usually, but not necessarily, the self-consistent field (SCF) determinant. The space of all possible determinants with  $n$  electrons formed from the spin orbitals is represented by  $|\mathbf{h}\rangle$ . The space  $|\mathbf{h}\rangle$  is then divided into  $|\mathbf{h}\rangle = |\mathbf{p}\rangle \oplus |\mathbf{q}\rangle$ . Here,  $|\mathbf{p}\rangle$  represents the space spanned by the operators  $\mathcal{L}$  and  $\mathcal{R}$ , where it is assumed that  $T$ ,  $\mathcal{L}$ , and  $\mathcal{R}$  all have the same rank. Finally,  $|\mathbf{p}\rangle$  is divided into  $|\mathbf{p}\rangle = |0\rangle \oplus |\mathbf{g}\rangle$ . For EOM-CCSD  $|\mathbf{g}\rangle$  consists of all determinants singly and doubly excited with respect to  $|0\rangle$ . This is the same notation used by Stanton.<sup>7</sup>

The ground state coupled-cluster equations can be written as

$$\langle 0 | \bar{H} | 0 \rangle = E_{CC}, \quad (2)$$

and

$$\langle \mathbf{g} | \bar{H} | 0 \rangle = \mathbf{0}. \quad (3)$$

The  $T$  operator has the form

$$T = \sum_{i,a} t_i^a a^\dagger i + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} a^\dagger i b^\dagger j + \dots, \quad (4)$$

i.e., it is an excitation operator. It accounts for the ground state correlation.

The EOM-CC equations can be written as<sup>3</sup>

$$\langle 0 | \mathcal{L} \bar{H} | \mathbf{p} \rangle = E \langle 0 | \mathcal{L} | \mathbf{p} \rangle, \quad (5)$$

and

$$\langle \mathbf{p} | \bar{H} \mathcal{R} | 0 \rangle = E \langle \mathbf{p} | \mathcal{R} | 0 \rangle. \quad (6)$$

Here,  $E$  is the total energy for the excited state,

$$\mathcal{L} = l_0 + \sum_{a,i} l_i^a a^\dagger i + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} l_{ij}^{ab} i^\dagger a j^\dagger b + \dots \quad (7)$$

is the left eigenvector of  $\bar{H}$ , and

$$\mathcal{R} = r_0 + \sum_{i,a} r_i^a a^\dagger i + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} r_{ij}^{ab} a^\dagger i b^\dagger j + \dots \quad (8)$$

is the right eigenvector of  $\bar{H}$ . It is also possible to include the equation of motion in the  $\mathcal{R}$  equation. Equation (6) then becomes<sup>2</sup>

$$\langle \mathbf{p} | [\bar{H}, \mathcal{R}] | 0 \rangle = \omega \langle \mathbf{p} | \mathcal{R} | 0 \rangle, \quad (9)$$

where  $\omega = E - E_{CC}$  is the excitation energy.

It can be seen that in EOM-CC the excited states are represented as eigenvectors of  $\bar{H}$ , with the corresponding eigenvalues being the energies. Since  $\bar{H}$  is formed from a similarity transformation, it is not Hermitian, but its eigenvectors form a biorthogonal set. Choosing the norm of the excited state vectors appropriately gives that

$$\langle 0 | \mathcal{L}_j \mathcal{R}_k | 0 \rangle = \delta_{jk} \quad (10)$$

for all states  $j$  and  $k$ . Therefore, from either Eq. (5) or (6) we can get an expression for the excited state energy

$$E = \langle 0 | \mathcal{L} \bar{H} \mathcal{R} | 0 \rangle. \quad (11)$$

When Stanton first derived the equations for EOM-CC gradients,<sup>7</sup> he followed the same development as that of Refs. 10, 11, and 13 by taking the derivative of Eq. (11) with respect to a general external perturbation. In the process, he had to introduce the perturbation independent quantity zeta ( $Z$ ) to account for the effect of the perturbation on the ground state  $T$  amplitudes. Since  $\mathcal{L}$  and  $\mathcal{R}$  are eigenvectors for the excited state, the excited state energy is stationary with respect to their variation. On the other hand, the energy is never stationary with respect to a variation of  $T$  (even for the ground state), and another operator must be included to account for the response of  $T$  with respect to the external perturbation.

Szalay<sup>22</sup> then used the approach of a general functional analogous to the  $\Lambda$  functional in ground state coupled-cluster theory<sup>23,24</sup> by introducing  $Z$  to force the value of the functional to be stationary with respect to a variation of  $T$ . Following this approach, we introduce an EOM-CC functional which has the property that its value is stationary with respect to variations of all of its components, and therefore the functional will satisfy the generalized Hellmann–Feynman theorem.<sup>25,26</sup> Such a functional is

$$F = \langle 0 | \mathcal{L} \bar{H} \mathcal{R} | 0 \rangle + \langle 0 | Z \bar{H} | 0 \rangle + E(1 - \langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle). \quad (12)$$

By construction

$$Z = \sum_{a,i} \zeta_i^a a^\dagger i + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} \zeta_{ij}^{ab} i^\dagger a j^\dagger b + \dots \quad (13)$$

is a pure deexcitation operator of rank equal to  $T$ . Since the last two terms of Eq. (12) do not contribute to the value of the functional, the value of the functional is just the energy. By taking the derivative of each of the quantities on the right-hand side of Eq. (12) and setting them equal to zero, we will recover the EOM-CC gradient equations. For example,

$$\frac{\partial F}{\partial E} = 0 = 1 - \langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle \quad (14)$$

is a restatement of Eq. (10), the normalization condition for  $\mathcal{L}$  and  $\mathcal{R}$ .

Since the energy is a scalar, taking the derivative of the functional with respect to it is straightforward. However, all of the other terms which appear are operators, and some care must be exercised with what is meant by taking the derivative with respect to them. The actual operation is to take the derivative with respect to each coefficient in the operator and

set the resulting scalar equation to zero. For example, for a given  $l$  coefficient  $\kappa$ , the derivative of the functional with respect to  $l_\kappa$  is

$$\frac{\partial F}{\partial l_\kappa} = 0 = \langle \Phi_\kappa | \bar{H} \mathcal{R} | 0 \rangle - E \langle \Phi_\kappa | \mathcal{R} | 0 \rangle. \quad (15)$$

Note that the creation and annihilation operators associated with  $l_\kappa$  remain and create the determinant  $\langle \Phi_\kappa |$ . Since the derivative must be taken with respect to every coefficient, a vector of equations results. Writing Eq. (15) in vector notation gives

$$\frac{\partial F}{\partial \mathbf{l}} = \mathbf{0} = \langle \mathbf{p} | \bar{H} \mathcal{R} | 0 \rangle - E \langle \mathbf{p} | \mathcal{R} | 0 \rangle. \quad (16)$$

This is simply Eq. (6), the equation for  $\mathcal{R}$ .

Similarly, taking the derivative of the functional with respect to the coefficients of  $\mathcal{R}$  gives Eq. (5), which is the equation for  $\mathcal{L}$ . Taking the derivative of the functional with respect to the coefficients of  $Z$  gives Eq. (3), which is the ground state  $T$  equation.

However, taking the derivative of the functional with respect to the  $T$  amplitudes is more complicated. Since the form of  $\bar{H}$ , and therefore the equations for  $T$ , vary between different CC methods, it should not be surprising that the equations for  $Z$  also vary between different EOM-CC methods. Here we will assume a pure EOM-CC method (an EOM-CC method based on a pure CC method). The derivative then becomes

$$\begin{aligned} \frac{\partial F}{\partial \mathbf{t}} = \mathbf{0} &= \langle 0 | \mathcal{L} (-\Omega_{\mathbf{g}} e^{-T} H e^T + e^{-T} H e^T \Omega_{\mathbf{g}}) \mathcal{R} | 0 \rangle \\ &+ \langle 0 | Z (-\Omega_{\mathbf{g}} e^{-T} H e^T + e^{-T} H e^T \Omega_{\mathbf{g}}) | 0 \rangle \\ &= \langle 0 | \mathcal{L} [\bar{H}, \Omega_{\mathbf{g}}] \mathcal{R} | 0 \rangle + \langle 0 | Z [\bar{H}, \Omega_{\mathbf{g}}] | 0 \rangle. \end{aligned} \quad (17)$$

The operator array  $\Omega_{\mathbf{g}}$  is a column array containing all excitation operators from Eq. (4) and is defined such that  $\Omega_{\mathbf{g}}$  acting on  $|0\rangle$  creates  $|\mathbf{g}\rangle$ .

After significant simplification, Eq. (17) reduces to

$$\langle 0 | Z |\mathbf{g}\rangle = \langle 0 | \mathcal{L} \bar{H} |\mathbf{q}\rangle \langle \mathbf{q} | \mathcal{R} |\mathbf{g}\rangle (\langle \mathbf{g} | (E_{\text{CC}} \mathbf{1} - \bar{H}) |\mathbf{g}\rangle)^{-1}, \quad (18)$$

where  $\mathbf{1}$  stands for a unit matrix of rank  $|\mathbf{g}\rangle$ . This is exactly equivalent to the equation for  $Z$  in Ref. 7.

Finally, since the functional satisfies the generalized Hellmann–Feynman theorem, for any perturbation  $\chi$ ,

$$\frac{\partial F}{\partial \chi} = \frac{\partial E}{\partial \chi} = \langle 0 | \mathcal{L} \bar{H}^\chi \mathcal{R} | 0 \rangle + \langle 0 | Z \bar{H}^\chi | 0 \rangle. \quad (19)$$

Here,  $\bar{H}^\chi$  represents the derivative of the bare Hamiltonian elements with respect to the perturbation  $\chi$  within the similarity transformed Hamiltonian  $\bar{H}$ . For the pure EOM-CC methods this means  $\bar{H}^\chi = e^{-T} (\partial H / \partial \chi) e^T$ . Equation (19) is the same as Eq. (36) of Ref. 7. Although we simply postulated the form of the functional, the fact that it produces equations (and therefore density matrices) identical to those produced through straightforward differentiation of the en-

ergy expression (Ref. 7) proves that the functional is valid. For a discussion of the properties of the density matrices resulting from these equations, see Ref. 27.

It is also possible to derive an energy expression from Eq. (9). By projecting on the left-hand side by  $\langle 0 | \mathcal{L} | \mathbf{p} \rangle$  we get the expression

$$E = \langle 0 | \mathcal{L} [\bar{H}, \mathcal{R}] | 0 \rangle + \langle 0 | \bar{H} | 0 \rangle, \quad (20)$$

where the second term,  $E_{\text{CC}}$ , is added to give a total energy instead of just the excitation energy. The functional which corresponds to this energy expression is

$$\begin{aligned} F &= \langle 0 | \mathcal{L} [\bar{H}, \mathcal{R}] | 0 \rangle + \langle 0 | \bar{H} | 0 \rangle + \langle 0 | Z \bar{H} | 0 \rangle \\ &+ \omega (1 - \langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle). \end{aligned} \quad (21)$$

Superficially, Eqs. (12) and (21) appear similar. Both functionals have the same value, the total energy  $E$ , and the EOM-CC equations can be derived from either.<sup>28</sup> However, these energy functionals contain several differences. The most important is that the equations for and the value of  $Z$  have changed. For a pure EOM-CC method the equation for  $Z$  with this functional is<sup>28</sup>

$$\begin{aligned} \langle 0 | Z |\mathbf{g}\rangle &= \langle 0 | \mathcal{L} \bar{H} |\mathbf{q}\rangle \langle \mathbf{q} | \mathcal{R} |\mathbf{g}\rangle (\langle \mathbf{g} | (E_{\text{CC}} \mathbf{1} - \bar{H}) |\mathbf{g}\rangle)^{-1} \\ &+ \langle 0 | \mathcal{L} \mathcal{R} |\mathbf{g}\rangle. \end{aligned} \quad (22)$$

The first term in Eq. (22) is the same as Eq. (18). However, the second term is new.

The expression for the energy derivative corresponding to this functional is

$$\frac{\partial E}{\partial \chi} = \langle 0 | \mathcal{L} [\bar{H}^\chi, \mathcal{R}] | 0 \rangle + \langle 0 | \bar{H}^\chi | 0 \rangle + \langle 0 | Z \bar{H}^\chi | 0 \rangle. \quad (23)$$

Equations (23) and (19) produce the same density matrices. Therefore, either may be used. Hence, the operator  $Z$  is not unique but only has meaning within the context of its functional.

## B. P-EOM-MBPT(2) gradients

Detailed equations for P-EOM-MBPT(2) have been given previously.<sup>21</sup> The P-EOM-MBPT(2) functional is

$$\begin{aligned} F &= \langle 0 | (\mathcal{L}_1 + \mathcal{L}_2) [(H^{[0]} + H^{[1]} + H^{[1]} T^{[1]}) \mathcal{R}_1]_c | 0 \rangle \\ &+ \langle 0 | \mathcal{L}_1 [(H^{[0]} + H^{[1]} + H^{[1]} T^{[1]}) \mathcal{R}_2]_c | 0 \rangle \\ &+ \langle 0 | \mathcal{L}_2 (H^{[0]} \mathcal{R}_2)_c | 0 \rangle \\ &+ \langle 0 | H^{[0]} + H^{[1]} + (H^{[1]} T^{[1]})_c | 0 \rangle \\ &+ \langle 0 | Z [(H^{[0]} - E^{[0]}) T^{[1]} + H^{[1]}] | 0 \rangle \\ &+ E (1 - \langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle). \end{aligned} \quad (24)$$

Here we assume the usual many-body perturbation theory partitioning of the Hamiltonian.  $H^{[n]}$  is the  $n$ th order term of the Hamiltonian, and  $T^{[n]}$  is the  $n$ th order  $T$  amplitude from many-body perturbation theory. The subscript  $c$  means that  $T^{[1]}$  or  $\mathcal{R}$  is connected to  $H$ , and  $(HT^{[1]})_c$  is equivalent to  $[H, T^{[1]}]$ . When all three symbols are included,  $T^{[1]}$  and  $\mathcal{R}$

both must be connected to  $H$ , and  $(HT^{[1]}\mathcal{R})_c$  is equivalent to  $[[H, T^{[1]}], \mathcal{R}]$ . The fifth term comes from the defining equation for the  $T^{[1]}$  amplitudes.<sup>20</sup>

For the rest of the paper we will assume that the reference determinant is the Hartree–Fock solution. In this case,

$$H^{[0]} = \sum_i \epsilon_i \{i^\dagger i\} + \sum_a \epsilon_a \{a^\dagger a\}, \quad (25)$$

and

$$H^{[1]} = H - H^{[0]} = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{p^\dagger q^\dagger sr\}. \quad (26)$$

Also,  $T^{[1]}$  is a double excitation operator, and therefore  $\langle 0 | \mathcal{L}_1 [H^{[1]} T^{[1]} \mathcal{R}_2]_c | 0 \rangle$  must vanish. Another consequence of  $T^{[1]}$  only being a double excitation is that now  $Z$  consists of only double deexcitation operators.

Taking derivatives of the (simplified) Eq. (24) gives the equations for the gradients. It can be shown that taking derivatives with respect to the coefficients of the various  $\mathcal{R}$  and  $\mathcal{L}$  operators recovers the energy expression. Again, by construction, taking the derivative with respect to the coefficients of  $Z$  recovers the  $T^{[1]}$  equation. Finally, taking the derivative with respect to the  $T^{[1]}$  amplitudes gives

$$\begin{aligned} \frac{\partial F}{\partial T^{[1]}} = \mathbf{0} = & \langle 0 | \mathcal{L}(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}})_c | 0 \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle \\ & + \langle 0 | Z(H^{[0]} - E^{[0]}) | \mathbf{d} \rangle. \end{aligned} \quad (27)$$

---


$$\begin{aligned} \frac{\partial E}{\partial \chi} = \frac{\partial F}{\partial \chi} = & \langle 0 | (\mathcal{L}_1 + \mathcal{L}_2) \left[ \left( \frac{\partial H^{[0]}}{\partial \chi} + \frac{\partial H^{[1]}}{\partial \chi} + \frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \right) \mathcal{R}_1 \right]_c | 0 \rangle + \langle 0 | \mathcal{L}_1 \left[ \left( \frac{\partial H^{[0]}}{\partial \chi} + \frac{\partial H^{[1]}}{\partial \chi} + \frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \right) \mathcal{R}_2 \right]_c | 0 \rangle \\ & + \langle 0 | \mathcal{L}_2 \left( \frac{\partial H^{[0]}}{\partial \chi} \mathcal{R}_2 \right)_c | 0 \rangle + \langle 0 | \frac{\partial H^{[0]}}{\partial \chi} + \frac{\partial H^{[1]}}{\partial \chi} + \left( \frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \right)_c | 0 \rangle + \langle 0 | Z \left( \frac{\partial H^{[0]}}{\partial \chi} T^{[1]} + \frac{\partial H^{[1]}}{\partial \chi} \right)_c | 0 \rangle. \end{aligned} \quad (31)$$


---

This expression only contains quantities which are independent of the perturbation plus derivatives of the Hamiltonian elements. Thus, the derivative can be recast as one- and two-particle effective density matrices times derivatives of integrals;

$$\frac{\partial E}{\partial \chi} = \sum_{p,q} \rho_q^p \frac{\partial f_{pq}}{\partial \chi} + \sum_{p,q} \rho_{rs}^{pq} \frac{\partial \langle pq || rs \rangle}{\partial \chi}. \quad (32)$$

The equations for  $\rho$  and for  $\xi$  are subsets of the corresponding equations for EOM-MBPT(2) gradients,<sup>20</sup> where all terms except those including both a  $\mathcal{L}_2$  and a  $\mathcal{R}_2$  coefficient are kept.<sup>28</sup> Please note that the term on the right-hand side of Eq. (60) in Ref. 20 and the third term on the right-hand side of Eq. (61) in Ref. 20 have been incorrectly included in their equations. The P-EOM-MBPT(2) gradients have been implemented in the ACES II program system<sup>29</sup> starting from Stanton and Gauss' EOM-MBPT(2) gradient code.<sup>20</sup>

Here,  $\Omega_{\mathbf{d}}$  is a pure doubles operator analogous to  $\Omega_{\mathbf{g}}$ . Diagrammatically, having  $H^{[1]}$  connected to  $\Omega_{\mathbf{d}}$  means that lines from  $H^{[1]}$  are dangling from the bottom. We have used the fact that  $\mathcal{R}$  commutes with  $\Omega_{\mathbf{d}}$ . Solving for  $Z$  gives

$$\begin{aligned} \langle 0 | Z | \mathbf{d} \rangle = & \{ \langle 0 | \mathcal{L}(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}})_c | 0 \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle \} \\ & \times (\langle \mathbf{d} | (E^{[0]} \mathbf{1} - H^{[0]}) | \mathbf{d} \rangle)^{-1}. \end{aligned} \quad (28)$$

Previously, solving for  $Z$  involved inverting the full  $\bar{H}$ , but now we only need the inverse of  $\langle \mathbf{d} | (E^{[0]} - H^{[0]}) | \mathbf{d} \rangle$  which, in the Hartree–Fock case, is just the denominator from MBPT(2). It is now convenient to introduce a new operator,  $\Xi$ , which is the inhomogeneous part of the  $Z$  equation. For P-EOM-MBPT(2),

$$\Xi = \frac{1}{4} \sum_{\substack{a,b \\ i,j}} \xi_{ab}^{ij} i^\dagger a j^\dagger b \quad (29)$$

and

$$\langle 0 | \Xi | \mathbf{d} \rangle = \langle 0 | \mathcal{L}(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}})_c | 0 \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle. \quad (30)$$

Computationally, to solve for  $Z$ , we first solve for  $\Xi$  and then apply the denominator.

Now the derivative with respect to a general perturbation can be written as

One final note should be made about the cost of the P-EOM-MBPT(2) gradients. Previously we argued that the iterative  $n_{\text{occ}}^2 N_{\text{virt}}^3$  steps should dominate the time over the noniterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  step for normal vertical excitation energy calculations. This was partially because the cost of the  $n_{\text{occ}}^2 N_{\text{virt}}^4$  step can be amortized over multiple excited states. However, the gradient for only one excited state can be calculated at a time. Hence, this amortization cannot occur. More important, there are now many more  $n_{\text{occ}}^3 N_{\text{virt}}^3$  steps, which, when added together will also contribute significantly to the cost of the calculation. Therefore, P-EOM-MBPT(2) gradients is most accurately considered a noniterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  method.

### III. APPLICATION TO DIATOMIC MOLECULES

In order to assess the performance of the CIS(D)<sup>30</sup> method for excited state potential energy surfaces, Stanton *et al.*<sup>31</sup> studied singlet excited states for six diatomic molecules. In order to compare our new work with the methods

TABLE I. Vertical excitation energies (in eV) for the excited singlet states.

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ
H <sub>2</sub>	CIS <sup>a</sup>	15.354	12.639	12.714
	CIS(D) <sup>a</sup>	15.341	12.574	12.832
	P-EOM-MBPT(2)	15.349	12.574	12.835
	EOM-CCSD <sup>a</sup>	15.257	12.484	12.717
BH	CIS <sup>a</sup>	3.029	2.849	2.852
	CIS(D) <sup>a</sup>	2.991	2.864	2.810
	P-EOM-MBPT(2)	2.991	2.875	2.824
	EOM-CCSD <sup>a</sup>	3.117	2.972	2.914
CO	CIS <sup>a</sup>	9.385	9.272	9.330
	CIS(D) <sup>a</sup>	8.911	8.768	8.767
	P-EOM-MBPT(2)	9.196	9.047	9.076
	EOM-CCSD <sup>a</sup>	8.833	8.638	8.666
N <sub>2</sub>	CIS <sup>a</sup>	10.378	10.360	10.550
	CIS(D) <sup>a</sup>	9.444	9.389	9.532
	P-EOM-MBPT(2)	9.883	9.805	9.980
	EOM-CCSD <sup>a</sup>	9.425	9.339	9.514
BF	CIS <sup>a</sup>	6.888	6.559	6.601
	CIS(D) <sup>a</sup>	6.865	6.481	6.455
	P-EOM-MBPT(2)	6.935	6.560	6.545
	EOM-CCSD <sup>a</sup>	6.898	6.482	6.454
C <sub>2</sub>	CIS <sup>a</sup>	-1.180	-1.258	-1.229
	CIS(D) <sup>a</sup>	1.310	1.151	1.222
	P-EOM-MBPT(2)	1.423	1.261	1.328
	EOM-CCSD <sup>a</sup>	1.526	1.283	1.308

<sup>a</sup>Reference 31.

presented there, we have also studied those systems. The six diatomics are CO, N<sub>2</sub>, C<sub>2</sub>, H<sub>2</sub>, BH, and BF. Except for N<sub>2</sub>, the studied states are the lowest singlet excited state of the molecule. For N<sub>2</sub> the 1<sup>1</sup>Π<sub>g</sub> state was studied.

The basis sets used were 6-31G\*,<sup>32,33</sup> aug-cc-pVDZ,<sup>34</sup> and aug-cc-pVTZ.<sup>34</sup> From attempting to match their reported numbers, it would appear that for the 6-31G\* and aug-cc-pVDZ basis sets they used all six Cartesian *d* functions, and for the aug-cc-pVTZ basis set they used only the spherical *d* and *f* functions. We have followed suit.

These states have been carefully studied with very accurate calculations. However, the point of this work is to compare the current method with other single reference excited state methods. Therefore, we will not attempt to review the voluminous literature on these molecules. Instead we will compare the three inexpensive single reference methods [CIS, CIS(D), and P-EOM-MBPT(2)] to the more expensive and more complete EOM-CCSD and to experiment.<sup>35</sup> All of the other methods can be viewed as various approximations to EOM-CCSD. For valence excited states there are frequently important contributions from triples to consider.<sup>36-39</sup>

Our results for the diatomic molecules are presented in Tables I–V. There are some small differences between the numbers reported here and the values given in Ref. 31. Several values given in that paper were in error. Those errors have been corrected here. All optimizations were done using analytic gradients, and all vibrational frequencies and intensities were calculated from finite differences of analytical gradients. Intensities are calculated in the double harmonic approximation.

TABLE II. Adiabatic excitation energies (in eV) for the excited singlet states.

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt. <sup>a</sup>
H <sub>2</sub>	CIS <sup>b</sup>	12.765	11.269	11.352	
	CIS(D) <sup>b</sup>	12.980	11.290	11.429	
	P-EOM-MBPT(2)	12.943	11.274	11.408	
	EOM-CCSD <sup>b</sup>	13.110	11.228	11.353	11.3694
BH	CIS <sup>b</sup>	3.024	2.845	2.849	
	CIS(D) <sup>b</sup>	2.989	2.861	2.807	
	P-EOM-MBPT(2)	2.989	2.872	2.821	
	EOM-CCSD <sup>b</sup>	3.117	2.972	2.913	2.8685
CO	CIS <sup>b</sup>	8.784	8.739	8.802	
	CIS(D) <sup>b</sup>	8.269	8.219	8.246	
	P-EOM-MBPT(2)	8.566	8.527	8.580	
	EOM-CCSD <sup>b</sup>	8.330	8.229	8.256	8.0684
N <sub>2</sub>	CIS <sup>b</sup>	9.413	9.432	9.582	
	CIS(D) <sup>b</sup>	8.802	8.775	8.864	
	P-EOM-MBPT(2)	9.264	9.231	9.346	
	EOM-CCSD <sup>b</sup>	8.760	8.714	8.839	8.5900
BF	CIS <sup>b</sup>	6.806	6.519	6.563	
	CIS(D) <sup>b</sup>	6.760	6.428	6.404	
	P-EOM-MBPT(2)	6.822	6.507	6.495	
	EOM-CCSD <sup>b</sup>	6.811	6.444	6.417	6.3427
C <sub>2</sub>	CIS <sup>b</sup>	-1.275	-1.350	-1.319	
	CIS(D) <sup>b</sup>	1.143	0.997	1.075	
	P-EOM-MBPT(2)	1.293	1.138	1.208	
	EOM-CCSD <sup>b</sup>	1.301	1.066	1.103	1.0404

<sup>a</sup>Reference 35.<sup>b</sup>Reference 31.

TABLE III. Equilibrium distances (in Å) for the ground states.

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt. <sup>a</sup>
H <sub>2</sub>	SCF <sup>b</sup>	0.7300	0.7481	0.7345	
	MBPT(2) <sup>b</sup>	0.7375	0.7549	0.7374	
	CCSD <sup>b</sup>	0.7462	0.7617	0.7431	0.7414
BH	SCF <sup>b</sup>	1.225	1.233	1.221	
	MBPT(2) <sup>b</sup>	1.233	1.241	1.216	
	CCSD <sup>b</sup>	1.244	1.249	1.220	1.2324
CO	SCF <sup>b</sup>	1.114	1.110	1.104	
	MBPT(2) <sup>b</sup>	1.150	1.147	1.134	
	CCSD <sup>b</sup>	1.141	1.138	1.124	1.1283
N <sub>2</sub>	SCF <sup>b</sup>	1.078	1.078	1.067	
	MBPT(2) <sup>b</sup>	1.130	1.131	1.110	
	CCSD <sup>b</sup>	1.113	1.113	1.093	1.0977
BF	SCF <sup>b</sup>	1.260	1.270	1.249	
	MBPT(2) <sup>b</sup>	1.279	1.294	1.264	
	CCSD <sup>b</sup>	1.281	1.296	1.263	1.2626
C <sub>2</sub>	SCF <sup>b</sup>	1.245	1.253	1.241	
	MBPT(2) <sup>b</sup>	1.264	1.276	1.254	
	CCSD <sup>b</sup>	1.252	1.265	1.241	1.2425

<sup>a</sup>Reference 35.<sup>b</sup>Reference 31.

TABLE IV. Equilibrium distances (in Å) for the excited singlet states.

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt. <sup>a</sup>
H <sub>2</sub>	CIS <sup>b</sup>	1.544	1.239	1.239	
	CIS(D) <sup>b</sup>	1.599	1.256	1.273	
	P-EOM-MBPT(2)	1.626	1.273	1.295	
	EOM-CCSD <sup>b</sup>	1.616	1.267	1.283	1.2928
BH	CIS <sup>b</sup>	1.204	1.214	1.204	
	CIS(D) <sup>b</sup>	1.219	1.223	1.199	
	P-EOM-MBPT(2)	1.216	1.223	1.199	
	EOM-CCSD <sup>b</sup>	1.241	1.242	1.211	1.2186
CO	CIS <sup>b</sup>	1.228	1.220	1.213	
	CIS(D) <sup>b</sup>	1.295	1.286	1.263	
	P-EOM-MBPT(2)	1.293	1.282	1.259	
	EOM-CCSD <sup>b</sup>	1.252	1.242	1.224	1.2353
N <sub>2</sub>	CIS <sup>b</sup>	1.200	1.200	1.192	
	CIS(D) <sup>b</sup>	1.250	1.249	1.231	
	P-EOM-MBPT(2)	1.245	1.244	1.227	
	EOM-CCSD <sup>b</sup>	1.221	1.220	1.202	1.2203
BF	CIS <sup>b</sup>	1.316	1.312	1.287	
	CIS(D) <sup>b</sup>	1.350	1.349	1.312	
	P-EOM-MBPT(2)	1.353	1.349	1.312	
	EOM-CCSD <sup>b</sup>	1.345	1.342	1.304	1.3038
C <sub>2</sub>	CIS <sup>b</sup>	1.293	1.301	1.289	
	CIS(D) <sup>b</sup>	1.333	1.346	1.320	
	P-EOM-MBPT(2)	1.325	1.337	1.312	
	EOM-CCSD <sup>b</sup>	1.334	1.347	1.318	1.3184

<sup>a</sup>Reference 35.<sup>b</sup>Reference 31.

### A. Vertical and adiabatic excitation energies

The vertical excitation energies are given for the six molecules, for the four methods, and for the three basis sets in Table I. The adiabatic excitation energies are given in Table II. The ground state minimum geometries used are listed in Table III, with the excited state minimum geometries in Table IV. The appropriate ground state minimum for CIS is the SCF minimum. The appropriate ground state minimum for CIS(D) and P-EOM-MBPT(2) is the MBPT(2) minimum. The appropriate minimum for EOM-CCSD is the CCSD minimum.

As has been noted before,<sup>31</sup> the CIS answers are too poor to be reliable. CIS has several errors greater than 1 eV, and for C<sub>2</sub> CIS even predicts the wrong sign for the excitation energy. The mean absolute deviation with respect to experiment for the adiabatic excitation energies with the aug-cc-pVTZ basis is 0.724 eV. These failings are directly attributable to the method's complete lack of dynamic correlation.

CIS(D) improves on the CIS in all cases, except those four where the CIS is accidentally already in good agreement. In all cases, the CIS(D) energies are within 0.2 eV of the EOM-CCSD energies, and in all of the cases with the best basis set, the error with respect to experiment is less than 0.3 eV. The mean absolute deviation with respect to experiment for the adiabatic excitation energies with the aug-cc-pVTZ basis is 0.112 eV. This is partially due to the choice of excited states considered and is actually better accuracy than was initially reported for the method.<sup>30</sup>

The P-EOM-MBPT(2) method, on the other hand, performs worse than originally reported.<sup>21</sup> The vertical excitation energies are slightly worse than the CIS(D) energies.

TABLE V. Harmonic vibrational frequencies (in cm<sup>-1</sup>) for the excited singlet states.

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt. <sup>a</sup>
H <sub>2</sub>	CIS <sup>b</sup>	1495	1610	1589	
	CIS(D) <sup>b</sup>	1438	1485	1422	
	P-EOM-MBPT(2)	1407	1410	1337	
	EOM-CCSD <sup>b</sup>	1428	1439	1368	1358.09
BH	CIS <sup>b</sup>	2576	2536	2544	
	CIS(D) <sup>b</sup>	2426	2441	2517	
	P-EOM-MBPT(2)	2445	2443	2515	
	EOM-CCSD <sup>b</sup>	2180	2243	2372	2251.0
CO	CIS <sup>b</sup>	1646	1615	1633	
	CIS(D) <sup>b</sup>	1282	1238	1323	
	P-EOM-MBPT(2)	1281	1244	1330	
	EOM-CCSD <sup>b</sup>	1559	1517	1592	1518.2
N <sub>2</sub>	CIS <sup>b</sup>	1939	1909	1897	
	CIS(D) <sup>b</sup>	1612	1583	1615	
	P-EOM-MBPT(2)	1638	1612	1635	
	EOM-CCSD <sup>b</sup>	1856	1825	1854	1694.21
BF	CIS <sup>b</sup>	1339	1273	1367	
	CIS(D) <sup>b</sup>	1173	1097	1239	
	P-EOM-MBPT(2)	1160	1095	1241	
	EOM-CCSD <sup>b</sup>	1199	1130	1279	1264.9
C <sub>2</sub>	CIS <sup>b</sup>	1830	1797	1794	
	CIS(D) <sup>b</sup>	1618	1577	1631	
	P-EOM-MBPT(2)	1674	1635	1687	
	EOM-CCSD <sup>b</sup>	1605	1563	1630	1608.35

<sup>a</sup>Reference 35.<sup>b</sup>Reference 31.

The adiabatic energies are slightly better to somewhat worse than the CIS(D) energies, with their mean absolute deviation with respect to experiment for the aug-cc-pVTZ basis being 0.279 eV.

The fact that the P-EOM-MBPT(2) energies are worse than the CIS(D) energies seems to be caused by the choice of states and by a curious feature of CIS(D). In the previous study,<sup>21</sup> it was noted that P-EOM-MBPT(2) performed better on Rydberg states than on valence states. This can be understood, since Rydberg excitations essentially involve pulling an electron out of the valence region and putting it in a very diffuse orbital, while valence excitations put the electron back into the valence space in a different arrangement. Thus valence excitations should involve more orbital relaxation and differential dynamic correlation compared to Rydberg excitations. Therefore, it is reasonable that a method as simple as P-EOM-MBPT(2) could have more trouble accurately describing valence excitations than Rydberg excitations. EOM-CCSD is also more accurate for Rydberg states than valence states, where it takes triples to partially correct the problem.<sup>40</sup>

CIS(D), on the other hand, performs better for valence states than for Rydberg states.<sup>21</sup> This is curious, since the method does not allow the states to relax in the presence of electron correlation. All of the states studied here are valence states, which is probably why the CIS(D) energies are better than the P-EOM-MBPT(2) energies. Also, these states are well separated from other states of the same symmetry, meaning that mixing of states, which the zeroth-order wave

TABLE VI. Geometries (in Å), harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ), infrared intensities (in  $\text{km/mol}$ ), and energies (in hartrees) for the  $D_{3h}$  equilibrium geometry of the  $S_1$  state of  $\text{NH}_3$ .

	CIS <sup>a</sup>	CIS(D) <sup>a</sup>	P-EOM-MBPT(2)	EOM-MBPT(2) <sup>b</sup>	EOM-CCSD <sup>b</sup>
$r_{\text{NH}}$	1.021 3	1.044 1	1.042 0	1.048 7	1.051 2
$\omega_1(a_1')$	3180.8	2814.0	2971.4	3180.8	2993.1
$\omega_2(a_2'')$	842.4	736.5	767.2	769.6	741.2
$\omega_3(e')$	3356.7	3277.2	3185.5	3021.0	2997.5
$\omega_4(e')$	1517.9	1378.6	1370.6	1331.1	1335.2
$I_2$	0.1	57.6	48.3	14.7	9.7
$I_3$	5803.2	1538.5	3620.2	4622.1	4447.1
$I_4$	19.4	981.9	464.4	293.0	376.0
Energy	-55.968 635	-56.240 376	-56.225 152	-56.234 687	-56.246 539

<sup>a</sup>Reference 31.<sup>b</sup>Reference 20.

function, the CIS, would have trouble handling, does not occur in these problems.

The EOM-CCSD aug-cc-pVTZ results agree quite well with experiment, which is not unexpected for such relatively simple states. The mean absolute deviation with respect to experiment for the adiabatic excitation energies is 0.106 eV.

## B. Bond lengths and vibrational frequencies

Excited state equilibrium bond lengths are presented in Table IV and excited state vibrational frequencies are presented in Table V. Certain trends hold true. CIS bond lengths are always too short and vibrational frequencies are all too high. This is completely analogous to the situation for Hartree–Fock for the ground state. However, like Hartree–Fock, the bond lengths and vibrational frequencies are reasonable. The CIS(D) and P-EOM-MBPT(2) bond lengths and vibrational frequencies are quite similar to each other. And, as should be expected, the EOM-CCSD is superior to the other methods.

For CIS, the mean absolute deviation in the bond length is 0.028 Å, and the mean absolute deviation in the frequency is 188  $\text{cm}^{-1}$ . For comparison, the mean absolute deviation in the ground state bond lengths for the SCF was 0.015 Å. The mean absolute deviation in the bond length drops to 0.015 Å for CIS(D), with the mean absolute deviation in the vibrational frequencies being 108  $\text{cm}^{-1}$ . This compares to a mean absolute deviation of 0.011 Å for the P-EOM-MBPT(2) bond lengths, 106  $\text{cm}^{-1}$  for the P-EOM-MBPT(2) vibrational frequencies, and 0.009 Å for the MBPT(2) ground state bond lengths. The EOM-CCSD bond lengths have a mean absolute error of 0.008 Å, and the vibrational frequencies have a mean absolute error of 67  $\text{cm}^{-1}$ . The ground state CCSD has a mean absolute deviation of 0.004 Å for the bond length. All comparisons were made between the aug-cc-pVTZ results and the experimental results. In general, the ground state methods were slightly better than the excited state methods, and EOM-CCSD was better than P-EOM-MBPT(2), which was slightly better than CIS(D).

## IV. APPLICATION TO POLYATOMIC MOLECULES

### A. The $S_1$ state of ammonia

The  $S_1$  state of ammonia has been studied extensively.<sup>41,42</sup> As a methods test, one of its attractive features is its predissociative nature. The character of the state

changes from Rydberg-like near its  $D_{3h}$  minimum to valence-like near the  $C_{2v}$  transition state.<sup>43</sup> Therefore for a method to properly describe the barrier height, it must equally treat the valence and Rydberg parts of the potential energy surface. Studying the  $S_1$  state of ammonia will also let us compare the P-EOM-MBPT(2) with the (nonpartitioned) EOM-MBPT(2) method<sup>20</sup> in order to assess the effect of the partitioning apart from the effect of replacing the CCSD ground state with the MBPT(2) ground state.

The basis set used for this study was the ‘‘A’’ basis set of Ref. 44. This basis set contains 65 contracted functions and includes multiple diffuse functions at each atom. It is flexible enough to give a reasonable description of the entire area of interest of the potential energy surface. Table VI gives the geometry and vibrational spectrum for the  $D_{3h}$  minimum. It is believed that the N–H bond distance is  $1.055 \pm 0.008$  Å.<sup>45</sup> The EOM-CCSD bond distance falls within these error bars. However, a larger basis set would tend to shorten it.<sup>46</sup> The CIS bond length is once again too short and the frequencies are too large. The CIS(D), P-EOM-MBPT(2), and EOM-MBPT(2) bond lengths are all similar and slightly shorter than the EOM-CCSD bond length. For the vibrational frequencies, the CIS(D) results are slightly more erratic compared to the EOM-CCSD than are the P-EOM-MBPT(2) and EOM-MBPT(2), which are similar.

The infrared intensities show some interesting patterns. In every case CIS(D) substantially overestimates the correlation correction to the intensity. The P-EOM-MBPT(2) is only partially able to correct that behavior. Most of the error in the P-EOM-MBPT(2) can be traced to the very approximate treatment of the doubles–doubles block, since the EOM-MBPT(2) intensities are much closer to the EOM-CCSD intensities. The intensities provide a very sensitive measure of the quality of the wave function, and these large errors for the P-EOM-MBPT(2) and especially the CIS(D) methods suggest that their descriptions of the wave function are not as good as the bond lengths and vibrational frequencies suggest.

The structure and vibrational spectrum of the transition state are presented in Table VII. The CIS(D) bond length for the hydrogen being extracted is much too long. This bond length for the P-EOM-MBPT(2) method is also too long, although shorter than for CIS(D). CIS actually manages to get this bond length right compared to EOM-CCSD. These elongated bonds for CIS(D) and P-EOM-MBPT(2) cause  $\omega_6$

TABLE VII. Geometries (in Å and degrees), harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ), infrared intensities (in  $\text{km/mol}$ ), dipole moments (in D), energies (in hartrees), and barrier heights (in  $\text{cm}^{-1}$ ) for the  $C_{2v}$  predissociative transition state of the  $S_1$  state of  $\text{NH}_3$ . The symmetry unique hydrogen is denoted by an asterisk.

	CIS <sup>a</sup>	CIS(D) <sup>a</sup>	P-EOM-MBPT(2)	EOM-MBPT(2) <sup>b</sup>	EOM-CCSD <sup>b</sup>
$r_{\text{NH}^*}$	1.349 7	1.437 1	1.410 8	1.321 9	1.342 1
$r_{\text{NH}}$	1.010 6	1.042 1	1.037 0	1.042 3	1.044 1
$\theta(\text{H}^*\text{NH})$	123.43	126.78	125.82	124.51	124.27
$\omega_1(a_1)$	3538.5	3133.7	3203.6	3069.0	3051.6
$\omega_2(a_1)$	1568.5	1539.1	1525.9	1478.5	1456.0
$\omega_3(a_1)$	1446.6i	1510.3i	1543.2i	1977.3i	1897.3i
$\omega_4(b_1)$	1025.3	1276.0	1191.1	1042.0	1023.1
$\omega_5(b_2)$	3737.2	3313.9	3384.0	3274.9	3255.2
$\omega_6(b_2)$	498.8	104.8i	129.9	396.5	419.6
$I_1$	293.7	640.4	590.5	1081.2	1010.6
$I_2$	5.4	0.3	0.0	48.9	41.0
$I_3$	463.7	5.5	112.1	2301.1	1921.3
$I_4$	50.2	88.4	68.0	43.9	69.9
$I_5$	2.0	6.7	3.7	58.1	56.5
$I_6$	73.0	66.5	103.4	158.0	167.5
$\mu$	3.750	2.951	2.985	2.631	2.727
Energy	-55.952 723	-56.214 426	-56.205 848	-56.223 512	-56.234 405
Barrier Height	3492	5695	4237	2452	2663

<sup>a</sup>Reference 31.

<sup>b</sup>Reference 20.

to be too small,<sup>31</sup> with CIS(D) actually predicting that the transition state is not  $C_{2v}$ .

Once again, CIS(D) and P-EOM-MBPT(2) have problems with the intensities, with  $I_2$ ,  $I_3$ , and  $I_5$  having significant errors with respect to EOM-CCSD and EOM-MBPT(2). On the other hand, the CIS(D) and P-EOM-MBPT(2) dipole moments are pretty reasonable. The barrier heights, though, are much too large, with the CIS(D) barrier height being much worse than the P-EOM-MBPT(2) barrier height. Even the EOM-CCSD barrier height is well above the experimental barrier height, estimated to be about  $2100 \text{ cm}^{-1}$ .<sup>45</sup>

## B. Simple carbonyls

As the simplest of the carbonyls, formaldehyde's spectrum has been studied extensively.<sup>47,48</sup> The first excited state,  $n \rightarrow \pi^*$ , has two distinctive geometrical features. The C–O bond lengthens and the molecule becomes pyramidal. CIS severely underestimates the bond lengthening,<sup>49</sup> while CIS(D) severely overestimates the bond lengthening.<sup>31</sup> Also, CIS(D) predicts the molecule to be almost flat.<sup>31</sup>

Table VIII presents our P-EOM-MBPT(2) results. Other than predicting a C–O bond that is  $0.02 \text{ Å}$  too long, the

TABLE VIII. Geometries (in Å and degrees), harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ), infrared intensities (in  $\text{km/mol}$ ), dipole moments (in D), and energies (in hartrees) for the equilibrium geometry of the  $\tilde{A} \ ^1A'$  state of formaldehyde. Experimental frequencies are fundamentals.

	CIS <sup>a</sup>	CIS(D) <sup>b</sup>	P-EOM-MBPT(2)	EOM-CCSD <sup>b</sup>	Expt. <sup>a</sup>
$r_{\text{CO}}$	1.258	1.384	1.340	1.324	1.321
$r_{\text{CH}}$	1.085	1.088	1.093	1.096	1.097
$\theta(\text{OCH})$	117.3	117.8	117.0	115.8	118.0
$\tau(\text{HOCH})$	148.4	171.5	153.0	145.9	148.3
$\omega_1(a')$	3209.5	3154.1	3102.3	3072.9	2847
$\omega_2(a')$	1437.9	1420.5	1412.7	1407.9	1290
$\omega_3(a')$	1660.8	895.7	1187.2	1248.5	1173
$\omega_4(a')$	561.6	172.6	564.9	719.8	683
$\omega_5(a'')$	3299.6	3295.8	3223.6	3189.5	2968
$\omega_6(a'')$	993.5	914.0	932.9	934.3	898
$I_1$	29.6	2.6	0.7	2.8	
$I_2$	52.0	6.3	0.8	3.5	
$I_3$	2.1	109.6	66.8	93.7	
$I_4$	108.2	38.3	36.0	30.8	
$I_5$	0.0	1.6	2.9	2.8	
$I_6$	3.4	3.6	3.4	4.0	
Dipole moment	1.507	2.374	2.094	1.776	1.56(7) <sup>c</sup>
Energy	-113.669 47	-114.043 84	-114.028 60	-114.052 75	

<sup>a</sup>Reference 49.

<sup>b</sup>Reference 31.

<sup>c</sup>Reference 53.

TABLE IX. A comparison of the geometries of the  $n \rightarrow \pi^*$  states in formaldehyde, acetaldehyde, and acetone using the 6-31G\* basis set. The acetone values in parentheses are for the aug'-cc-pVDZ basis set. Geometries are in angstroms and degrees.

	Formaldehyde	Acetaldehyde	Acetone
$r_{\text{CO}}$	1.340	1.359	1.376 (1.376)
$r_{\text{CC}}$		1.494	1.494 (1.502)
$r_{\text{CH}_a}$	1.093	1.095	
$r_{\text{CH}_b}$		1.091	1.092 (1.099)
$r_{\text{CH}_c}$		1.099	1.101 (1.109)
$r_{\text{CH}_d}$		1.094	1.094 (1.100)
$\theta(\text{OCC})$		116.0	113.4 (113.1)
$\theta(\text{OCH}_a)$	117.0	114.3	
$\theta(\text{CCH}_b)$		110.2	110.3 (109.8)
$\theta(\text{CCH}_c)$		110.6	110.2 (109.8)
$\theta(\text{CCH}_d)$		110.2	110.6 (110.9)
$\tau(\text{H}_a\text{COH})$	153.0		
$\tau(\text{H}_a\text{COC})$		149.9	
$\tau(\text{CCOC})$			146.9 (144.4)
$\tau(\text{H}_b\text{CCO})$		-177.5	-174.5 (-175.1)
$\tau(\text{H}_c\text{CCO})$		61.6	65.0 (64.8)
$\tau(\text{H}_d\text{CCO})$		-57.1	-53.7 (-54.1)

P-EOM-MBPT(2) geometry agrees well with experiment, especially considering the relatively poor basis set used (6-31G\*,<sup>32</sup> the same that was used in Ref. 31). The frequencies are also reasonable, except for  $\omega_4$ . The dipole is somewhat too large, but is still in better agreement with experiment than the CIS(D) dipole.

In Table IX we present a comparison of the formaldehyde, acetaldehyde, and acetone geometries, all with the 6-31G\* basis set.<sup>32</sup> Hydrogen "a" is a hydrogen attached to the carbonyl carbon. Hydrogen "b" is the "in-plane" hydrogen. Hydrogen "c" is the hydrogen pointing into the pyramid. Finally, hydrogen "d" is the hydrogen pointing away from the pyramid. Since acetaldehyde and acetone are pyramidal in their first excited state like formaldehyde is, there is no true in-plane hydrogen. However, in both cases there is a hydrogen with a dihedral angle only about five

degrees out of planarity. The difference with the ground state, however, is that the in-plane hydrogen points away from the oxygen instead of being hydrogen bound to it.<sup>50</sup> In Table IX we also present results for acetone using a bigger basis set, consisting of the aug-cc-pVDZ basis<sup>34</sup> on carbon and oxygen and the cc-pVDZ basis on the hydrogen.<sup>51</sup> This basis set has sometimes been referred to as aug'-cc-pVDZ.

Zuckermann *et al.*<sup>52</sup> carefully measured the spectrum of acetone around the origin of the  $n \rightarrow \pi^*$  band. Their analysis led to the positive assignment of three vibrational bands, with uncertainty about two others. In Table X we present their assignments along with our calculated vibrational frequencies using the aug'-cc-pVDZ basis. They could not definitely distinguish between the first possibility and the second possibility, although they preferred the first. Determining which is correct depends upon the frequency of  $\nu_{19}$ . The computed frequency of  $360.1 \text{ cm}^{-1}$  is well below the  $465.4 \text{ cm}^{-1}$  for the second possibility. On the other hand we are low on all of the other frequencies except for  $\nu_{12}$ , considering we are comparing harmonic frequencies to fundamental frequencies. Also, in acetaldehyde we get good agreement between our calculated vibrational frequency ( $368.4 \text{ cm}^{-1}$ ) and the measured frequency ( $370 \text{ cm}^{-1}$ )<sup>50</sup> for the corresponding mode. The next mode we calculate in acetone is at  $802.5 \text{ cm}^{-1}$ . Hence, our calculated spectrum supports the second possibility over the first possibility. Note that in  $C_s$ ,  $\nu_9$  and  $\nu_{23}$  are both  $A'$ , and they mix strongly. Therefore, the labels as to the nature of the modes should be interpreted loosely.

## V. CONCLUSIONS

We present an alternative and simpler derivation for EOM-CCSD gradients based upon an excited state EOM-CC functional and have derived gradients for the P-EOM-MBPT(2) method and discussed its cost. Then, by studying a series of diatomics and prototypical polyatomics we studied the performance of P-EOM-MBPT(2) for low-lying valence potential energy surfaces versus other single reference methods for excited states for which gradients have been derived.

The performance of CIS, CIS(D), and EOM-CCSD has been discussed previously,<sup>31</sup> and so they will only briefly be discussed here. The CIS energies are too poor to be even qualitatively reliable. However, the CIS geometries are normally quite reasonable. CIS(D) has the opposite behavior. Its energies for valence states often have errors of 0.3 eV or less, but its geometries sometimes fail dramatically. Even

TABLE X. A comparison of two possible assignments of the low frequency vibrations in the  $S_1$  state of acetone to the calculated frequencies. All frequencies are in  $\text{cm}^{-1}$ .

	First possibility <sup>a</sup>	Second possibility <sup>a</sup>	P-EOM-MBPT(2)
$\nu_{12}$ torsion (antigearing)	155.5	155.5	185.7
$\nu_{24}$ torsion (gearing)	172.5	172.5	184.9
$\nu_8$ C-C-C bend	373	373	373.8
$\nu_{23}$ C=O out-of-plane wagging	...	333	330.6
$\nu_{19}$ C=O in-plane wagging	177.5	465.4	360.1

<sup>a</sup>Reference 52.

worse, there seems to be no indication of when the CIS(D) geometries will fail. EOM-CCSD performed quite well in all of the tests presented here, both for the energies and for the geometries.

Overall, the performance of the P-EOM-MBPT(2) method was mixed. The energies were reasonable but were not as good as had been reported previously.<sup>21</sup> The geometries were also reasonable but were noticeably worse than the EOM-CCSD geometries. Overall, in these tests P-EOM-MBPT(2) performed very similarly to CIS(D) when CIS(D) did not fail and was qualitatively correct for those cases for which CIS(D) did fail.

The discrepancy between the P-EOM-MBPT(2) and the EOM-CCSD geometries is attributable primarily to the partitioning of the doubles–doubles block in P-EOM-MBPT(2), since the (nonpartitioned) EOM-MBPT(2) performed similarly to the EOM-CCSD for ammonia. However, it is this partitioning that makes the method attractive, since it is the partitioning that reduces the cost from an iterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$  to an iterative  $n_{\text{occ}}^2 N_{\text{virt}}^3$  plus a noniterative  $n_{\text{occ}}^2 N_{\text{virt}}^4$ .

## ACKNOWLEDGMENTS

This work has been supported by AFOSR Grant No. F49620-95-1-0130 and by AFOSR AASERT Grant No. F49620-I-0421. The authors would like to thank Professor John F. Stanton, University of Texas, and Professor Jürgen Gauss, Universität Mainz, for access to their EOM-CCSD gradient code. We would also like to thank Professor Stanton for his help in correcting the literature data in Tables I–V. Finally, we would like to thank Professor Marcel Nooijen, Princeton University, for his very helpful discussions about excited state gradients.

- <sup>1</sup>J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).
- <sup>2</sup>D. C. Comeau and R. J. Bartlett, Chem. Phys. Lett. **207**, 414 (1993).
- <sup>3</sup>J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
- <sup>4</sup>H. Monkhorst, Int. J. Quantum Chem., Symp. **11**, 421 (1977).
- <sup>5</sup>H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990).
- <sup>6</sup>H. Koch, H. J. A. Jensen, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **93**, 3345 (1990).
- <sup>7</sup>J. F. Stanton, J. Chem. Phys. **99**, 8840 (1993).
- <sup>8</sup>J. F. Stanton and J. Gauss, J. Chem. Phys. **100**, 4695 (1994).
- <sup>9</sup>J. F. Stanton and J. Gauss, Theor. Chim. Acta **91**, 267 (1995).
- <sup>10</sup>L. Adanowicz, W. D. Laidig, and R. J. Bartlett, Int. J. Quantum Chem., Symp. **18**, 245 (1984).
- <sup>11</sup>R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jørgensen and J. Simons, NATO ASI Series C Vol. 166 (Reidel, Dordrecht, 1986), pp. 35–61.
- <sup>12</sup>A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer, III, J. Chem. Phys. **87**, 5361 (1987).
- <sup>13</sup>E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989).
- <sup>14</sup>J. F. Stanton and J. Gauss, J. Chem. Phys. **103**, 8931 (1995).
- <sup>15</sup>J. F. Stanton and J. Gauss, J. Chem. Phys. **101**, 8938 (1994).
- <sup>16</sup>A. Dalgarno and A. L. Stewart, Proc. R. Soc. London, Ser. A **247**, 245 (1958).
- <sup>17</sup>N. C. Handy and H. F. Schaefer, III, J. Chem. Phys. **81**, 5031 (1984).
- <sup>18</sup>E. S. Nielsen, P. Jørgensen, and J. Oddershede, J. Chem. Phys. **73**, 6238 (1980).
- <sup>19</sup>M. Nooijen and J. G. Snijders, J. Chem. Phys. **102**, 1681 (1995).
- <sup>20</sup>J. F. Stanton and J. Gauss, J. Chem. Phys. **103**, 1064 (1995).
- <sup>21</sup>S. R. Gwaltney, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **248**, 189 (1996).
- <sup>22</sup>P. Z. Szalay, Int. J. Quantum Chem. **55**, 151 (1995).
- <sup>23</sup>R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Pt. II, pp. 1047–1113.
- <sup>24</sup>P. G. Szalay, M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **103**, 281 (1995).
- <sup>25</sup>P.-O. Löwdin, Adv. Chem. Phys. **2**, 270 (1959).
- <sup>26</sup>R. J. Bartlett, S. A. Kucharski, J. Noga, J. D. Watts, and G. W. Trucks, in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor, Lecture Notes in Chemistry Vol. 52 (Springer, Berlin, 1989), pp. 125–149.
- <sup>27</sup>J. F. Stanton, J. Chem. Phys. **101**, 8928 (1994).
- <sup>28</sup>S. R. Gwaltney, Ph.D. thesis, University of Florida, 1997.
- <sup>29</sup>The ACES II program is a product of the Quantum Theory Project, University of Florida Authors: J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baek, H. Sekino, P. Rozyczko, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor), VPROPS (P. R. Taylor), and a modified version of the ABACUS integral derivative package (T. U. Helgaker, H. J. Aa. Jensen, J. Olsen, P. Jørgensen, and P. R. Taylor).
- <sup>30</sup>M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, Chem. Phys. Lett. **219**, 21 (1994).
- <sup>31</sup>J. F. Stanton, J. Gauss, N. Ishikawa, and M. Head-Gordon, J. Chem. Phys. **103**, 4160 (1995).
- <sup>32</sup>P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).
- <sup>33</sup>Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.
- <sup>34</sup>R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- <sup>35</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
- <sup>36</sup>J. D. Watts and R. J. Bartlett, J. Chem. Phys. **101**, 3073 (1994).
- <sup>37</sup>J. D. Watts and R. J. Bartlett, Chem. Phys. Lett. **233**, 81 (1995).
- <sup>38</sup>O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **103**, 7429 (1995).
- <sup>39</sup>J. D. Watts and R. J. Bartlett, Chem. Phys. Lett. **258**, 581 (1996).
- <sup>40</sup>J. D. Watts, S. R. Gwaltney, and R. J. Bartlett, J. Chem. Phys. **105**, 6979 (1996).
- <sup>41</sup>G. R. Burton, W. F. Chan, G. Cooper, and C. E. Brion, Chem. Phys. **177**, 217 (1993), and references therein.
- <sup>42</sup>R. J. Bartlett, J. E. Del Bene, S. A. Perera, and R. P. Mattie, J. Mol. Struct.: THEOCHEM **400**, 157 (1997).
- <sup>43</sup>J. Müller and S. Canuto, Chem. Phys. Lett. **70**, 236 (1980).
- <sup>44</sup>P. Rosmus, P. Botschwina, H.-J. Werner, V. Vaida, P. C. Engelking, and M. I. McCarthy, J. Chem. Phys. **86**, 6677 (1987).
- <sup>45</sup>S. A. Henck, M. A. Mason, W.-B. Yan, K. K. Lehmann, and S. L. Coy, J. Chem. Phys. **102**, 4772 (1995).
- <sup>46</sup>J. F. Stanton and N. S. Kadagathur, J. Chem. Phys. **102**, 1096 (1995).
- <sup>47</sup>D. C. Moule and A. D. Walsh, Chem. Rev. **75**, 67 (1975).
- <sup>48</sup>E. R. Davidson and L. E. McMurchie, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982), Vol. 5, pp. 1–39.
- <sup>49</sup>C. M. Hadad, J. B. Foresman, and K. B. Wiberg, J. Phys. Chem. **97**, 4293 (1993).
- <sup>50</sup>M. Noble and E. K. C. Lee, J. Chem. Phys. **81**, 1632 (1984).
- <sup>51</sup>T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- <sup>52</sup>H. Zuckermann, Y. Haas, M. Drabbel, J. Heinze, W. L. Meerts, J. Reuss, and J. van Bladel, Chem. Phys. **163**, 193 (1992).
- <sup>53</sup>D. E. Freeman and W. Klemperer, J. Chem. Phys. **45**, 52 (1966).