COUPLED-CLUSTER BASED METHODS FOR EXCITED STATE ENERGIES AND GRADIENTS

By

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Coupled-cluster based methods have become widely used for calculating energies and properties of molecular ground states. In this dissertation, I present a new method, the partitioned equation-of-motion coupled-cluster method based on a second order many-body perturbation theory ground state (P-EOM-MBPT(2)) for calculating energies of molecular electronic excited states. I also describe how to calculate gradients for two excited state methods, P-EOM-MBPT(2) and the similarity transformed equation-of-motion coupled-cluster singles and doubles (STEOM-CCSD) method. These new methods are then applied to several example molecules.

CHAPTER 1
AN OVERVIEW OF CURRENT METHODS FOR EXCITED STATES

Coupled-Cluster Methods

Coupled-cluster theory[1–14] provides a routinely applicable method for calculating energies and properties of molecules in the lowest state of a given spin and symmetry. By adding triple,[15, 16] quadruple,[17, 18] and higher excitations, it is possible to converge on the exact answer within a given basis set. The perturbative inclusion of triple excitation effects[19–21] is now routine, meaning that energies and properties can approach near chemical accuracy for many molecules. Unfortunately, these methods do not, in general, work for electronic excited states.

The primary problem with describing excited states with normal coupled-cluster (CC) theory is its inherent single reference nature. The wavefunction for the state can be expressed as a linear combination of determinants, with the reference determinant having a coefficient of one. Although in principle coupled-cluster theory can be made exact, the cost of such a calculation would increase in cost at the same rate as full configuration interaction (CI), i.e. as the size of the system factorial.[22] Therefore, the set of excitations used in the calculation are truncated. In such a truncated CC, a second determinant with a coefficient of more than 0.2 to 0.3 can cause the accuracy of the computed results to drop significantly. However, for an open-shell singlet excited state, the second determinant must have a coefficient of one.

Coupled-cluster theory has been extended in order to be able to describe such multireference states. Multireference coupled-cluster theories can be divided into two main categories. They are the Hilbert space approaches[23–31] and the Fock spaces approaches.[32–45] A very simplified view of Hilbert space multireference coupled-cluster theory is that each determinant in the active space gets its own set of T amplitudes, and a small effective Hamiltonian is diagonalized over the space of these wavefunctions. In the Fock space coupled-cluster method, a single exponential operator is used for all determinants in the active space, but this exponential contains operators that change the number of electrons in the system. Hilbert space coupled-cluster theory is more suited to studying one or a few states, while Fock space coupled-cluster theory is more suited to studying energy differences between many states and to calculating spectra.

An alternative method for calculating excitation energies within a coupled-cluster framework is to follow the response of the system to an external time dependent perturbation. This was introduced by Monkhorst,[46] and has been developed into the coupled-cluster linear response (CCLR) method.[47–54] The same equations can also be derived from an equations-of-motion[55] framework based on a coupled-cluster ground state. This gives the equation-of-motion coupled-cluster (EOM-CC) method.[56–59] In EOM-CC (or CCLR) the ground state coupled-cluster operator is used to perform a similarity transformation of the Hamiltonian, which is then diagonalized over a space of excited determinants. EOM-CC and CCLR are identical for excited state energies, but the approximations made by the two methods differ for oscillator strengths and polarizabilities. Typically, the ground state operator and the space of excited determinants is truncated to include only single and double excitations. This gives the EOM-CCSD[58, 59] (or CCSDLR)[53, 54] method. Models have also been developed which partially include the effects of triple excitations.[60–63]

Recently, Nooijen and Bartlett have developed a new method for calculating excited state energies and properties. It is the similarity transformed equation-of-motion coupled-cluster (STEOM-CC) method.[64–66] For singly excited states, STEOM-CC is closely related to the Fock space coupled-cluster method,[66] but conceptually they are very different. In STEOM-CC, ionization potential EOM-CCSD[67] and electron attachment EOM-CCSD[68] calculations are done. Information about the states with one fewer and one more electron is then used to perform a second similarity transformation on the Hamiltonian[69] such that the terms which directly couple single and double excitations are set to zero. A detailed description of STEOM-CC will be given in Chapter 4.

Other Current Excited State Methods

An attempt to catalog all *ab initio* methods currently used for calculating excited states would be futile and will not be attempted. Instead, several of the methods which are used most often will be reviewed. But first it will be useful to take a more general view of excited states and break down how the various methods describe excited states. In this view, the excited state energy is divided into several components. They are the zeroth order description of the wavefunction, the orbital relaxation, and the dynamic correlation in the excited state.

Properly describing the zeroth order description simply means being able to include all of the determinants which play a dominant role in the excited state. For example, this means being able to give the two determinants in an open-shell singlet the same weight. The orbital relaxation refers to how much the orbitals are allowed to rearrange themselves in response to the excitation.

The dynamic correlation for the excited state is further broken down into the dynamic correlation for the ground state and the differential dynamic correlation between the ground and excited states. The reason for this division of the dynamic correlation is that, especially for the single reference theories, first a ground state is calculated and then the excited states are built upon it. The justification for this division is that most electrons do not take part in the excitation and therefore still interact with each other in the same way in the excited state as in the ground state.

These definitions are not unique, especially when considering orbital relaxation versus differential dynamic correlation. The coupled-cluster viewpoint will be taken here. The key to the coupled-cluster viewpoint is Thouless' theorem,[70] which states that any two non-orthogonal determinants can be written as

$$|\Phi_i\rangle = e^{T_1}|\Phi_j\rangle, \tag{1–1}$$

where T_1 is a single excitation operator. Therefore, any set of single excitations or any product of single excitations will be considered orbital relaxation, and dynamic correlation will be reserved for "connected" double and higher excitations.[13]

Table 1–1 provides a convenient representation for how the selected methods break down into the four terms. A "+" means that the method treats this term adequately. Two pluses mean that the method treats the term very well. A "-" means that the term is included, but poorly. Finally, a "0" means that the term is completely neglected. The question mark means that how well the term in question is treated varies based on specifics of the calculation.

The first method to be considered is probably the simplest of all *ab initio* excited state methods. It is the Tamm-Dancoff approximation,[71, 72] also known as the configuration

Table 1–1: An overview of excited state methods.

	zeroth order description	orbital relaxation	ground state dynamic correlation	differential dynamic correlation
CIS	+	-	0	0
RPA	+	+	0	0
MCSCF	++ (?)	++	-	-
CASPT2	++ (?)	++	+	+
CIS(D)	+	-	+	+
EOM-CCSD	++	+	++	+
STEOM-CCSD	+	+	++	++ (?)
MRCI	++ (?)	++ (?)	++ (?)	++ (?)

interaction singles (CIS)[73–75] method. The names will be used interchangeably. In CIS the excited state is determined from diagonalizing a Hamiltonian matrix made up of single excitations with respect to the Hartree-Fock reference determinant. Since, by Brillouin's theorem,[22] single excitations cannot couple with the Hartree-Fock determinant, this diagonalization leaves the ground state unchanged and gives excited states. Because all possible single excitations are included, any excited state which corresponds to a single electron being promoted can be described. However, the orbital relaxation is extremely limited and the method contains no dynamic correlation.

The next method is the random phase approximation (RPA).[76, 77] Although RPA can be derived several ways, the one most useful here is to consider RPA as the response of a wavefunction written as[12, 13] $|\Psi\rangle = \big(1 + T_1 + \frac{1}{2}T_1^2\big)|\Phi_0\rangle$. Clearly, then, RPA also contains no dynamic correlation, but it does contain more orbital relaxation than CIS.

The next method to be considered is multiconfigurational SCF (MCSCF).[78, 79] In MCSCF, a set of configurations is chosen. Then the coefficient for each configuration is variationally optimized while simultaneously optimizing the orbitals from which the configurations are built. Since the procedure involves variationally choosing the optimal orbitals, orbital relaxation can be treated quite well. Because of the flexibility to choose any configurations wanted, any excited state, no matter its excitation level, can be described. Thus the zeroth order description can also be very good if the configurations are chosen properly. Because of the multideterminantal nature of the final wavefunction, some dynamic correlation is recovered, but normally the amount is small. A special way of choosing the configurations is to choose a set of orbitals and to create all possible configurations with a given number of electrons distributed among that set of orbitals. This gives rise to the complete active space SCF (CASSCF)[80] variant of MCSCF.

The CASSCF wavefunction can be used as the zeroth order wavefunction in a multireference perturbation theory expansion. The most popular of the methods derived this way is the CASPT2 method.[81, 82] Since it is based on a CASSCF wavefunction, the arguments above about the zeroth order description and the orbital relaxation still apply. The perturbation theory then allows a treatment of the dynamic correlation. Overall, this method works well, but because of issues involving properly choosing the active space and a potential intruder state problem, it is sometimes difficult to get consistently good results.

Starting with the CIS wavefunction being used as the zeroth order wavefunction in a perturbation expansion, it is possible to derive the CIS(D) method.[83] CIS(D) shares CIS's weakness in term of orbital relaxation, but it does allow for a second order perturbation description of both the ground state dynamic correlation and the differential dynamic correlation.

The next method to be considered is EOM-CCSD,[58, 59] discussed above. Since the excited state wavefunction consists of both single and double excitations, it can have a proper zeroth order description of not only singly excited states, but also doubly excited states and states which are mixtures of singles and doubles. On the other hand, since the reference state determines the orbitals, they are fixed, and the excited state wavefunction has only limited flexibility to relax them through the other singles and through the doubles acting as a single times a single. This linear excited state also limits to what extent differential dynamic correlation is included. More is probably included than for any other method considered so far, but in EOM-CCSD, unlike CASPT2, the differential dynamic correlation needs to compensate for the orbital relaxation. The ground state dynamic correlation is very well described through the ground state coupled-cluster calculation, and therefore for states without large orbital relaxation and differential correlation, EOM-CCSD works well.

In STEOM-CCSD,[64, 66] the use of a singles only excited state operator limits the zeroth order description to those kinds of states describable in CIS. The orbital relaxation is also somewhat limited, but some orbital relaxation comes indirectly from the consideration of the ionized and electron-attached states. The ground state coupled-cluster calculation again describes the ground state dynamic correlation very well. The differential dynamic correlation is handled through the second similarity transformation, which is built from an active space of ionized and electron-attached states. How well this works in practice for a large variety of molecules is not clear yet, but the amount of differential correlation included will depend heavily on the completeness of the active space.[66]

Finally, there is multireference CI (MRCI).[84] Because of the flexibility offered by a MRCI calculation, it is possible to achieve extremely good accuracy by properly accounting for all four parts of the excited state energy. But MRCI has two very significant drawbacks. It often takes an experienced practitioner to properly build the trial wavefunction, and the cost of the method is such that it can only be applied to very small systems. It is not size extensive, either, and its lack of size extensivity will cause the error in the calculation to grow as the molecule grows.

Gradients for Excited State Methods

One of the most important advances in quantum chemistry was Pulay's derivation of gradients for SCF wavefunctions.[85] This allowed for the convenient computation of the derivative of the energy with respect to a general perturbation. By taking the perturbation to be moving an atom, his discovery made practical the exploration of ground state potential energy surfaces.[86] People could readily find minima and transition states and calculate vibrational frequencies. Pople *et al.*[87] extended gradient technology to correlated methods with the development of gradients for MBPT(2). For a review of current analytical gradient techniques, see Ref. 88.

In terms of excited states, gradients were first introduced for the MCSCF method.[86] Although not in general use, gradients are also available for MRCI wavefunctions.[89] Gradients for CIS were first developed in 1992.[75] Then came gradients for EOM-CCSD in 1993,[90–92] followed by CIS(D) gradients.[93] For a general overview of gradients for coupled-cluster based methods for excited states, see Ref. 94.

CHAPTER 2
PARTITIONED EQUATION-OF-MOTION COUPLED-CLUSTER METHODS FOR EXCITED STATE ENERGIES

Introduction

The equation-of-motion coupled-cluster (EOM-CC) method[57–59] is a conceptually single reference, generally applicable, unambiguous approach for the description of excited,[57–59] electron-attached[68] or ionized states.[67] All follow from simple consideration of the Schrödinger equation for two states, a reference state $|\Psi_0\rangle$ (not necessarily the ground state), and an excited (electron-attached or ionized) state $|\Psi_\kappa\rangle$. Considering H to be in second quantization, where the number of particles is irrelevant, the Schrödinger equations for the two states are

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \tag{2–1}$$

and

$$H|\Psi_\kappa\rangle = E_\kappa|\Psi_\kappa\rangle. \tag{2–2}$$

By choosing to represent the excited state eigenfunction as

$$|\Psi_\kappa\rangle = \mathcal{R}_\kappa|\Psi_0\rangle, \tag{2–3}$$

it is readily obtained that

$$[H, \mathcal{R}_\kappa]|\Psi_0\rangle = \omega_\kappa \mathcal{R}_\kappa|\Psi_0\rangle \tag{2–4}$$

for $\omega_\kappa = E_\kappa - E_0$, from subtracting Eq. (2–1) from Eq. (2–2) after left multiplication by $\mathcal{R}_\kappa$.

The choice of $\mathcal{R}_\kappa$ defines the particular EOM with *i*, *j*, *k*, . . . indicating occupied orbital indices and operators, while *a*, *b*, *c*, . . . are unoccupied orbitals and operators. Also, *p*, *q*, *r*, . . . refer to orbitals and operators of either occupation. For electronic excited states,

$$\mathcal{R}_\kappa^{EE} = r_0(\kappa) + \sum_{i,a} r_i^a(\kappa)\left\{a^\dagger i\right\} + \frac{1}{4}\sum_{\substack{i,j\\a,b}} r_{ij}^{ab}(\kappa)\left\{a^\dagger i b^\dagger j\right\} + \cdots, \tag{2–5}$$

for electron attachment

$$\mathcal{R}_\kappa^{EA} = \sum_{a} r^a(\kappa)\left\{a^\dagger\right\} + \frac{1}{2}\sum_{a,b,j} r_j^{ab}(\kappa)\left\{a^\dagger j b^\dagger\right\} + \cdots, \tag{2–6}$$

and for ionization

$$\mathcal{R}_\kappa^{IP} = \sum_{i} r_i(\kappa)\{i\} + \frac{1}{2}\sum_{i,j,a} r_{ij}^a(\kappa)\left\{i a^\dagger j\right\} + \cdots, \tag{2–7}$$

Coupled-cluster theory is introduced by choosing

$$|\Psi_0\rangle = e^T|0\rangle \tag{2–8}$$

where T is the usual excitation operator, and $|0\rangle$ represents some independent particle model reference. Since $[\mathcal{R}_\kappa, T] = 0$ for any of the above choices, we can commute the operators to give

$$[\bar{H}, \mathcal{R}_\kappa]|0\rangle = \left(\bar{H}\mathcal{R}_\kappa\right)_c|0\rangle = \omega_\kappa\mathcal{R}_\kappa|0\rangle, \tag{2–9}$$

where

$$\bar{H} = e^{-T}He^T, \tag{2–10}$$

and $\left(\bar{H}\mathcal{R}_\kappa\right)_c$ indicates the open, connected terms that remain in the commutator. Two operators being connected means that they share at least one index. In this way, all of the ground state CC information is contained in $\bar{H}$, now generalized to have three- and four-body terms.[58] Note, $\bar{H}$ is also non-Hermitian, necessitating that both its left $\mathcal{L}_\kappa$ and right $\mathcal{R}_\kappa$ eigenvectors, which form a biorthogonal set, $\mathcal{L}_i\mathcal{R}_j = \delta_{ij}$, be considered for a treatment of properties. In matrix form,

$$\begin{aligned} \left(\bar{\mathbf{H}}\mathbf{R}_\kappa\right)_c &= \mathbf{R}_\kappa\omega_\kappa \\ \mathbf{L}_\kappa\bar{\mathbf{H}} &= \mathbf{L}_\kappa\omega_\kappa. \end{aligned} \tag{2–11}$$

Consequently, EOM-CC reduces to a CI-like equation that provides the relevant excitation energies directly.

Besides the obvious approximations, such as $T = T_1 + T_2$, and $\mathcal{R}_\kappa$ being limited to single and double excitations, which defines EOM-CCSD, and various triple excitation extensions, EOM-CCSD(T),[61] EOM-CCSDT-1,[61], EOM-CCSD(T̃),[63] and EOM-CCSDT-3,[63] one can conceive of many other approximations to the basic EOM-CC structure. Instead of Eq. (2–8), for the reference state a perturbation approximation might be chosen, such as

$$\left| \Psi_0^{(m)} \right\rangle = \left(1 + T^{(1)} + \frac{1}{2}T^{(1)}T^{(1)} + T^{(2)} + \cdots\right) \left| 0 \right\rangle, \tag{2–12}$$

where one truncates at a particular order, *m*. (See Ref. 95 for the coupled-cluster, non-Hartree-Fock definition of the various orders.) Alternatively, rather than retaining the full perturbation approximation to $|\Psi_0^{(m)}\rangle$, we could truncate $\bar{H}$ itself to some order.[96, 97]

It is possible to conceive of perturbative approximations to $\mathcal{R}_\kappa$, too. The latter are, perhaps, most easily viewed from the partitioning approach to perturbation theory.[98] That is, Eq. (2–12) can be partitioned into the spaces *P* and *Q*, where *P* represents the principal configuration space (of dimension *p*) and *Q* (of dimension *q*) represents its orthogonal complement. Then it is well known that we can consider an effective Hamiltonian,

$$\bar{\bar{\mathbf{H}}}_{PP}(\omega_\kappa) = \bar{\mathbf{H}}_{PP} + \bar{\mathbf{H}}_{PQ}\left(\omega_\kappa - \bar{\mathbf{H}}_{QQ}\right)^{-1}\bar{\mathbf{H}}_{QP}, \tag{2–13}$$

whose eigenvectors are solely defined in the *P* space

$$\bar{\bar{\mathbf{H}}}_{PP}\bar{\mathbf{c}}_P = \bar{\mathbf{c}}_P\omega_\kappa \tag{2–14}$$

for the first several eigenvalues, ω_κ. Expanding the inverse in Eq. (2–13) provides a series of perturbative approximations to $\bar{\bar{\mathbf{H}}}_{PP}$ or to the eigenvectors $\bar{\mathbf{c}}_P$ in Eq. (2–14).[98] With *P* chosen to be the space of single excitations, and *Q* that of double excitations, such partitioned EOM-CCSD results, first presented in 1989[57] have been shown to retain most of the accuracy of the full EOM-CCSD method. Other approximations can be made. To introduce triple and quadruple excitations, selective double excitations could be retained in *P* and at least diagonal approximations could be made for the triple and quadruple excitation blocks of $\bar{\mathbf{H}}_{QQ}$.

In this chapter such partitioned and perturbation-based approximations to the full EOM-CCSD method will be reconsidered. It will be demonstrated that very good accuracy may be obtained within a much less expensive computational structure. In particular, whereas the full EOM-CCSD is proportional to $n_{occ}^2 N_{virt}^4 \propto n^6$, for *n* basis functions, a $n_{occ}^2 N_{virt}^3 \propto n^5$ procedure will be developed that shows promise for large molecules.

Theory

Partitioned EOM-CC for Excited States

In a typical EOM-CCSD calculation, the excitation energy and excited state properties are calculated via diagonalization of the non-symmetric matrix,[58]

$$(\bar{\mathbf{H}}) = \begin{bmatrix} \bar{\mathbf{H}}_{\mathrm{SS}} & \bar{\mathbf{H}}_{\mathrm{SD}} \\ \bar{\mathbf{H}}_{\mathrm{DS}} & \bar{\mathbf{H}}_{\mathrm{DD}} \end{bmatrix} \tag{2–15}$$

where $\bar{\mathbf{H}}_{\mathrm{SS}}$ stands for the singles-singles block of the matrix, etc. The major step in an iterative diagonalization[99] of the matrix is multiplying the matrix by a trial vector **C**. In the *EE* case, the equations for this multiplication are as follows:[58, 60]

$$[\bar{\mathbf{H}}_{\mathrm{SS}}\mathbf{C}]_i^a = \sum_e F_{ae}C_i^e - \sum_m F_{mi}C_m^a + \sum_{em} W_{amie}C_m^e, \tag{2–16}$$

$$[\bar{\mathbf{H}}_{\mathrm{SD}}\mathbf{C}]_i^a = \sum_{em} F_{me}C_{im}^{ae} + \frac{1}{2}\sum_{mef} W_{amef}C_{im}^{ef} - \frac{1}{2}\sum_{mne} W_{mnie}C_{mn}^{ae}, \tag{2–17}$$

$$\begin{aligned}
[\bar{\mathbf{H}}_{\mathrm{DS}}\mathbf{C}]_{ij}^{ab} =& P(ab)\sum_m W_{maij}C_m^b + P(ij)\sum_e W_{abej}C_i^e \\
&+ P(ab)\sum_f \left(\sum_{me} W_{bmfe}C_m^e\right) t_{ij}^{af} \\
&- P(ij)\sum_n \left(\sum_{me} W_{nmje}C_m^e\right) t_{in}^{ab},
\end{aligned} \tag{2–18}$$

$$\begin{aligned}
[\bar{\mathbf{H}}_{\mathrm{DD}}\mathbf{C}]_{ij}^{ab} =& P(ab)\sum_e F_{be}C_{ij}^{ae} - P(ij)\sum_m F_{mj}C_{im}^{ab} + \frac{1}{2}\sum_{ef} W_{abef}C_{ij}^{ef} \\
&+ \frac{1}{2}\sum_{mn} W_{mnij}C_{mn}^{ab} + P(ab)P(ij)\sum_{em} W_{bmje}C_{im}^{ae} \\
&- \frac{1}{2}P(ab)\sum_f \left(\sum_{mne} W_{nmfe}C_{mn}^{ea}\right) t_{ij}^{fb} \\
&+ \frac{1}{2}P(ij)\sum_n \left(\sum_{mef} W_{nmfe}C_{im}^{fe}\right) t_{jn}^{ab},
\end{aligned} \tag{2–19}$$

The permutation operator *P(qr)* is defined as

$$P(qr)\xi(\ldots q \ldots r \ldots) = \xi(\ldots q \ldots r \ldots) - \xi(\ldots r \ldots q \ldots) \tag{2–20}$$

F_{pq} and W_{pqrs} are presented elsewhere.[58]

In the partitioned scheme, $\bar{\mathbf{H}}_{\mathrm{DD}}$ is replaced by $\mathbf{H}_{0_{\mathrm{DD}}}$, where H_0 is the usual Møller-Plesset unperturbed Hamiltonian from many-body perturbation theory.[13] In other words, the unfolded matrix analogous to Eq. (2–13) to be diagonalized is approximated by

$$\bar{\mathbf{H}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathrm{SS}} & \bar{\mathbf{H}}_{\mathrm{SD}} \\ \bar{\mathbf{H}}_{\mathrm{DS}} & \mathbf{H}_{0_{\mathrm{DD}}} \end{pmatrix} \tag{2–21}$$

and Eq. (2–19) becomes

$$[\mathbf{H}_{0_{\mathrm{DD}}}\mathbf{C}]_{ij}^{ab} = P(ab)\sum_{e} f_{be}C_{ij}^{ae} - P(ij)\sum_{m} f_{mj}C_{im}^{ab}, \tag{2–22}$$

Here, f_{pq} is the Fock operator. In the case when the reference function is composed of canonical or semi-canonical Hartree-Fock orbitals, $\mathbf{H}_{0_{DD}}$ becomes diagonal with differences of orbital energies on the diagonal. From examining the equations, it is clear that the method is formally an iterative n^5 method, and the results are invariant to rotations among occupied or unoccupied orbitals. This partitioning scheme differs from that presented in Ref. 57 in two ways. Geertsen *et al.*[57] included the full $\bar{H}$ elements on the diagonal instead of just including H_0 elements in the doubles-doubles block, thus destroying the orbital invariance. Also, Geertsen *et al.*[57] did not include the three body terms (the last two terms in Eq. (2–18)) in their work.

After a matrix in the form of Eq. (2–13) has been diagonalized, the eigenvectors consisting of single excitations and double excitations are built. Therefore, the same techniques used to calculate the properties of a full EOM-CCSD wavefunction[58] can be used to calculate properties of the partitioned EOM-CCSD (i.e. P-EOM-CCSD) wavefunction.

Since $\bar{H}$ is not Hermitian, its left and right hand eigenvalues are the same, but the eigenvectors differ.[58] The equations for the left hand side are similar to those presented above.

MBPT[2] Ground State

The first logical perturbative approximation to

$$\begin{aligned}\bar{H} =& e^{-T}He^{T} = (He^{T})_c \\ =& \sum_{pq} F_{pq}\{p^{\dagger}q\} + \sum_{pqrs} W_{pqrs}\{p^{\dagger}q^{\dagger}sr\} + \text{higher order terms}\end{aligned} \tag{2–23}$$

is obtained by keeping only terms through second order. Such an approximation defines an EOM-MBPT[2] method for excited states (i.e. an EOM-CC calculation based on a MBPT[2] ground state instead of a coupled-cluster ground state).[97] If we insist upon a method correct through second-order for the non-Hartree-Fock case, the explicit equations for $\bar{H}^{(2)}$ are

$$F_{ai} = 0, \tag{2–24}$$

$$F_{ab} = f_{ab} + \sum_{m} t_m^a f_{mb} + \sum_{fm} t_m^f \langle ma||fb\rangle - \frac{1}{2}\sum_{emn} t_{mn}^{ae}\langle mn||be\rangle, \tag{2–25}$$

$$F_{ij} = f_{ij} + \sum_{e} t_j^e f_{ie} + \sum_{em} t_m^e \langle im||je\rangle - \frac{1}{2}\sum_{efm} t_{mj}^{ef}\langle im||ef\rangle, \tag{2–26}$$

$$F_{ia} = f_{ia} + \sum_{em} t_m^e \langle im||ae\rangle, \tag{2–27}$$

$$W_{abij} = 0, \tag{2–28}$$

$$W_{ijkl} = \langle ij||kl\rangle + P(kl)\sum_{e} t_l^e \langle ij||ke\rangle + \frac{1}{2}\sum_{ef} t_{kl}^{ef}\langle ij||ef\rangle, \tag{2–29}$$

$$W_{abcd} = \langle ab||cd\rangle - P(ab)\sum_m t_m^b \langle am||cd\rangle + \frac{1}{2}\sum_{mn} t_{mn}^{ab}\langle mn||cd\rangle, \tag{2–30}$$

$$W_{aibc} = \langle ai||bc\rangle - \sum_m t_m^a \langle mi||bc\rangle, \tag{2–31}$$

$$W_{ijka} = \langle jk||ia\rangle + \sum_e t_i^e \langle jk||ea\rangle, \tag{2–32}$$

$$W_{ijab} = \langle ij||ab\rangle, \tag{2–33}$$

$$W_{aijb} = \langle ai||jb\rangle + \sum_e t_j^e\langle ai||eb\rangle - \sum_m t_m^a \langle mi||jb\rangle - \sum_{em} t_{mj}^{ae}\langle mi||eb\rangle, \tag{2–34}$$

$$\begin{aligned} W_{abci} =& \langle ab||ci\rangle - P(ab)\sum_{em} t_{im}^{eb}\langle am||ce\rangle + \frac{1}{2}\sum_{mn} t_{mn}^{ab}\langle ci||mn\rangle \\ &+ \sum_m t_{im}^{ab} f_{mc} + \sum_e t_i^e \langle ab||ce\rangle - P(ab)\sum_m t_m^a \langle mb||ci\rangle, \end{aligned} \tag{2–35}$$

$$\begin{aligned} W_{iajk} =& \langle ia||jk\rangle - P(ij)\sum_{em} t_{mk}^{ae}\langle im||je\rangle + \frac{1}{2}\sum_{ef} t_{jk}^{ef}\langle ia||ef\rangle \\ &+ \sum_e t_{jk}^{ae} f_{ie} + \sum_m t_m^a \langle im||jk\rangle - P(ij)\sum_e t_j^e \langle ia||ek\rangle. \end{aligned} \tag{2–36}$$

In all of these equations t_i^a and t_{ij}^{ab} refer to their values through first order. That is, $t^{[1]a}_{\ i} = \frac{f_{ia}}{\varepsilon_i - \varepsilon_a}$, and $t^{[1]ab}_{\ ij} = \frac{\langle ab||ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$.

Since approximating the excited state with a partitioned EOM-CC calculation and approximating the ground state with a MBPT(2) calculation are independent approximations, we can obviously combine them into a partitioned EOM-MBPT(2) (P-EOM-MBPT(2)) method. When combined, the $\bar{H}$ elements W_{ijkl}, W_{ijab}, and the most numerous, W_{abcd}, are not needed. Therefore, in the Hartree-Fock case, the $\langle ab||cd\rangle$ integrals never need to be calculated. The $\langle ab||cd\rangle$ integrals would contribute to the W_{abci} $\bar{H}$ element multiplied by a $T_1^{[1]}$, but in the Hartree-Fock case all $T_1^{[1]}$'s are zero. A few n^6 terms still remain in the calculation of the $\bar{H}$ elements, but these terms only need to be calculated once. In most calculations the cost of the iterative n^5 step in the excited state calculation will dominate over the n^6 step involved in calculating the $\bar{H}$ elements.

Calculations

Be Atom

Table 2–1 lists energies calculated using the four methods described above (EOM-CCSD, P-EOM-CCSD, EOM-MBPT(2), and P-EOM-MBPT(2)) for the first few singlet excited states in beryllium. The basis set from Ref. 100 was used in the calculations. From the mean absolute errors, it would appear that only the EOM-CCSD calculation is able to reproduce the full CI excitation energies (which are exact within the basis set used). However, if the 1^1D state is excluded from the determination of the mean absolute error, the errors become 0.010 eV for EOM-CCSD, 0.151 eV for P-EOM-CCSD, 0.431 eV for EOM-MBPT(2), and 0.300 eV for P-EOM-MBPT(2). With an approximate excitation level (AEL) value of 1.60, the 1^1D state is dominated by double excitation character. The AEL is a measure of the number of electrons excited in an excitation.[58] A value of 1.00 is a pure single excitation, while 2.00 corresponds to a pure double excitation. Since the doubles-doubles block of the EOM wavefunction is approximated in this partitioned scheme, it is reasonable to expect any state with appreciable double excitation character will be poorly described by this partitioned EOM calculation.

Even with the 1^1D excluded, the calculations based on a MBPT(2) ground state are still very poor. This poor behavior can be ascribed to the inadequacy of the MBPT(2) wavefunction in describing the ground state of Be. In a CCSD calculation the largest T_2 amplitude is 0.065, while the largest $T_2^{[1]}$ amplitude in the MBPT(2) calculation is only 0.034. Also, the MBPT(2) calculation only obtains 73% of the correlation energy recovered by the CCSD calculation. Clearly, MBPT(2) is not adequate to describe the ground state, and any excited state calculation based on that MBPT(2) ground state will suffer accordingly.

In Table 2–2 the first few triplet excited states of beryllium starting from the singlet ground state are presented. Since all of the calculated states are single excitations, the EOM-CCSD method does exceedingly well, while the P-EOM-CCSD also does a good job of describing the states.

Example Molecules

While comparisons with full CI calculations are useful, it is also informative to look at the performance of the methods for more common molecules. These calculations will also provide an opportunity to compare the current methods with other single reference methods used today. Tables 2–3 to 2–6 present calculations on four molecules: formaldehyde, acetaldehyde, ethylene, and butadiene. The calculations are performed at the MP2/6–31G* geometries given in Refs. 101–103. A 6–311(2+,2+)G** basis set[101] is used for formaldehyde and ethylene, with a 6–311(2+)G* basis set[102] being used for acetaldehyde and butadiene. All electrons are correlated except in butadiene, where the first four core orbitals are dropped.

All of the methods presented, except for the CIS-MP2,[75] can be viewed as approximations to the full EOM-CCSD method. TDA (or CIS)[104] is the crudest of the methods in that the excited state is given as a linear combination of single excitations out of a single reference ground state. This method includes no dynamic correlation. CIS(D)[83] provides a non-iterative n^5 perturbation correction to the CIS energy. CIS-MP2 also provides a correction to the CIS energy, but the method is not size-consistent and scales as n^6.[83] The partitioned methods provide an iterative n^5 excited state method based on either a

n^5 ground state (P-EOM-MBPT(2)) or an iterative n^6 ground state (P-EOM-CCSD). The full EOM-CCSD method is an iterative n^6 method.

Except for two differences, our assignment of states agrees with the assignments of Wiberg *et al.* and with the corrected assignments of Head-Gordon *et al.*,[105]. The states have been ordered based on their experimental excitation energies, or, where not available, their EOM-CCSD excitation energies, instead of their CIS excitation energies. Also, Head-Gordon *et al.*[83] had incorrectly assigned the $^1A_1$ EOM-CCSD state at 9.27 eV in formaldehyde to the valence 4^1A_1 state. Based upon the state's properties, including an $<r^2>$ value of 54.4 au^2 (compared to the ground state $<r^2>$ value of 20.5 au^2), the $^1A_1$ EOM-CCSD state has been reassigned to the Rydberg 3^1A_1 state. The 4^1A_1 state (the $\pi^* \leftarrow \pi$ state), with an $<r^2>$ value of 32.6 au^2, has an EOM-CCSD excitation energy of 10.00 eV.

Considering the basis sets and the relatively inexpensive methods used here, these calculations are not meant to be definitive. For previous results on these molecules see the references in Refs. 101–103. Instead, the mean absolute errors of the methods compared to experiment and compared to EOM-CCSD will be used to access the quality of the methods. The mean absolute error for each of the methods with respect to the experimental values given is 0.66 eV for CIS, 0.41 eV for CIS-MP2, 0.32 eV for CIS(D), 0.17 eV for P-EOM-MBPT(2), 0.20 eV for P-EOM-CCSD, and 0.14 eV for the full EOM-CCSD method. Compared to the more complete EOM-CCSD method, the mean absolute errors of the various methods are 0.70 eV for CIS, 0.39 eV for CIS-MP2, 0.35 for CIS(D), 0.12 eV for P-EOM-MBPT(2), and 0.16 eV for P-EOM-CCSD.

As should be expected from its simple nature, TDA performs poorly. The average errors for CIS-MP2 and CIS(D) are similar, although, as previously noted,[83] the CIS-MP2 energies are more erratic. The P-EOM-MBPT(2) and P-EOM-CCSD energies are also similar, seldom differing by 0.1 eV. This suggests that for these cases where MBPT(2) is able to well represent the ground state, P-EOM-MBPT(2) should be able to well describe singly excited states. A balance argument between the ground and excited state would also tend to favor the P-EOM-MBPT(2) method, since the partitioning, as discussed above, can be viewed as a second-order in H perturbation expansion for the excited state.

Looking only at the valence states, as designated by Wiberg *et al.*,[101–103] the mean absolute errors from the EOM-CCSD energies are 0.45 eV for CIS, 0.68 eV for CIS-MP2, 0.33 eV for CIS(D), 0.23 for P-EOM-MBPT(2), and 0.38 eV for P-EOM-CCSD. This is compared to the Rydberg states, where the mean absolute errors from the EOM-CCSD energies are 0.76 eV for CIS, 0.32 eV for CIS-MP2, 0.35 eV for CIS(D), 0.10 for P-EOM-MBPT(2), and 0.11 eV for P-EOM-CCSD. It appears that the partitioned methods on average do not describe valence states as well as they describe Rydberg states. Since orbital relaxation is often greater for valence states, it is possible the reduced relaxation available by approximating the doubles vector might cause larger errors for valence states.

These calculations also give a good chance to measure the time savings of the partitioned method. For example, for butadiene the full EOM-CCSD calculation took 25905 seconds on an IBM RS/6000 model 590 to calculate eighteen excited states (both right and left hand sides). To calculate the same states with the P-EOM-CCSD method took 3998 seconds. These times only include the time for the excited states. P-EOM-

MBPT(2) also saves time in the calculation of the ground state and in the formation of $\bar{H}$, as well as saves disk space.

Conclusions

In this chapter a formalism is presented and results are given for partitioned methods based on the equation-of-motion coupled-cluster theory, where the ground state can be described by either a CCSD or an MBPT(2) wavefunction. The partitioned methods provide an iterative n^5 method (plus an n^6 step for forming $\bar{H}$ elements) for excited states. When the ground state of the system is well described by an MBPT(2) wavefunction, the P-EOM-MBPT(2) method provides an inexpensive way to accurately calculate the energies and properties of singly excited states. For systems less well described by a MBPT(2) wavefunction, the P-EOM-CCSD method is a generally accurate, but more economical, alternative to a full EOM-CCSD calculation. For vertical excitation energies, P-EOM-MBPT(2) is a superior n^5 method to CIS(D).

Table 2–1: Be singlet excitation energies (in eV)

state	AEL[a]	EOM-CCSD	P-EOM-CCSD[b]	EOM-MBPT(2)	P-EOM-MBPT(2)	full CI[c]
1^1P	1.07	5.323	5.666	4.869	5.228	5.318
2^1S	1.06	6.773	6.985	6.329	6.576	6.765
1^1D	1.60	7.139	10.579	6.682	10.170	7.089
2^1P	1.06	7.468	7.653	7.023	7.224	7.462
2^1D	1.21	8.055	7.892	7.618	7.477	8.034
3^1S	1.04	8.084	8.203	7.648	7.788	8.076
3^1P	1.05	8.309	8.432	7.873	8.011	8.302
3^1D	1.09	8.548	8.548	8.115	8.132	8.536
4^1S	1.04	8.583[d]	8.694		8.278	8.600
4^1P	1.04	8.700	8.792	8.267	8.374	8.693
mean abs. error		0.014 (0.010)[e]	0.485 (0.151)[e]	0.428 (0.431)[e]	0.578 (0.300)[e]	

a)Ref. 60. The AEL is for the EOM-CCSD wavefunction.

b)Because of a different implementation of the partitioning, these numbers are slightly different than those in Ref. 57.

c)Ref. 100.

d)Ref. 60.

e)Average error without 1^1D double excited state.

Table 2–2: Be triplet excitation energies (in eV)

state	AEL[a]	EOM-CCSD	P-EOM-CCSD[b]	EOM-MBPT(2)	P-EOM-MBPT(2)	full CI[c]
1^3P	1.01	2.729	2.819	2.271	2.366	2.733
2^3S	1.04	6.447	6.583	5.997	6.140	6.444
2^3P	1.04	7.301	7.424	6.868	7.006	7.295
1^3D	1.04	7.748	7.866	7.316	7.448	7.741
3^3S	1.04	7.991	8.089	7.557	7.668	7.985
4^3P	1.03	8.278	8.366		7.949	8.272
2^3D	1.03	8.456	8.539	8.025	8.121	8.449
4^3S		8.58[d]	8.647		8.228	8.560
5^3P		8.70[d]	8.766		8.348	8.686
mean abs. error		0.008	0.104	0.436	0.321	

a)The AEL is for the EOM-CCSD wavefunction.

b)See footnote b, Table 2–1.

c)Ref. 100.

d)Ref. 59.

Table 2–3: Formaldehyde (energies in eV)

	CIS[a]	CIS-MP2[a]	CIS(D)[b]	P-EOM-MBPT(2)[c]	P-EOM-CCSD[c]	EOM-CCSD	Exp.[a]
1^1A_2(V)	4.48	4.58	3.98	4.31	4.41	3.95[b]	4.07
1^1B_2(R)	8.63	6.85	6.44	7.10	7.10	7.06[b]	7.11
2^1B_2(R)	9.36	7.66	7.26	7.97	7.95	7.89[b]	7.97
2^1A_1(R)	9.66	8.47	8.12	8.02	8.01	8.00[b]	8.14
2^1A_2(R)	9.78	7.83	7.50	8.25	8.23	8.23[b]	8.37
3^1B_2(R)	10.61	8.46	8.21	8.99	8.97	9.07[b]	8.88
1^1B_1(V)	9.66	9.97	9.37	9.61	9.68	9.26[b]	
3^1A_1(R)	10.88	8.75	8.52	9.24	9.21	9.27[c]	
4^1B_2(R)	10.86	8.94	8.63	9.39	9.38	9.40[b]	
4^1A_1(V)	9.45	9.19	8.80	10.08	10.24	10.00[c]	

a)Ref. 102.

b)Ref. 83.

c)Present work.

Table 2–4: Acetaldehyde (energies in eV)

	CIS[a]	CIS-MP2[a]	CIS(D)[b]	P-EOM-MBPT(2)[c]	P-EOM-CCSD[c]	EOM-CCSD	Exp.[a]
1^1A"(V)	4.89	5.27	4.28	4.65	4.71	4.26[b]	4.28
2^1A'(R)	8.51	6.71	6.13	6.88	6.84	6.78[b]	6.82
3^1A'(R)	9.22	7.57	7.04	7.57	7.52	7.49[b]	7.46
2^1A"(R)	9.37	7.37	6.90	7.70	7.64	7.64[b]	
4^1A'(R)	9.30	8.00	7.42	7.77	7.70	7.68[b]	7.75
5^1A'(R)	10.19	8.09	7.70	8.42	8.35	8.39[b]	8.43
6^1A'(R)	10.26	8.08	7.70	8.53	8.47	8.51[b]	8.69
3^1A"(R)	10.31	8.10	7.74	8.58	8.51	8.57[b]	
4^1A"(V)	9.78	10.34	9.34	9.61	9.65	9.23[c]	
7^1A'(V)	9.73	9.07	8.50	9.58	10.07	9.44[c]	

a)Ref. 102.

b)Ref. 83.

c)Present work.

Table 2–5: Ethylene (energies in eV)

	CIS[a]	CIS-MP2[a]	CIS(D)[b]	P-EOM-MBPT(2)[c]	P-EOM-CCSD[c]	EOM-CCSD	Exp.[a]
1^1B_{3u}(R)	7.13	7.52	7.21	7.45	7.51	7.31[b]	7.11
1^1B_{1u}(V)	7.74	8.39	8.04	8.20	8.36	8.14[b]	7.60
1^1B_{1g}(R)	7.71	8.14	7.84	8.08	8.14	7.96[b]	7.80
1^1B_{2g}(R)	7.86	8.12	7.86	8.12	8.18	7.99[b]	8.01
2^1A_g(R)	8.09	8.42	8.18	8.43	8.48	8.34[b]	8.29
2^1B_{3u}(R)	8.63	8.92	8.69	8.95	9.00	8.86[b]	8.62
1^1A_u(R)	8.77	9.00	8.80	9.07	9.12	9.01[b]	
3^1B_{3u}(R)	8.93	9.14	8.96	9.23	9.28	9.18[b]	
2^1B_{1u}(R)	9.09	9.38	9.18	9.42	9.51	9.39[c]	9.33
2^1B_{1g}(R)	9.09	9.31	9.12	9.42	9.48	9.38[c]	9.34

a)Ref. 101.

b)Ref. 83.

c)Present work.

Table 2–6: Butadiene (energies in eV)

	CIS[a]	CIS-MP2[a]	CIS(D)[b]	P-EOM-MBPT(2)[c]	P-EOM-CCSD[c]	EOM-CCSD	Exp.[a]
1^1B_u(V)	6.21	7.00	6.29	6.52	6.63	6.42[b]	5.91
1^1B_g(R)	6.11	6.73	6.11	6.40	6.39	6.20[b]	6.22
1^1A_u(R)	6.45	7.03	6.44	6.72	6.73	6.53[b]	
2^1A_u(R)	6.61	7.11	6.55	6.85	6.84	6.67[b]	6.66
2^1B_u(R)	6.99	7.58	7.03	7.29	7.34	7.17[b]	7.07
2^1B_g(R)	7.22	7.66	7.17	7.47	7.47	7.31[b]	7.36
2^1A_g(R)	7.19	7.74	7.19	7.43	7.44	7.10[b]	7.4
3^1B_g(R)	7.25	7.74	7.24	7.54	7.53	7.39[b]	7.62
4^1B_g(R)	7.39	7.87	7.40	7.70	7.69	7.55[b]	7.72
3^1A_g(R)	7.45	7.88	7.44	7.74	7.73	7.61[b]	
3^1B_u(R)	8.05	8.40	8.01	8.32	8.31	8.21[c]	8.00
3^1A_u(R)	7.78	6.75	7.73	8.07	8.07	7.92[c]	8.18
4^1A_u(R)	7.92	7.66	7.86	8.19	8.18	8.06[c]	8.21

a)Ref. 103.

b)Ref. 83.

c)Present work.

CHAPTER 3
GRADIENTS FOR THE PARTITIONED EQUATION-OF-MOTION MBPT(2) METHOD FOR EXCITED STATES

Introduction

The equation-of-motion coupled-cluster method with single and double excitations for excitation energies (EOM-CCSD)[58, 59] provides an accurate method for calculating the energy and properties of many excited states of molecules. With the development of gradients for EOM-CCSD[90–92] it has become possible to study the excited state potential energy surfaces, just as the development of coupled-cluster gradients for ground state methods[106–109] made routine the study of ground state potential energy surfaces. More recently, Stanton and Gauss have developed second derivatives for EOM-CCSD[110] and gradients for ionization potential EOM-CCSD (IP-EOM-CCSD).[67] The key to all coupled-cluster gradients has been the recognition of how the interchange theorem of Dalgarno and Stewart,[111] initially used by Adamowicz *et al.*[106] and Bartlett[107] for coupled-cluster gradients and sometimes known in quantum chemistry as the Z-vector method,[112] could be used to avoid computing the response of the ground state T amplitudes to each perturbation.

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 $n_{occ}^2 N_{virt}^4$, where n_{occ} stands for the number of orbitals occupied in the reference determinant, and N_{virt} stands for the number of orbitals unoccupied in the reference determinant . These iterative $n_{occ}^2 N_{virt}^4$ steps are calculating the ground state T amplitudes, calculating the right hand eigenvector $\mathcal{R}$, calculating the left hand eigenvector $\mathcal{L}$, and inverting $\bar{H}$ as part of calculating the Z vector.

In the philosophy of replacing ground state cluster amplitudes with second-order perturbation approaches,[113, 96] Stanton and Gauss[97] developed an EOM-CC method based on a $\bar{H}$ 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 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 an non-iterative $n_{occ}(n_{occ} + N_{virt})^4$ step and reduced the cost of inverting $\bar{H}$ to $n_{occ}^2 N_{virt}^2$.[97] However, the iterative $n_{occ}^2 N_{virt}^4$ 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,[114] 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 $n_{occ}^2 N_{virt}^4$ steps in calculating $\mathcal{R}$ and $\mathcal{L}$ arise. In practice this means replacing $\bar{H}$ in the doubles-doubles block with H_0, which is diagonal in the Hartree-Fock case. Thus, the iterative $n_{occ}^2 N_{virt}^4$ steps involved in calculating $\mathcal{R}$ and $\mathcal{L}$ are replaced with iterative $n_{occ}^2 N_{virt}^3$ steps. The overall effect is that the cost is significantly reduced, with little loss in accuracy in vertical excitation energies.[114]

Now, however, the non-iterative $n_{occ}^2 N_{virt}^4$ step involved in calculating $\bar{H}$ elements can also become significant. The point at which the cost of calculating the one $n_{occ}^2 N_{virt}^4$ step in $\bar{H}$ becomes dominant over the cost of calculating the three iterative $n_{occ}^2 N_{virt}^3$ 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 fifteen 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 ninety 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.

Theory

EOM-CC Gradients

Before we beginning with an overview of EOM-CC theory and EOM-CC gradients, it will be helpful to define some notation. Given a set of spin orbitals and a reference determinant $|0\rangle$, the labels *i*, *j*, *k*, . . . represent spin orbitals occupied in $|0\rangle$, the labels *a*, *b*, *c*, . . . represent spin orbitals unoccupied in $|0\rangle$, and the labels *p*, *q*, *r*, . . . represent spin orbitals whose occupation is not specified. The reference determinant is usually, but not necessarily, the 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.[90]

The ground state coupled-cluster equations can be written as

$$\langle 0|\bar{H}|0\rangle = E_{CC}, \tag{3–1}$$

and

$$\langle \mathbf{g}|\bar{H}|0\rangle = 0. \tag{3–2}$$

In pure CC methods (e.g. CCSD or CCSDT), $\bar{H}$ can be written as

$$\bar{H} = e^{-T}He^{T} = \left(He^{T}\right)_c, \tag{3–3}$$

where the subscript *c* indicates that the terms are connected; they share at least one index in common.

$$T = \sum_{i,a} t_i^a \left\{a^\dagger i\right\} + \frac{1}{4}\sum_{\substack{i,j\\a,b}} t_{ij}^{ab}\left\{a^\dagger i b^\dagger j\right\} + \ldots \tag{3–4}$$

is an excitation operator which accounts for the ground state correlation. In the iterative triples methods such as the CCSDT-n methods,[115] or in many-body perturbation theory, $\bar{H}$ does not have such a concise form. Therefore, Eqs. (3–1) and (3–2) will be taken as the defining equations of $\bar{H}$.

It is now possible to write the EOM-CC equations[58] as

$$\langle 0|\mathcal{L}\bar{H}|\mathbf{p}\rangle = E\langle 0|\mathcal{L}|\mathbf{p}\rangle, \tag{3–5}$$

and

$$\langle \mathbf{p}|\bar{H}\mathcal{R}|0\rangle = E\langle \mathbf{p}|\mathcal{R}|0\rangle. \tag{3–6}$$

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

$$\mathcal{L} = l_0 + \sum_{a,i} l_a^i \left\{i^\dagger a\right\} + \frac{1}{4}\sum_{\substack{a,b\\i,j}} l_{ab}^{ij}\left\{i^\dagger a j^\dagger b\right\} + \ldots \tag{3–7}$$

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

$$\mathcal{R} = r_0 + \sum_{i,a} r_i^a \left\{a^\dagger i\right\} + \frac{1}{4}\sum_{\substack{i,j\\a,b}} r_{ij}^{ab}\left\{a^\dagger i b^\dagger j\right\} + \ldots \tag{3–8}$$

is a right eigenvector of $\bar{H}$. It is also possible to include the equation–of–motion in the $\mathcal{R}$ equation. Eq. (3–6) then becomes[59]

$$\langle\mathbf{p}|\big[\bar{H},\mathcal{R}\big]|0\rangle = \omega\langle\mathbf{p}|\mathcal{R}|0\rangle, \tag{3–9}$$

where

$$\omega = E - E_{CC} \tag{3–10}$$

is the excitation energy.

It can be seen that in EOM-CC the excited states are the 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 do form a biorthogonal set. Choosing the norm of the excited state vectors to be one gives that

$$\langle 0|\mathcal{L}_j\mathcal{R}_k|0\rangle = \delta_{jk} \tag{3–11}$$

for all states *j* and *k*. Therefore, from either Eq. (3–5) or (3–6) we can get an expression for the excited state energy

$$E = \langle 0|\mathcal{L}\bar{H}\mathcal{R}|0\rangle. \tag{3–12}$$

When Stanton first derived the equations for EOM-CC gradients,[90] he followed the same development as that of Refs. 106, 107, 109 by taking the derivative of Eq. (3–12) 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 excited state perturbation on the ground state *T* amplitudes. Since $\mathcal{L}$ and R are eigenvectors for the excited state, they are variationally optimum and therefore stationary with respect to the perturbation. On the other hand, T is never stationary (even for the ground state), and another operator must be included to account for its response.

Szalay[94] then used the approach of a general functional analogous to the Λ functional in ground state coupled-cluster theory[14, 116] by introducing Z to force T to be stationary with respect to the external perturbation. Following this approach, here is introduced an EOM-CC functional which has the property that all quantities are stationary, and therefore the functional will satisfy the generalized Hellmann-Feynman theorem.[117, 118] Such a functional is

$$F = \langle 0|\mathcal{L}\bar{H}\mathcal{R}|0\rangle + \langle 0|\mathrm{Z}\bar{H}|0\rangle + E(1 - \langle 0|\mathcal{L}\mathcal{R}|0\rangle). \tag{3–13}$$

By construction

$$\mathrm{Z} = \sum_{a,i} \zeta_a^i \left\{ i^\dagger a \right\} + \frac{1}{4} \sum_{\substack{a,b \\ i,j}} \zeta_{ab}^{ij} \left\{ i^\dagger a j^\dagger b \right\} + \ldots \tag{3–14}$$

is a pure deexcitation operator of rank equal to T. Since the last two terms of Eq. (3–13) 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. (3–13) and setting them equal to zero, the EOM-CC gradient equations will be recovered. For example,

$$\frac{\partial F}{\partial E} = 0 = 1 - \langle 0|\mathcal{L}\mathcal{R}|0\rangle \tag{3–15}$$

is a restatement of Eq. (3–11), the normalization condition for $\mathcal{L}$ and R. Taking the derivative of the functional with respect to R ($\mathcal{L}$) gives Eq. (3–5) (Eq. (3–6)), which is the equation for $\mathcal{L}$ (R). Taking the derivative of the functional with respect to Z gives Eq. (3–2), which is the ground state T equation.

However, taking the derivative of the functional with respect to *T* is much 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 will be assumed a pure EOM-CC method (e.g. EOM-CCSD, EOM-CCSDT, ...). When the derivative with respect to one of the operators is taken, $\mathcal{L}$, R, *T*, or Z, what is really being done is separately taking the derivative with respect to every coefficient in the operator. For example, $\frac{\partial}{\partial T}$ really means $\frac{\partial}{\partial t}$ for all *t* amplitudes in *T*. This still leaves the excitation or deexcitation part of the operator. So when $\frac{\partial \bar{H}}{\partial T}$ is taken as a part of getting $\frac{\partial F}{\partial T}$, what results is

$$\begin{aligned} \frac{\partial \bar{H}}{\partial T} &= -\Omega_T e^{-T} H e^{T} + e^{-T} H e^{T} \Omega_T \\ &= \left[\bar{H}, \Omega_T\right]. \end{aligned} \tag{3–16}$$

Here

$$\Omega_T = \sum_{i,a} \left\{a^\dagger i\right\} + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} \left\{a^\dagger i b^\dagger j\right\} + \dots \tag{3–17}$$

is the pure excitation operator without any coefficients. Therefore,

$$\frac{\partial F}{\partial T} = 0 = \langle 0|\mathcal{L}\left[\bar{H}, \Omega_T\right]\mathcal{R}|0\rangle + \langle 0|\mathrm{Z}\left[\bar{H}, \Omega_T\right]|0\rangle. \tag{3–18}$$

After significant simplification, Eq. (3–18) reduces to

$$\langle 0|\mathrm{Z}|\mathbf{g}\rangle = \langle 0|\mathcal{L}\bar{H}|\mathbf{q}\rangle\langle \mathbf{q}|\mathcal{R}|\mathbf{g}\rangle\left(\langle \mathbf{g}|\left(E_{CC}\mathbf{1} - \bar{H}\right)|\mathbf{g}\rangle\right)^{-1}, \tag{3–19}$$

where **1** stands for a unit matrix of rank $|\mathrm{g}\rangle$. This is exactly equivalent to the equation for Z in Ref. 90.

Finally, since the functional satisfies the generalized Hellmann-Feynman theorem, for any perturbation χ

$$\frac{\partial F}{\partial \chi} = \frac{\partial E}{\partial \chi} = \langle 0|\mathcal{L}\bar{H}^{\chi}\mathcal{R}|0\rangle + \langle 0|\mathrm{Z}\bar{H}^{\chi}|0\rangle. \tag{3–20}$$

Here, $\bar{H}^{\chi}$ represents the derivative of the bare Hamiltonian elements with respect to the perturbation χ within the similarity transformed Hamiltonian $\bar{H}$. For the pure EOM-CC methods this means

$$\bar{H}^{\chi} = e^{-T}\frac{\partial H}{\partial \chi}e^{T}. \tag{3–21}$$

Eq. (3–20) is the same as Eq. (36) of Ref. 90. Although the form of the functional was simply postulated, the fact that it produces equations (and therefore density matrices) identical to those produced through straightforward derivation of the energy expression[90] proves that the functional is valid. For a discussion of the properties of the density matrices resulting from these equations, see Ref. 119.

It is also possible to derive an energy expression from Eq. (3–9). Projecting on the left by $\langle 0|\mathcal{L}|\mathbf{p}\rangle$ gives the expression

$$E = \langle 0|\mathcal{L}\big[\bar{H}, \mathcal{R}\big]|0\rangle + \langle 0|\bar{H}|0\rangle, \tag{3–22}$$

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

$$F = \langle 0|\mathcal{L}\big[\bar{H}, \mathcal{R}\big]|0\rangle + \langle 0|\bar{H}|0\rangle + \langle 0|\mathrm{Z}\bar{H}|0\rangle + \omega(1 - \langle 0|\mathcal{L}\mathcal{R}|0\rangle). \tag{3–23}$$

Superficially, Eqs. (3–13) and (3–23) appear similar. In fact, Eq. (3–22) can be straightforwardly derived from Eq. (3–12), and both functionals have the same value, the total energy *E*. However, these energy functionals contain several important differences. The first is that ω, the excitation energy, appears on the right instead of *E*. More importantly, though, the equations for and value of Z have changed. This will seen later, but first it is important to see that the EOM-CC equations are still contained in the new functional.

As before, the derivative of each of the quantities on the right hand side of the functional will be taken and set to zero. First,

$$\frac{\partial F}{\partial \omega} = 0 = 1 - \langle 0|\mathcal{L}\mathcal{R}|0\rangle \tag{3–24}$$

again gives the normalization condition for $\mathcal{L}$ and R.

$$\frac{\partial F}{\partial \mathrm{Z}} = 0 = \langle \mathbf{g}|\bar{H}|0\rangle \tag{3–25}$$

again gives the coupled-cluster equations.

Next, taking the derivative of the functional with respect to $\mathcal{L}$ gives

$$\frac{\partial F}{\partial \mathcal{L}} = 0 = \langle \mathbf{p}|\left[\bar{H}, \mathcal{R}\right]|0\rangle - \omega\langle \mathbf{p}|\mathcal{R}|0\rangle, \tag{3–26}$$

which is equivalent to Eq. (3–9). Expanding the commutator gives

$$\omega\langle \mathbf{p}|\mathcal{R}|0\rangle = \langle \mathbf{p}|\bar{H}\mathcal{R}|0\rangle - \langle \mathbf{p}|\mathcal{R}\bar{H}|0\rangle. \tag{3–27}$$

Inserting a resolution of the identity $|\mathbf{h}\rangle\langle\mathbf{h}|$ into the last term gives

$$\begin{aligned}\omega\langle \mathbf{p}|\mathcal{R}|0\rangle &= \langle \mathbf{p}|\bar{H}\mathcal{R}|0\rangle - \langle \mathbf{p}|\mathcal{R}|\mathbf{q}\rangle\langle \mathbf{q}|\bar{H}|0\rangle \\ &\qquad - \langle \mathbf{p}|\mathcal{R}|\mathbf{g}\rangle\langle \mathbf{g}|\bar{H}|0\rangle - \langle \mathbf{p}|\mathcal{R}|0\rangle\langle 0|\bar{H}|0\rangle \\ &= \langle \mathbf{p}|\bar{H}\mathcal{R}|0\rangle - \langle \mathbf{p}|\mathcal{R}|0\rangle E_{CC},\end{aligned} \tag{3–28}$$

or

$$(E_{CC} + \omega)\langle \mathbf{p}|\mathcal{R}|0\rangle = \langle \mathbf{p}|\bar{H}\mathcal{R}|0\rangle. \tag{3–29}$$

The third term in the first equality of Eq. (3–28) disappears because of the solution of the coupled-cluster equations. The second term in the first equality of Eq. (3–28) disappears because R, being an excitation operator, can never decrease the excitation level. Thus it cannot have any non-vanishing terms between $\langle \mathbf{p}|$ and $|\mathbf{q}\rangle$. Note that Eq. (3–29) is equivalent to Eq. (3–6).

Taking the derivative of the functional with respect to R gives

$$\frac{\partial F}{\partial \mathcal{R}} = 0 = \langle 0|\mathcal{L}\big[\bar{H}, \Omega_{\mathcal{R}}\big]|0\rangle - \omega\langle 0|\mathcal{L}\Omega_{\mathcal{R}}|0\rangle. \tag{3–30}$$

In analogy to Ω_T above, $\Omega_{\mathcal{R}}$ is the excitation part of the operator R without any coefficients. The difference is that Ω_T acting on $|0\rangle$ gives $|\mathbf{g}\rangle$, while $\Omega_{\mathcal{R}}$ acting on $|0\rangle$ gives $|\mathbf{p}\rangle$, since $\Omega_{\mathcal{R}}$ contains a constant part and Ω_T does not. Rewriting Eq. (3–30) gives

$$\omega\langle 0|\mathcal{L}|\mathbf{p}\rangle = \langle 0|\mathcal{L}\bar{H}\Omega_{\mathcal{R}}|0\rangle - \langle 0|\mathcal{L}\Omega_{\mathcal{R}}\bar{H}|0\rangle. \tag{3–31}$$

Inserting a resolution of the identity into the last term gives

$$\begin{aligned}\omega\langle 0|\mathcal{L}|\mathbf{p}\rangle &= \langle 0|\mathcal{L}\bar{H}|\mathbf{p}\rangle - \langle 0|\mathcal{L}\Omega_{\mathcal{R}}|0\rangle\langle 0|\bar{H}|0\rangle - \langle 0|\mathcal{L}\Omega_{\mathcal{R}}|\mathbf{p}\rangle\langle \mathbf{p}|\bar{H}|0\rangle \\ &\quad - \langle 0|\mathcal{L}\Omega_{\mathcal{R}}|\mathbf{q}\rangle\langle \mathbf{q}|\bar{H}|0\rangle \\ &= \langle 0|\mathcal{L}\bar{H}|\mathbf{p}\rangle - \langle 0|\mathcal{L}|\mathbf{p}\rangle E_{CC},\end{aligned} \tag{3–32}$$

or

$$(\omega + E_{CC})\langle 0|\mathcal{L}|\mathbf{p}\rangle = \langle 0|\mathcal{L}\bar{H}|\mathbf{p}\rangle. \tag{3–33}$$

This is simply Eq. (3–5). The third term in the top equality of Eq. (3–32) disappears because of the solution of the coupled-cluster equations. The last term in top equality of Eq. (3–32) disappears because $\Omega_{\mathcal{R}}$ acting on $|\mathbf{q}\rangle$ gives back $|\mathbf{q}\rangle$, and $\mathcal{L}$ cannot give non-vanishing terms between $\langle 0|$ and $|\mathbf{q}\rangle$.

For the Zeta equations a pure EOM-CC method will again be assumed. Taking the derivative of the functional with respect to T gives

$$\begin{aligned}\frac{\partial F}{\partial T} = 0 &= \langle 0|\mathcal{L}\big[\big[\bar{H}, \Omega_T\big], \mathcal{R}\big]|0\rangle + \langle 0|\big[\bar{H}, \Omega_T\big]|0\rangle + \langle 0|\mathrm{Z}\big[\bar{H}, \Omega_T\big]|0\rangle \\ &= \langle 0|\mathcal{L}\big[\bar{H}, \Omega_T\big]\mathcal{R}|0\rangle - \langle 0|\mathcal{L}\mathcal{R}\big[\bar{H}, \Omega_T\big]|0\rangle + \langle 0|\big[\bar{H}, \Omega_T\big]|0\rangle \\ &\quad + \langle 0|\mathrm{Z}\big[\bar{H}, \Omega_T\big]|0\rangle.\end{aligned} \tag{3–34}$$

Notice that the first and last terms are the same as Eq. (3–18). Expanding the commutators and inserting resolutions of the identity gives

$$\begin{aligned} 0 =&\langle 0|\mathcal{L}\bar{H}|\mathbf{q}\rangle\langle\mathbf{q}|\Omega_T\mathcal{R}|0\rangle + \langle 0|\mathcal{L}\bar{H}|\mathbf{p}\rangle\langle\mathbf{p}|\Omega_T\mathcal{R}|0\rangle - \langle 0|\mathcal{L}\Omega_T|\mathbf{q}\rangle\langle\mathbf{q}|\bar{H}\mathcal{R}|0\rangle \\ &- \langle 0|\mathcal{L}\Omega_T|\mathbf{p}\rangle\langle\mathbf{p}|\bar{H}\mathcal{R}|0\rangle - \langle 0|\mathcal{L}\mathcal{R}|\mathbf{q}\rangle\langle\mathbf{q}|\big[\bar{H},\Omega_T\big]|0\rangle \\ &- \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\big[\bar{H},\Omega_T\big]|0\rangle - \langle 0|\mathcal{L}\mathcal{R}|0\rangle\langle 0|\big[\bar{H},\Omega_T\big]|0\rangle + \langle 0|\big[\bar{H},\Omega_T\big]|0\rangle \\ &+ \langle 0|\mathrm{Z}|\mathbf{q}\rangle\langle\mathbf{q}|\bar{H}\Omega_T|0\rangle + \langle 0|\mathrm{Z}|\mathbf{g}\rangle\langle\mathbf{g}|\bar{H}\Omega_T|0\rangle + \langle 0|\mathrm{Z}|0\rangle\langle 0|\bar{H}\Omega_T|0\rangle \\ &- \langle 0|\mathrm{Z}\Omega_T|\mathbf{q}\rangle\langle\mathbf{q}|\bar{H}|0\rangle - \langle 0|\mathrm{Z}\Omega_T|\mathbf{g}\rangle\langle\mathbf{g}|\bar{H}|0\rangle - \langle 0|\mathrm{Z}\Omega_T|0\rangle\langle 0|\bar{H}|0\rangle. \end{aligned} \tag{3–35}$$

The third, fifth, and twelfth term disappear for the same reason that the $\langle 0|\mathcal{L}\Omega_{\mathcal{R}}|\mathbf{q}\rangle$ disappeared above. Since the norm is chosen to be one, the seventh and eighth terms cancel. The ninth and eleventh terms disappear since Z cannot connect $\langle 0|$ to either $|0\rangle$ or $|\mathbf{q}\rangle$. The thirteenth term disappears because of the solution of the coupled-cluster equations. Eqs. (3–5) and (3–6) can be used to simplify the second and fourth terms. Doing this gives

$$\begin{aligned} 0 =&\langle 0|\mathcal{L}\bar{H}|\mathbf{q}\rangle\langle\mathbf{q}|\mathcal{R}|\mathbf{g}\rangle + E\langle 0|\mathcal{L}|\mathbf{p}\rangle\langle\mathbf{p}|\Omega_T\mathcal{R}|0\rangle - E\langle 0|\mathcal{L}\Omega_T|\mathbf{p}\rangle\langle\mathbf{p}|\mathcal{R}|0\rangle \\ &- \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\bar{H}\Omega_T|0\rangle + \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\Omega_T|\mathbf{q}\rangle\langle\mathbf{q}|\bar{H}|0\rangle \\ &+ \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\Omega_T|\mathbf{g}\rangle\langle\mathbf{g}|\bar{H}|0\rangle + \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\Omega_T|0\rangle\langle 0|\bar{H}|0\rangle \\ &+ \langle 0|\mathrm{Z}|\mathbf{g}\rangle\langle\mathbf{g}|\bar{H}|\mathbf{g}\rangle - \langle 0|\mathrm{Z}|\mathbf{g}\rangle E_{CC}. \end{aligned} \tag{3–36}$$

The fact that R and Ω_T, both being excitation operators, commute has been used. Since R acting on $|0\rangle$ only connects with $\langle\mathbf{p}|$ and since $\mathcal{L}$ acting on $\langle 0|$ only connects with $|\mathbf{p}\rangle$, the second and third terms cancel. The fifth term disappears since Ω_T cannot connect $\langle\mathrm{g}|$ to $|\mathbf{q}\rangle$. The sixth term disappears because of the solution of the coupled-cluster equations. Finally, the Zeta equation becomes

$$\begin{aligned} \langle 0|\mathrm{Z}|\mathbf{g}\rangle\langle\mathbf{g}|\big(E_{CC}\mathbf{1} - \bar{H}\big)|\mathbf{g}\rangle =&\langle 0|\mathcal{L}\bar{H}|\mathbf{q}\rangle\langle\mathbf{q}|\mathcal{R}|\mathbf{g}\rangle \\ &+ \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle\langle\mathbf{g}|\big(E_{CC}\mathbf{1} - \bar{H}\big)|\mathbf{g}\rangle, \end{aligned} \tag{3–37}$$

or

$$\langle 0|\mathrm{Z}|\mathbf{g}\rangle = \langle 0|\mathcal{L}\bar{H}|\mathbf{q}\rangle\langle\mathbf{q}|\mathcal{R}|\mathbf{g}\rangle\big(\langle\mathbf{g}|\big(E_{CC}\mathbf{1} - \bar{H}\big)|\mathbf{g}\rangle\big)^{-1} + \langle 0|\mathcal{L}\mathcal{R}|\mathbf{g}\rangle. \tag{3–38}$$

The first term in Eq. (3–38) is the same as Eq. (3–19). However, the second term is new.

The expression for the energy derivative corresponding to this functional is

$$\frac{\partial E}{\partial \chi} = \langle 0|\mathcal{L}\big[\bar{H}^{\chi}, \mathcal{R}\big]|0\rangle + \langle 0|\bar{H}^{\chi}|0\rangle + \langle 0|\mathrm{Z}\bar{H}^{\chi}|0\rangle. \tag{3–39}$$

In fact, this equation and Eq. (3–20) produce the same density matrices. In the first term of Eq. (3–20) $\bar{H}^{\chi}$ and $\mathcal{R}$ are not required to be connected, as they are in Eq. (3–39). Those disconnected term can be divided up into two categories. In the first, $\mathcal{L}$ is connected to only $\mathcal{R}$. When all such terms are added up, the norm can be factored out, leaving the second term of Eq. (3–39). The other category is when $\mathcal{L}$ is connected to $\bar{H}^{\chi}$. These terms lead to the extra term in Eq. (3–38).

It is important to note that the two different functionals have different equations for Z, but since they give the same density matrices, either may be used. Therefore, the operator Z is not unique, but only has meaning within the context of its functional.

To better understand the differences between the functionals, let us examine how the ground state fits into each. In EOM-CC theory, the ground state is just an eigenstate of $\bar{H}$ with the special property that $\mathcal{R} = 1$, and $\mathcal{L} = 1 + \Lambda$, where Λ, a pure deexcitation operator, is the usual Λ from coupled-cluster theory.[107] Substituting these values into the first functional gives

$$F = \langle 0|(1 + \Lambda)\bar{H}|0\rangle, \tag{3–40}$$

the usual ground state functional. In this functional Z for the ground state is zero. This can be seen from Eq. (3–19), where the constant operator 1 cannot connect $\langle \mathbf{q}|$ and $|\mathbf{g}\rangle$. These give for the energy derivative, Eq. (3–20),

$$\frac{\partial E}{\partial \chi} = \langle 0|(1+\Lambda)\bar{H}^{\chi}|0\rangle, \qquad (3\text{–}41)$$

again the usual coupled-cluster expression.

For the second functional the picture is somewhat more complicated. Substituting the appropriate values for $\mathcal{R}$ and $\mathcal{L}$ into Eq. (3–38) gives that $\langle 0|\mathrm{Z}|\mathbf{g}\rangle = \langle 0|(1+\Lambda)1|\mathbf{g}\rangle = \langle 0|\Lambda|\mathbf{g}\rangle$. In other words, Z for the ground state in the second functional is Λ. But in this case, $\mathcal{R}$ for the ground state, a constant operator, gives zero for the commutators in the first terms of Eqs. (3–23) and (3–39). So the usual coupled-cluster expressions, Eqs. (3–40) and (3–41), are still obtained.

The above equations derived from the second functional have a small computational advantage over those derived from the first functional. Specifically, the second Zeta equation suggests a simpler way to calculate some of the terms in the density matrix equations. Stanton and Gauss[92] suggest combining Z and $r_0\mathcal{L}$ into a composite operator, and using this new operator in a ground state coupled-cluster gradient code to calculate many of the excited state density matrix contributions. The approach presented here suggests including all of $\langle 0|\mathcal{L}\mathcal{R}|\mathrm{g}\rangle$ into the composite operator, reducing even further the number of terms which would need to be calculated separately. In practice, this should make very little difference in terms of how long a calculation takes. However, it should make programming somewhat easier.

It is possible to derive a third Z equation. Starting with the first line of Eq. (3–34) and not breaking the commutators gives

$$\langle 0|\mathrm{Z}|\mathbf{g}\rangle = \Big(\langle 0|\mathcal{L}\big[\big[\bar{H},\mathcal{R}\big],\Omega_T\big]|0\rangle + \langle 0|\big[\bar{H},\Omega_T\big]|0\rangle\Big)\Big(\langle\mathbf{g}|\big(E_{CC}\mathbf{1}-\bar{H}\big)|\mathbf{g}\rangle\Big)^{-1}. \tag{3–42}$$

In the first term $\bar{H}$ must be connected to both $\mathcal{R}$ and Ω_T, while in the second term $\bar{H}$ is connected to just Ω_T, but $\mathcal{R}$ and $\mathcal{L}$ cannot appear. In diagrammatic language saying that $\bar{H}$ is connected to Ω_T is equivalent to saying that at least one of the lines from $\bar{H}$ must be dangling from the bottom.

Since the second and third Z equations were derived starting from the same place, they must be equivalent. For EOM-CCSD the third Z equation has two more diagrams than the first Z equation. None of the diagrams where the two differ would change the overall computational scaling of the method.

P-EOM-MBPT(2) Gradients

The defining equations for P-EOM-MBPT(2) are identical to Eqs. (3–4) and (3–5), but with a modified $\bar{H}$. Detailed equations for $\bar{H}$, $\mathcal{R}$, and $\mathcal{L}$ have been given previously.[114] For (non-partitioned) EOM-MBPT(2) the functional is[97]

$$\begin{aligned} F =& \Big\langle 0 \,\Big|\, \mathcal{L}\Big[\Big(H^{[0]} + H^{[1]} + H^{[1]}T^{[1]}\Big)\mathcal{R}\Big]_c \,\Big|\, 0\Big\rangle \\ &+ \Big\langle 0 \,\Big|\, H^{[0]} + H^{[1]} + \Big(H^{[1]}T^{[1]}\Big)_c \,\Big|\, 0\Big\rangle \\ &+ \Big\langle 0 \,\Big|\, \mathrm{Z}\Big[\Big(H^{[0]} - E^0\Big)T^{[1]} + H^{[1]}\Big] \,\Big|\, 0\Big\rangle \\ &+ E\Big(1 - \Big\langle 0 \,\Big|\, \mathcal{L}\mathcal{R} \,\Big|\, 0\Big\rangle\Big). \end{aligned} \tag{3–43}$$

The *c* means that the operators are connected; they share at least one index. Here, the usual many-body perturbation theory partitioning of the Hamiltonian is assumed. $H^{[n]}$

is the nth order term of the Hamiltionian, and $T^{[n]}$ is the nth order T amplitude from many-body perturbation theory. For P-EOM-MBPT(2) the functional becomes

$$\begin{aligned} F =& \Big\langle 0 \Big| (\mathcal{L}_1 + \mathcal{L}_2)\Big[\Big(H^{[0]} + H^{[1]} + H^{[1]}T^{[1]}\Big)\mathcal{R}_1\Big]_c \Big| 0 \Big\rangle \\ &+ \Big\langle 0 \Big| \mathcal{L}_1\Big[\Big(H^{[0]} + H^{[1]} + H^{[1]}T^{[1]}\Big)\mathcal{R}_2\Big]_c \Big| 0 \Big\rangle \\ &+ \Big\langle 0 \Big| \mathcal{L}_2\Big(H^{[0]}\mathcal{R}_2\Big)_c \Big| 0 \Big\rangle \\ &+ \Big\langle 0 \Big| H^{[0]} + H^{[1]} + \Big(H^{[1]}T^{[1]}\Big)_c \Big| 0 \Big\rangle \\ &+ \Big\langle 0 \Big| \mathrm{Z}\Big[\Big(H^{[0]} - E^{[0]}\Big)T^{[1]} + H^{[1]}\Big] \Big| 0 \Big\rangle \\ &+ E\Big(1 - \Big\langle 0 \Big| \mathcal{L}\mathcal{R} \Big| 0 \Big\rangle\Big). \end{aligned} \tag{3–44}$$

This form of the Zeta operator comes from the defining equation for the $T^{[1]}$ amplitudes, which is

$$\Big\langle \mathbf{g} \Big| \Big(H^{[0]} - E^{[0]}\Big)T^{[1]} + H^{[1]} \Big| 0 \Big\rangle = 0. \tag{3–45}$$

For the rest of the paper it will be assumed that the reference determinant is the Hartree-Fock solution. In this case,

$$H^{[0]} = \sum_i \varepsilon_i \Big\{ i^\dagger i \Big\} + \sum_a \varepsilon_a \Big\{ a^\dagger a \Big\}, \tag{3–46}$$

and

$$\begin{aligned} H^{[1]} &= H - H^{[0]} \\ &= \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \Big\{ p^\dagger q^\dagger s r \Big\}. \end{aligned} \tag{3–47}$$

Also,

$$T^{[1]} = \frac{1}{4} \sum_{\substack{i,j\\a,b}} t_{ij}^{ab[1]} \Big\{ a^\dagger i b^\dagger j \Big\}, \tag{3–48}$$

where

$$t_{ij}^{ab[1]} = \frac{\langle ab||ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \tag{3–49}$$

Since $T^{[1]}$ is now a double excitation operator, $\left\langle 0 \,\middle|\, \mathcal{L}_1 \left[H^{[1]} T^{[1]} \mathcal{R}_2\right]_c \,\middle|\, 0 \right\rangle$ must vanish, and the functional is slightly simpler. Another consequence of $T^{[1]}$ being a pure double excitation is that Z consists only of double deexcitation operators.

Taking derivatives of the (simplified) Eq. (3–44) gives the equations for the gradients. It can be shown that taking derivatives with respect to the various $\mathcal{R}$ and $\mathcal{L}$ operators recovers the energy expression. Again, by construction, taking the derivative with respect to Z recovers the $T^{[1]}$ equation. Finally, taking the derivative with respect to $T^{[1]}$ gives

$$\begin{aligned} \frac{\partial F}{\partial T^{[1]}} = 0 = &\left\langle 0 \,\middle|\, \mathcal{L}\left(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}}\right)_c \,\middle|\, 0 \right\rangle + \left\langle 0 \,\middle|\, H^{[1]} \,\middle|\, \mathbf{d} \right\rangle \\ &+ \left\langle 0 \,\middle|\, \mathrm{Z}\left(H^{[0]} - E^{[0]}\right) \,\middle|\, \mathbf{d} \right\rangle. \end{aligned} \tag{3–50}$$

Here, $\Omega_{\mathbf{d}} = \frac{1}{4} \sum\limits_{i,j,a,b} \left\{a^\dagger i b^\dagger j\right\}$ is the pure doubles excitation operator. The fact that $\mathcal{R}$ commutes with $\Omega_{\mathbf{d}}$ has been used. Solving for Z gives

$$\begin{aligned} \left\langle 0 \,\middle|\, \mathrm{Z} \,\middle|\, \mathbf{d} \right\rangle = &\left\{ \left\langle 0 \,\middle|\, \mathcal{L}\left(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}}\right)_c \,\middle|\, 0 \right\rangle + \left\langle 0 \,\middle|\, H^{[1]} \,\middle|\, \mathbf{d} \right\rangle \right\} \\ &\times \left(\left\langle \mathbf{d} \,\middle|\, \left(E^{[0]} \mathbf{1} - H^{[0]}\right) \,\middle|\, \mathbf{d} \right\rangle \right)^{-1}. \end{aligned} \tag{3–51}$$

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

$$\begin{aligned} \Xi &= \frac{1}{4} \sum_{\substack{a,b \\ i,j}} \xi_{ab}^{ij} \left\{ i^\dagger a j^\dagger b \right\} \\ &= \left\langle 0 \,\middle|\, \mathcal{L}\left(H^{[1]} \mathcal{R}_1 \Omega_{\mathbf{d}}\right)_c \,\middle|\, 0 \right\rangle + \left\langle 0 \,\middle|\, H^{[1]} \,\middle|\, \mathbf{d} \right\rangle. \end{aligned} \tag{3–52}$$

Computationally, to solve for Z, Ξ must first be calculated and then the denominator applied.

Now the derivative can be rewritten as

$$\begin{aligned}\frac{\partial E}{\partial\chi}=\frac{\partial F}{\partial\chi}=&\Big\langle 0\,\Big|\,(\mathcal{L}_1+\mathcal{L}_2)\left[\left(\frac{\partial H^{[0]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}T^{[1]}\right)\mathcal{R}_1\right]_c\,\Big|\,0\Big\rangle\\&+\Big\langle 0\,\Big|\,\mathcal{L}_1\left[\left(\frac{\partial H^{[0]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}T^{[1]}\right)\mathcal{R}_2\right]_c\,\Big|\,0\Big\rangle\\&+\Big\langle 0\,\Big|\,\mathcal{L}_2\Big(H^{[0]}\mathcal{R}_2\Big)_c\,\Big|\,0\Big\rangle\\&+\Big\langle 0\,\Big|\,\frac{\partial H^{[0]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}+\frac{\partial H^{[1]}}{\partial\chi}T^{[1]}\,\Big|\,0\Big\rangle\\&+\Big\langle 0\,\Big|\,\mathrm{Z}\left(\frac{\partial H^{[0]}}{\partial\chi}T^{[1]}+\frac{\partial H^{[1]}}{\partial\chi}\right)\,\Big|\,0\Big\rangle.\end{aligned}\tag{3–53}$$

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;

$$\frac{\partial E}{\partial x}=\rho^p_q\frac{\partial f_{pq}}{\partial\chi}+\rho^{pq}_{rs}\frac{\partial\langle pq||rs\rangle}{\partial\chi}.\tag{3–54}$$

Explicit spin orbital equations for the effective density matrix elements in terms of $\mathcal{R}$, $\mathcal{L}$, $T^{[1]}$, and Z are

$$\rho^i_j=-\sum_e l^i_e r^e_j-\frac{1}{2}\sum_{m,e,f}\zeta^{im}_{ef}t^{ef}_{jm}+\delta_{ij},\tag{3–55}$$

$$\rho^a_b=\sum_b l^m_b r^a_m+\frac{1}{2}\sum_{m,n,a}\zeta^{mn}_{be}t^{ae}_{mn},\tag{3–56}$$

$$\rho^a_i=-\frac{1}{2}\sum_{m,n,e,f}l^{mn}_{ef}r^f_i t^{ea}_{mn}-\frac{1}{2}\sum_{m,n,e,f}l^{mn}_{ef}r^a_n t^{ef}_{mi}+\sum_{m,e}l^m_e r^{ae}_{im},\tag{3–57}$$

$$\rho^i_a=0,\tag{3–58}$$

$$\rho^{ij}_{kl}=\frac{1}{4}P_-(ij)P_-(kl)\delta_{ik}\delta_{jl},\tag{3–59}$$

$$\rho^{ij}_{ka}=-\frac{1}{4}\sum_e l^{ij}_{ea}r^e_k,\tag{3–60}$$

$$\begin{aligned}\rho^{ia}_{jk} =& -\frac{1}{4}\sum_{e} l^{i}_{e} r^{ea}_{jk} + \frac{1}{4}P_{-}(jk)\sum_{m,e,f} l^{im}_{ef} r^{f}_{k} t^{ea}_{jm} + \frac{1}{8}\sum_{m,e,f} l^{im}_{ef} r^{a}_{m} t^{ef}_{jk} \\ & -\frac{1}{8}P_{-}(jk)\sum_{m,e,f} l^{im}_{ef} r^{a}_{k} t^{ef}_{jm},\end{aligned} \tag{3–61}$$

$$\rho^{ia}_{bj} = -\frac{1}{16}P_{-}(ij)P_{-}(ab) l^{i}_{b} r^{a}_{j}, \tag{3–62}$$

$$\begin{aligned}\rho^{ab}_{ci} =& \frac{1}{4}\sum_{m} l^{m}_{e} r^{ba}_{im} - \frac{1}{4}P_{-}(ab)\sum_{m,n,e} l^{mn}_{ec} r^{b}_{m} t^{ea}_{in} - \frac{1}{8}\sum_{m,n,e} l^{mn}_{ec} r^{e}_{i} t^{ba}_{mn} \\ & + \frac{1}{8}P_{-}(ab)\sum_{m,n,e} l^{mn}_{ec} r^{b}_{i} t^{ea}_{mn},\end{aligned} \tag{3–63}$$

$$\rho^{ai}_{bc} = \frac{1}{4}\sum_{m} l^{mi}_{bc} r^{a}_{m}, \tag{3–64}$$

$$\begin{aligned}\rho^{ij}_{ab} =& \frac{1}{4}t^{ab}_{ij} - \frac{1}{4}P_{-}(ij)\sum_{m,e} l^{m}_{e} r^{e}_{i} t^{ab}_{mj} - \frac{1}{4}P_{-}(ab)\sum_{m,e} l^{m}_{e} r^{a}_{m} t^{eb}_{ij} \\ & + \frac{1}{4}P_{-}(ij)P_{-}(ab)\sum_{m,e} l^{m}_{e} r^{b}_{j} t^{ae}_{im} + \frac{1}{4}\zeta^{ij}_{ab},\end{aligned} \tag{3–65}$$

$$\rho^{ab}_{cd} = 0, \tag{3–66}$$

$$\rho^{ab}_{ij} = 0. \tag{3–67}$$

The explicit spin orbital equation for Ξ is

$$\begin{aligned}\xi^{ij}_{ab} =& -P_{-}(ab)\sum_{m,e} l^{m}_{a} r^{e}_{m}\langle ij||eb\rangle - P_{-}(ij)\sum_{m,e} l^{i}_{e} r^{e}_{m}\langle mj||ab\rangle \\ & + P_{-}(ij)P_{-}(ab)\sum_{m,e} l^{i}_{a} r^{e}_{m}\langle mj||eb\rangle \\ & - P_{-}(ij)P_{-}(ab)\sum_{m,n,e} l^{in}_{ae} r^{e}_{m}\langle mj||nb\rangle \\ & + P_{-}(ij)P_{-}(ab)\sum_{m,e,f} l^{im}_{af} r^{e}_{m}\langle fj||eb\rangle \\ & + P_{-}(ab)\sum_{m,e,f} l^{ij}_{af} r^{e}_{m}\langle fm||be\rangle \\ & - P_{-}(ij)\sum_{m,n,e} l^{in}_{ab} r^{e}_{m}\langle jm||ne\rangle - \sum_{m,e,f} l^{ij}_{ef} r^{e}_{m}\langle fm||ba\rangle \\ & - \sum_{m,n,e} l^{mn}_{ab} r^{e}_{m}\langle ij||en\rangle + \langle ij||ab\rangle.\end{aligned} \tag{3–68}$$

In these equations $P_{-}(pq)$ stands for $[1 - P(pq)]$, where $P(pq)$ means permute p and q.

The equations for ρ and for ξ are subsets of the corresponding equations for EOM-MBPT(2) gradients,[97] and the P-EOM-MBPT(2) gradients have been implemented in the ACES II program system* starting from Stanton and Gauss's EOM-MBPT(2) gradient code.[97]

One final note should be made about the cost of the P-EOM-MBPT(2) gradients. Previously it was argued that the iterative $n_{occ}^2 N_{virt}^3$ steps should dominate the time over the non-iterative $n_{occ}^2 N_{virt}^4$ step for normal vertical excitation energy calculations. This was partially because the cost of the $n_{occ}^2 N_{virt}^4$ step can be amortized over multiple excited states. However, the gradient for only one excited state can be calculated at a time. Therefore, this amortization cannot occur. More importantly, there are now many more $n_{occ}^3 N_{virt}^3$ 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 non-iterative $n_{occ}^2 N_{virt}^4$ method.

Application to Diatomic Molecules

In order to assess the performance of the CIS(D)[83] method for excited state potential energy surfaces, Stanton *et al.*[93] studied singlet excited states for six diatomic molecules.

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* 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. Baeck, H. Sekino, P. Rozyczko, C. Huber, and R. J. Bartlett. Integrals 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).

In order to compare this new work with the methods presented there, those systems have also been studied here. The six diatomics are CO, N_2, C_2, H_2, BH, and BF. Except for N_2, the studied states are the lowest singlet excited state of the molecule. For N_2 the $1^1\Pi_u$ state was studied.

The basis sets used were 6–31G*,[120] aug-cc-pVDZ,[121] and aug-cc-pVTZ.[121]† From attempting to match the reported numbers, it would appear that for the 6–31G* and aug-cc-pVDZ basis sets all six Cartesian *d* functions were used previously, and for the aug-cc-pVTZ basis set only the spherical *d* and *f* functions were used. The same was done here.

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, an attempt to review the volumous literature on these molecules will not be made. Instead the three inexpensive methods (CIS, CIS(D), and P-EOM-MBPT(2)) will be compared to the more expensive and more complete EOM-CCSD and to experiment.[122] 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.[60–63]

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† Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06–76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

Results for the diatomic molecules are presented in Tables 3–1 to 3–5. There are some small differences between the numbers reported here and the values given in Ref. 93. Several values given in the previous paper were in error. Those errors have been corrected here.

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 3–1. The adiabatic excitation energies are given in Table 3–2. The ground state minimum geometries used are listed in Table 3–3, with the excited state minimum geometries in Table 3–4. 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,[93] the CIS answers are too poor to be reliable CIS has several errors of greater than 1 eV, and for C_2 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.[83]

The P-EOM-MBPT(2) method, on the other hand, actually performs worse than originally reported.[114] The vertical excitation energies are slightly worse than the CIS(D) energies. 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,[114] 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 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.[123]

CIS(D), on the other hand, performs better for valence states than for Rydberg states.[114] 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 wavefunction, 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. Actually, there are not significant differences between the basis sets, except for H_2, where 6–31G* does not contain any polarization functions.

Bond Lengths and Vibrational Frequencies

Excited state equilibrium bond lengths are presented in Table 3–4 and excited state vibrational frequencies are presented in Table 3–5. 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. 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 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 cm^{-1}. This compares to a mean absolute deviation of 0.011 Å for the P-EOM-MBPT(2) bond lengths, 106 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 0.008Å, and the vibrational frequencies have a mean absolute error of 67 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).

Application to Polyatomic Molecules

The P-EOM-MBPT(2) method has also been applied to some prototypical polyatomic molecules. Because of the much more complicated chemistry possible, polyatomics can provide a much more demanding test of a method.

The S_1 State of Ammonia

The S_1 state of ammonia has been studied extensively.[124, 125] 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.[126] 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 provide an opportunity to compare the P-EOM-MBPT(2) with the (non-partitioned) EOM-MBPT(2) method[97] 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. 127. 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 3–6 gives the geometry and vibrational spectrum for the

D_{3h} minimum. It is believed that the N–H bond distance is 1.055 ± 0.008 Å.[128] The EOM-CCSD bond distance falls within these error bars. However, a larger basis set would tend to shorten it.[129] 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 the are 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 wavefunction, and these large errors for the P-EOM-MBPT(2) and especially the CIS(D) methods suggest that their descriptions of the wavefunction 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 3–7. 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 ω_6 to be too small[93] with the CIS(D) actually predicting that the transition state is not C_{2v}. Stanton *et al.*[93] suggested that the long bond length was caused by the tendency of CIS(D) to underestimate the energy of Rydberg states,[83] thus causing a “late” transition state. For P-EOM-MBPT(2) the problem is the opposite. It tends to overestimate the valence states. However, that will also lead to a “late” transition state and a longer C–H bond.

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 cm^{-1}.[128]

Trans-bent and Vinylidenic Isomers on the S_1 Surface of C_2H_2

The S_1 surface of acetylene provides a nice test for excited state methods. The C_{2h} *trans*-bent minimum for the S_1 state was described in the 1950’s.[130–132] However, in a recent theoretical paper, it was suggested that the global minimum was a C_{2v} vinylidenic structure with both hydrogens bonded to one of the carbons.[133] The vinylidenic structure was calculated to be 13 kcal/mol lower than the *trans*-bent acetylenic structure. This prediction that the vinylidenic state was lower was confirmed with multireference CI, approximate coupled-pair functional,[134] and averaged quadratic coupled-cluster[135] calculations. On the other hand, both CIS and CIS(D) predict the wrong ordering of the isomers.[93]

The structures, vibrational frequencies, and energies of the two isomers are presented in Tables 3–8 and 3–9. The calculations were performed with a TZ2P basis set.[136] Not including zero point energy corrections, CIS predicts the acetylenic structure to be more stable by 2.1 kcal/mol. The CIS(D) predicts the acetylenic structure to be more stable by 0.9 kcal/mol. The P-EOM-MBPT(2) also has the wrong order, with the acetylenic structure being 2.9 kcal/mol lower in energy than the vinylidenic structure.

Simple Carbonyls

As the simplest of the carbonyls, formaldehyde's spectrum has been studied extensively.[137, 138] 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,[102] while CIS(D) severely overestimates the bond lengthening.[93] Also, CIS(D) predicts the molecule to be almost flat.[93]

Table 3–10 presents the P-EOM-MBPT(2) results. Other than predicting a C–O bond that is 0.02 Å too long, the P-EOM-MBPT(2) geometry agrees well with experiment, especially considering the relatively poor basis set used (6–31G*,[120] the same that was used in Ref. 93). The frequencies are also reasonable, except for ω_4. The dipole is somewhat too large, but is still in better agreement with experiment than the CIS(D) dipole.

Table 3–11 presents a comparison of the formaldehyde, acetaldehyde, and acetone geometries, all with the 6–31G* basis set.[120] 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.[139] This can be attributed to the removal of one electron from the in plane lone pair on oxygen, letting the steric effects dominate over the weakened hydrogen bonding.

Zuckermann *et al.*[140] carefully measured the spectrum of acetone around the origin of the $n \rightarrow \pi^*$ band. Their analysis led to the positive analysis of three vibrational bands, with uncertainty about two others. Their assignments, along with the calculated vibrational frequencies, are presented in Table 3–12. Zuckermann *et al.* could not definitely distinguish between the first possibility and the second possibility; though they preferred the first. Determining which is correct depends upon the frequency of ν_{19}. The computed frequency of 368.4 cm^{-1} is well below the 465.4 cm^{-1} for the second possibility. On the other hand the P-EOM-MBPT(2) is low on all of the other frequencies except for ν_{12}, considering that the calculated frequencies are harmonic frequencies as opposed to the measured fundamental frequencies. Also, in acetaldehyde the P-EOM-MBPT(2) gets very good agreement between the calculated vibrational frequency (368.4 cm^{-1}) and the measured frequency (370 cm^{-1})[139] for the corresponding mode. The next calculated mode in acetone is at 811.1 cm^{-1}. Hence, the calculated spectrum supports the second possibility over the first possibility. It would take better calculations, for example an EOM-CCSD calculation with a better basis set and possibly with triples, to confirm which one it is.

Conclusions

An alternative and simpler derivation for EOM-CCSD gradients based upon an excited state EOM-CC functional is presented. Gradients for the P-EOM-MBPT(2) method have been derived and their cost discussed. Then, by studying a series of diatomics and prototypical polyatomics the performance of P-EOM-MBPT(2) for low-lying valence potential energy surfaces was studied 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[93], 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 has errors of 0.3 eV or less, but its geometries sometime fail dramatically. Even 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.[114] 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 (non-partitioned) 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 $n_{occ}^2 N_{virt}^4$ to an iterative $n_{occ}^2 N_{virt}^3$ plus a non-iterative $n_{occ}^2 N_{virt}^4$.

Table 3–1: Vertical excitation energies (in eV) for the excited singlet states

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ
H_2	CIS[a]	15.354	12.639	12.714
	CIS(D)[a]	15.341	12.574	12.832
	P-EOM-MBPT(2)	15.349	12.574	12.835
	EOM-CCSD[a]	15.257	12.484	12.717
BH	CIS[a]	3.029	2.849	2.852
	CIS(D)[a]	2.991	2.864	2.810
	P-EOM-MBPT(2)	2.991	2.875	2.824
	EOM-CCSD[a]	3.117	2.972	2.914
CO	CIS[a]	9.385	9.272	9.330
	CIS(D)[a]	8.911	8.768	8.767
	P-EOM-MBPT(2)	9.196	9.047	9.076
	EOM-CCSD[a]	8.833	8.638	8.666
N_2	CIS[a]	10.378	10.360	10.550
	CIS(D)[a]	9.444	9.389	9.532
	P-EOM-MBPT(2)	9.883	9.805	9.980
	EOM-CCSD[a]	9.425	9.339	9.514
BF	CIS[a]	6.888	6.559	6.601
	CIS(D)[a]	6.865	6.481	6.455
	P-EOM-MBPT(2)	6.935	6.560	6.545
	EOM-CCSD[a]	6.898	6.482	6.454
C_2	CIS[a]	-1.180	-1.258	-1.229
	CIS(D)[a]	1.310	1.151	1.222
	P-EOM-MBPT(2)	1.423	1.261	1.328
	EOM-CCSD[a]	1.526	1.283	1.308

a)Ref. 93.

Table 3–2: Adiabatic excitation energies (in eV) for the excited singlet states

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt.[a]
H_2	CIS[b]	12.765	11.269	11.352	
	CIS(D)[b]	12.980	11.290	11.429	
	P-EOM-MBPT(2)	12.943	11.274	11.408	
	EOM-CCSD[b]	13.110	11.228	11.353	11.3694
BH	CIS[b]	3.024	2.845	2.849	
	CIS(D)[b]	2.989	2.861	2.807	
	P-EOM-MBPT(2)	2.989	2.872	2.821	
	EOM-CCSD[b]	3.117	2.972	2.913	2.8685
CO	CIS[b]	8.784	8.739	8.802	
	CIS(D)[b]	8.269	8.219	8.246	
	P-EOM-MBPT(2)	8.566	8.527	8.580	
	EOM-CCSD[b]	8.330	8.229	8.256	8.0684
N_2	CIS[b]	9.413	9.432	9.582	
	CIS(D)[b]	8.802	8.775	8.864	
	P-EOM-MBPT(2)	9.264	9.231	9.346	
	EOM-CCSD[b]	8.760	8.714	8.839	8.5900
BF	CIS[b]	6.806	6.519	6.563	
	CIS(D)[b]	6.760	6.428	6.404	
	P-EOM-MBPT(2)	6.822	6.507	6.495	
	EOM-CCSD[b]	6.811	6.444	6.417	6.3427
C_2	CIS[b]	-1.275	-1.350	-1.319	
	CIS(D)[b]	1.143	0.997	1.075	
	P-EOM-MBPT(2)	1.293	1.138	1.208	
	EOM-CCSD[b]	1.301	1.066	1.103	1.0404

a)Ref. 122.

b)Ref. 93.

Table 3–3: Equilibrium distances (in Å) for the ground states

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt[a]
H_2	SCF[b]	0.7300	0.7481	0.7345	
	MBPT(2)[b]	0.7375	0.7549	0.7374	
	CCSD[b]	0.7462	0.7617	0.7431	0.7414
BH	SCF[b]	1.225	1.233	1.221	
	MBPT(2)[b]	1.233	1.241	1.216	
	CCSD[b]	1.244	1.249	1.220	1.2324
CO	SCF[b]	1.114	1.110	1.104	
	MBPT(2)[b]	1.150	1.147	1.134	
	CCSD[b]	1.141	1.138	1.124	1.1283
N_2	SCF[b]	1.078	1.078	1.067	
	MBPT(2)[b]	1.130	1.131	1.110	
	CCSD[b]	1.113	1.113	1.093	1.0977
BF	SCF[b]	1.260	1.270	1.249	
	MBPT(2)[b]	1.279	1.294	1.264	
	CCSD[b]	1.281	1.296	1.263	1.2626
C_2	SCF[b]	1.245	1.253	1.241	
	MBPT(2)[b]	1.264	1.276	1.254	
	CCSD[b]	1.252	1.265	1.241	1.2425

a)Ref. 122.

b)Ref. 93.

Table 3–4: Equilibrium distances (in Å) for the excited singlet states

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt.[a]
H_2	CIS[b]	1.544	1.239	1.239	
	CIS(D)[b]	1.599	1.256	1.273	
	P-EOM-MBPT(2)	1.626	1.273	1.295	
	EOM-CCSD[b]	1.616	1.267	1.283	1.2928
BH	CIS[b]	1.204	1.214	1.204	
	CIS(D)[b]	1.219	1.223	1.199	
	P-EOM-MBPT(2)	1.216	1.223	1.199	
	EOM-CCSD[b]	1.241	1.242	1.211	1.2186
CO	CIS[b]	1.228	1.220	1.213	
	CIS(D)[b]	1.295	1.286	1.263	
	P-EOM-MBPT(2)	1.293	1.282	1.259	
	EOM-CCSD[b]	1.252	1.242	1.224	1.2353
N_2	CIS[b]	1.200	1.200	1.192	
	CIS(D)[b]	1.250	1.249	1.231	
	P-EOM-MBPT(2)	1.245	1.244	1.227	
	EOM-CCSD[b]	1.221	1.220	1.202	1.2203
BF	CIS[b]	1.316	1.312	1.287	
	CIS(D)[b]	1.350	1.349	1.312	
	P-EOM-MBPT(2)	1.353	1.349	1.312	
	EOM-CCSD[b]	1.345	1.342	1.304	1.3038
C_2	CIS[b]	1.293	1.301	1.289	
	CIS(D)[b]	1.333	1.346	1.320	
	P-EOM-MBPT(2)	1.325	1.337	1.312	
	EOM-CCSD[b]	1.334	1.347	1.318	1.3184

a)Ref. 122.

b)Ref. 93.

Table 3–5: Harmonic vibrational frequencies (in cm^{-1}) for the excited singlet states

		6-31G*	aug-cc-pVDZ	aug-cc-pVTZ	Expt.[a]
H_2	CIS[b]	1495	1610	1589	
	CIS(D)[b]	1438	1485	1422	
	P-EOM-MBPT(2)	1407	1410	1337	
	EOM-CCSD[b]	1428	1439	1368	1358.09
BH	CIS[b]	2576	2536	2544	
	CIS(D)[b]	2426	2441	2517	
	P-EOM-MBPT(2)	2445	2443	2515	
	EOM-CCSD[b]	2180	2243	2372	2251.0
CO	CIS[b]	1646	1615	1633	
	CIS(D)[b]	1282	1238	1323	
	P-EOM-MBPT(2)	1281	1244	1330	
	EOM-CCSD[b]	1559	1517	1592	1518.2
N_2	CIS[b]	1939	1909	1897	
	CIS(D)[b]	1612	1583	1615	
	P-EOM-MBPT(2)	1638	1612	1635	
	EOM-CCSD[b]	1856	1825	1854	1694.21
BF	CIS[b]	1339	1273	1367	
	CIS(D)[b]	1173	1097	1239	
	P-EOM-MBPT(2)	1160	1095	1241	
	EOM-CCSD[b]	1199	1130	1279	1264.9
C_2	CIS[b]	1830	1797	1794	
	CIS(D)[b]	1618	1577	1631	
	P-EOM-MBPT(2)	1674	1635	1687	
	EOM-CCSD[b]	1605	1563	1630	1608.35

a)Ref. 122.

b)Ref. 93.

Table 3–6: Geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), and energies (in Hartrees) for the D_{3h} equilibrium geometry of the S_1 state of NH_3

	CIS[a]	CIS(D)[a]	P-EOM-MBPT(2)	EOM-MBPT(2)[b]	EOM-CCSD[b]
r_{NH}	1.0213	1.0441	1.0420	1.0487	1.0512
$\omega_1(a_1')$	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

a)Ref. 93.

b)Ref. 97.

Table 3–7: Geometries (in Å and degrees), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), dipole moments (in Debyes), energies (in Hartrees), and barrier heights (in cm^{-1}) for the C_{2v} predissociative transition state of the S_1 state of NH_3. The symmetry unique hydrogen is denoted by an asterisk.

	CIS[a]	CIS(D)[a]	P-EOM-MBPT(2)	EOM-MBPT(2)[b]	EOM-CCSD[b]
r_{NH*}	1.3497	1.4371	1.4108	1.3219	1.3421
r_{NH}	1.0106	1.0421	1.0370	1.0423	1.0441
$\theta(H^*NH)$	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
μ	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

a)Ref. 93.

b)Ref. 97.

Table 3–8: Geometries (in Å and degrees), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), and energies (in Hartrees) for the *trans*-bent isomer of the S_1 state of acetylene

	CIS[a]	CIS(D)[a]	P-EOM-MBPT(2)	EOM-CCSD[b]
r_{CH}	1.0788	1.0889	1.0890	1.0907
r_{CC}	1.3521	1.3724	1.3717	1.3575
θ(HCC)	124.55	122.06	121.86	123.64
$\omega_1(a_g)$	3293.5	3144.7	3141.7	3107.7
$\omega_2(a_g)$	1545.1	1423.6	1436.4	1471.4
$\omega_3(a_g)$	1162.4	1108.2	1114.1	1106.6
$\omega_4(a_u)$	1230.8	687.2	907.8	614.6
$\omega_5(b_u)$	3280.3	3131.6	3126.2	3083.7
$\omega_6(b_u)$	805.7	882.4	887.5	745.8
I_4	2.8	111.1	40.7	100.1
I_5	2.5	3.6	3.9	6.9
I_6	342.4	281.6	295.6	405.9
Energy	-76.681 20	-76.969 01	-76.966 77	-76.981 76

a)Ref. 93.

b)Ref. 133

Table 3–9: Geometries (in Å and degrees), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), and energies (in Hartrees) for the C_{2v} vinylidenic isomer of the S_1 state of acetylene

	CIS[a]	CIS(D)[a]	P-EOM-MBPT(2)	EOM-CCSD[b]
r_{CH}	1.0847	1.0881	1.0879	1.0890
r_{CC}	1.3877	1.4225	1.4174	1.4289
θ(HCC)	122.94	122.15	122.38	122.28
$\omega_1(a_1)$	3173.5	3086.1	3089.2	3060.1
$\omega_2(a_1)$	1618.8	1464.2	1476.7	1486.5
$\omega_3(a_1)$	1381.5	1225.7	1246.5	1213.1
$\omega_4(b_2)$	3235.5	3172.0	3171.0	3138.9
$\omega_5(b_2)$	1015.5	894.6	903.9	927.1
$\omega_6(a_2)$	977.1	702.3	708.6	763.2
I_1	17.1	0.1	0.2	3.2
I_2	1.3	29.1	24.5	14.4
I_3	0.3	57.0	41.7	31.3
I_4	9.7	2.2	2.1	7.0
I_5	4.7	3.9	3.5	5.3
I_6	1.6	1.1	0.4	2.1
Dipole moment	3.817	2.926	3.029	2.875
Energy	-76.677 85	-76.967 63	-76.962 08	-77.003 07

a)Ref. 93.

b)Ref. 133

Table 3–10: Geometries (in Å and degrees), harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), dipole moments (in Debyes), and energies (in Hartrees) for the equilibrium geometry of the $\tilde{A}$ $^1A''$ state of formaldehyde. Experimental frequencies are fundamentals.

	CIS[a]	CIS(D)[b]	P-EOM-MBPT(2)	EOM-CCSD[b]	Expt.[a]
r_{CO}	1.258	1.384	1.340	1.324	1.321
r_{CH}	1.085	1.088	1.093	1.096	1.097
θ(OCH)	117.3	117.8	117.0	115.8	118.0
τ(HOCH)	148.4	171.5	153.0	145.9	148.3
ω_1(a')	3209.5	3154.1	3102.3	3072.9	2847
ω_2(a')	1437.9	1420.5	1412.7	1407.9	1290
ω_3(a')	1660.8	895.7	1187.2	1248.5	1173
ω_4(a')	561.6	172.6	564.9	719.8	683
ω_5(a'')	3299.6	3295.8	3223.6	3189.5	2968
ω_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)[c)]
Energy	-113.669 47	-114.043 84	-114.028 60	-114.052 75	

[a)] Ref. 102.

[b)] Ref. 93.

[c)] Ref. 141.

Table 3–11: A comparison of the geometries of the n→π^* states in formaldehyde, acetaldehyde, and acetone. Geometries are in Angstroms and degrees.

	Formaldehyde	Acetaldehyde	Acetone
r_{CO}	1.340	1.359	1.376
r_{CC}		1.494	1.494
r_{CHa}	1.093	1.095	
r_{CHb}		1.091	1.092
r_{CHc}		1.099	1.101
r_{CHd}		1.094	1.094
θ(0CC)		116.0	113.4
θ(0CH$_a$)	117.0	114.3	
θ(CCH$_b$)		110.2	110.3
θ(CCH$_c$)		110.6	110.2
θ(CCH$_d$)		110.2	110.6
τ(H$_a$COH)	153.0		
τ(H$_a$COC)		149.9	
τ(CCOC)			146.9
τ(H$_b$CCO)		-177.5	-174.5
τ(H$_c$CCO)		61.6	65.0
τ(H$_d$CCO)		-57.1	-53.7

Table 3–12: 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 cm^{-1}.

	first possibility^{a}	second possibility^{a}	P-EOM-MBPT(2)
ν_{12} torsion (antigearing)	155.5	155.5	206.8
ν_{24} torsion (gearing)	172.5	172.5	190.1
ν_{8} C–C–C bend	373	373	353.8
ν_{23} C=O out-of-plane wagging	—	333	329.7
ν_{19} C=O in-plane wagging	177.5	465.4	368.4

a) Ref. 140.

CHAPTER 4
THE SIMILARITY TRANSFORMED EQUATION-OF-MOTION COUPLED-CLUSTER METHOD

Introduction

The equation-of-motion coupled-cluster (EOM-CC) method,[56, 57] especially when based on a coupled-cluster singles and doubles (CCSD)[9] ground state, offers an attractive and unified formalism to extend single reference coupled-cluster methods to excitation energies (EE-EOM-CCSD, sometimes just EOM-CCSD),[58, 59] ionization potentials (IP-EOM-CCSD),[67] and electron affinities (EA-EOM-CCSD).[68] The method is conceptually single reference, in that the entire calculation is built upon one reference determinant. Therefore, the only choices necessary in the method are the choice of basis set, the choice of reference determinant, usually the Hartree-Fock solution, and the choice of excitation level to include in the ground and excited state operators.

Several applications[58, 142–145, 123] of EE-EOM-CCSD and its twin, coupled-cluster singles and doubles linear response,[53, 54] have been made. The method has also been extended to include various effects of triple excitations.[60–63] But EOM-CCSD, and especially EE-EOM-CCSD, has some drawbacks. The first is the cost of the method. Every EE-EOM-CCSD excited state is approximately as expensive as a ground state CCSD calculation. Approximations can be made to reduce the cost,[114] with varying degrees of success. The second drawback is the accuracy of the method. For ethylene, butadiene, and cyclopentadiene, the average error for the Rydberg states was 0.17 eV, but the average error for the valence states was 0.26 eV.[123]

The key to EOM-CC theory is the similarity transformation of the Hamiltonian. After the ground state coupled-cluster equations have been solved, the cluster amplitudes are used to transform the Hamiltonian. A similarity transformation changes the eigenvectors of an operator without changing its eigenvalues. Hence, the energies of the excited states, electron attached states, and ionized states, which are all eigenvalues of the Hamiltonian matrix in terms of the appropriate bases, have not changed.

So far nothing has been accomplished. To calculate the energies of these states, it is still necessary to diagonalize a matrix that is, in principal, infinite. After a finite basis set has been introduced, the matrix is now finite, but its size grows as the size of the basis set factorial.[22] Therefore, approximations must be introduced. The typical approximations involve truncating the Hamiltonian matrix to include only a subset of possible excitations. In EE-EOM-CCSD the matrix is limited to only single and double excitations, i.e. determinants where one or two virtual orbitals replace one or two occupied orbitals. For EA-EOM-CCSD the space is limited to determinants where an electron has been added to a single virtual orbital and determinants where along with the electron being added to a virtual orbital, an occupied orbital is replaced with a virtual orbital. These are the so called $1p$ and $2p1h$ states. For IP-EOM-CCSD the space consists of the $1h$ and $2h1p$ determinants, which are those determinants with one electron removed from an occupied orbital and those determinants with one electron removed and one electron excited.

After the truncation of the matrix is when the similarity transformation becomes important. The truncation will change the eigenvalue spectrum. Many eigenvalues will no longer appear, and those that remain will be shifted by an amount which will depend on how much of the true eigenvector lies in the omitted space. What gives the similarity transformation its power is that by choosing the transformation so that the important eigenvectors are contained, to the greatest extent possible, in the space kept after the truncation, the effect of the truncation on the energies of the states of interest can be minimized. Note that an similarity transformation is needed, since a unitary transformation leaves the eigenvectors unchanged. An equivalent picture is to choose the transformation such that the parts of the matrix that couple the kept space with the excluded space are minimized, since these parts of the matrix determine the extent to which eigenvectors span both spaces.

For singly excited states, the most important terms deleted in the truncation to singles and doubles are the triple excitations. In the untransformed Hamiltonian matrix, the terms that couple single excitations to triple excitations are the two electron integrals $\langle ab||ij\rangle$, where a, b, c, and d are unoccupied in the reference determinant and i, j, k, and l are occupied in the reference determinant. These are precisely the terms which are set to zero by the similarity transformation. The transformation does add new coupling terms, but they are of the form of a t_2 amplitude times a different two electron integral. Since for a normal single reference problem, the largest t amplitudes are of the order of 0.1, the new coupling terms are at least an order of magnitude smaller than the former coupling terms. Therefore the “true” eigenvector for a singly excited state is contained more fully within the space of single and double excitations, and the eigenvalue for the state with the truncated similarity transformed Hamiltonian is much closer to the eigenvalue of the untruncated Hamiltonian than is the eigenvalue for that state with the truncated untransformed Hamiltonian.

In the similarity transformed equation-of-motion coupled-cluster (STEOM-CC) theory[64–66] the blocking of the matrix by similarity transformations is carried one step farther. Starting with the EOM-CC transformed Hamiltonian, a second similarity transformation[69] is performed in order to minimize the coupling between the singles space and the doubles space. The dominant terms that couple these two blocks in the EOM-CC Hamiltonian are the $\langle ab||ci\rangle$ and $\langle ia||jk\rangle$ two electron integrals. The most important of these coupling terms are set to zero in the second similarity transformation, leaving as the main coupling term between the singles and doubles blocks again a t_2 amplitude times a two electron integral. Once again, the coupling is reduced by at least an order of magnitude.

Since the second similarity transformation is done in such a way as to preserve the reduction of the singles-triples coupling from the first similarity transformation, the eigenvectors for states dominated by single excitations are almost exclusively composed of only single excitations, meaning that the truncation needs to leave only the space of singles. Now the final diagonalization to get the eigenvalues and eigenvectors only scales as the fourth power of the basis set, as opposed to the sixth power scaling for EOM-CCSD. The trade-off is having to perform the second similarity transformation, but the second transformation only scales as the fifth power of the size of the basis set.

If the final diagonalization is over the space where an electron has been removed from an occupied orbital and placed in an unoccupied orbital, then excited states are calculated, and the method is known as excitation energy STEOM-CC (EE-STEOM-CC).[64, 66] If the final space is over states with two electrons removed, the method is the double ionization potential STEOM-CC (DIP-STEOM-CC).[66] Finally, if the space is over determinants with two electrons added, the method is the double electron attachment STEOM-CC (DEA-STEOM-CC).[66] Each of these methods provides an important tool for describing interesting chemistry, and although the rest of the dissertation will focus on the EE-STEOM-CC variant, everything said can be applied to the other two with simple modifications.

The STEOM-CC Method

In STEOM-CC theory, the orbital space is divided into occupied and virtual orbitals, sometimes referred to as holes and particles, based on the orbital's occupancy in the reference determinant. The orbital space is then subdivided into active and inactive occupied orbitals and active and inactive virtual orbitals. To distinguish the sets, the labels i, j, k, and l will refer to generic occupied orbitals, and a, b, c, and d will refer to generic virtual orbitals. Active occupied orbitals will be m and n while active virtuals will be e and f. Explicitly inactive orbitals will be indicated with a prime, such as i' and a'. The labels p, q, r, and s can refer to any orbital. All such orbitals are spacial orbitals, as opposed to the previous chapters where spin orbitals have been used.

Although a STEOM-CC calculation could be based on any coupled-cluster or many-body perturbation theory treatment of the ground state, so far only CCSD and MBPT(2) have been used.[64] This discussion will focus on STEOM-CC with a CCSD[9] ground state, giving the STEOM-CCSD method.[64] In coupled-cluster theory, the ground state of the molecule is represented as

$$|\Psi_0\rangle = e^{T}|0\rangle, \tag{4–1}$$

where $|0\rangle$ is a closed shell single determinant, often the Restricted Hartree-Fock (RHF) determinant. For CCSD the operator *T* consists of pure excitation operators of the form

$$T = T_1 + T_2 = \sum_{i,a} t_i^a \left\{a^\dagger i\right\} + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} \left\{a^\dagger i b^\dagger j\right\}. \tag{4–2}$$

The curly brackets mean that the operator is normal ordered with respect to $|0\rangle$.

The untransformed Hamiltonian, in second quantization, is

$$H = h_0 + \sum_{p,q} f_{pq} \left\{p^\dagger q\right\} + \frac{1}{4} \sum_{\substack{p,q \\ r,s}} V_{qprs} \left\{p^\dagger r q^\dagger s\right\}. \tag{4–3}$$

The constant term, h_0, is the energy of the reference determinant. The f_{pq} refer to the appropriate parts of the Fock operator. The V_{qprs} are non-antisymmetrized two electron integrals.

After the first transformation the Hamiltonian becomes

$$\begin{aligned} \bar{H} &= e^{-T} H e^{T} \\ &= \bar{h}_0 + \sum_{p,q} \bar{h}_{pq} \left\{p^\dagger q\right\} + \frac{1}{4} \sum_{\substack{p,q \\ r,s}} \bar{h}_{pqrs} \left\{p^\dagger r q^\dagger s\right\} \\ &\quad + \frac{1}{36} \sum_{\substack{p,q,r \\ s,t,u}} \bar{h}_{pqrstu} \left\{p^\dagger s q^\dagger t r^\dagger u\right\} + \ldots . \end{aligned} \tag{4–4}$$

With a CCSD reference state, $\bar{H}$ will contain up to six-body terms, but the four- and higher body terms do not appear in the EOM-CCSD or STEOM-CCSD equations. Explicit equations for these $\bar{H}$ elements, as used here, can be found elsewhere.[146] In terms of $\bar{H}$, the CCSD equations can be written as

$$\begin{aligned} \langle \Phi_i^a | \bar{H} | 0 \rangle &= \bar{h}_{ai} = 0, \\ \langle \Phi_{ij}^{ab} | \bar{H} | 0 \rangle &= \bar{h}_{abij} = 0. \end{aligned} \tag{4–5}$$

The CCSD energy is

$$E_{CCSD} = \langle 0 | \bar{H} | 0 \rangle = \bar{h}_0. \tag{4–6}$$

Thus, solving the CCSD equations is equivalent to setting the one- and two-body pure excitation parts of $\bar{H}$ to zero.

In STEOM-CC, a second many-body similarity transformation[69] is performed in order to also set to zero selected remaining terms which increase the net excitation level by one. But since, in diagrammatic language, the necessary operators have a line on the bottom, they do not commute and can connect to each other. Thus instead of using a transformation of the form e^S, as originally done by Stolarczyk and Monkhorst,[37] a normal ordered exponential operator $\left\{e^S\right\}$ is used. The normal ordered exponential, introduced by Lindgren,[33] excludes terms inside the normal ordering from connecting to each other, and this simplifies the equations.

The S operator used in the transformation consists of two parts $S = S^+ + S^-$, where

$$S^+ = S_1^+ + S_2^+ = \sum_{a',e} s_e^{a'} \left\{a'^\dagger e\right\} + \frac{1}{2} \sum_{\substack{a,b\\ j,e}} s_{ej}^{ab} \left\{a^\dagger e b^\dagger j\right\}, \tag{4–7}$$

and

$$S^- = S_1^- + S_2^- = \sum_{i',m} s_{i'}^{m} \left\{m^\dagger i'\right\} + \frac{1}{2} \sum_{\substack{i,m\\ b,j}} s_{ij}^{mb} \left\{m^\dagger i b^\dagger j\right\}. \tag{4–8}$$

It is the presence of the active *q*-annihilation operators which cause the components of S to, in general, not commute.[66]

The double similarity transformed Hamiltonian takes the form

$$\begin{aligned} G &= \left\{e^S\right\}^{-1} \bar{H} \left\{e^S\right\} \\ &= g_0 + \sum_{p,q} g_{pq} \left\{p^\dagger q\right\} + \sum_{\substack{p,q\\ r,s}} g_{pqrs} \left\{p^\dagger r q^\dagger s\right\} + \ldots . \end{aligned} \tag{4–9}$$

The similarity transformation preserves the zeros for the one- and two-body pure excitation parts, so that[66]

$$\begin{aligned} g_{ai} &= \bar{h}_{ai} = 0, \\ g_{abij} &= \bar{h}_{abij} = 0. \end{aligned} \tag{4–10}$$

Also,

$$g_0 = \bar{h}_0 = E_{CCSD}. \tag{4–11}$$

In principle, like the CCSD equations for *T* above, the S equations could be derived by setting the appropriate parts of *G* to zero. These are[66]

$$\begin{aligned} g_{mi'} &= \langle \Phi_{i'} | G | \Phi_m \rangle = 0, \\ g_{a'e} &= \langle \Phi^{a'} | G | \Phi^e \rangle = 0, \\ g_{mbij} &= \langle \Phi_{ji}^{b} | G | \Phi_m \rangle = 0, \\ g_{abej} &= \langle \Phi_{j}^{ba} | G | \Phi^e \rangle = 0. \end{aligned} \tag{4–12}$$

Note that the second two equations set to zero the primary coupling terms between singly and doubly excited determinants. In practice, the S coefficients are not calculated this way. Doing so would lead to systems of nonlinear equations which in some situations can be numerically unstable.[64] Instead, the equivalence of IP-EOM-CC and EA-EOM-CC to Fock space coupled-cluster theory[147] is exploited to rewrite S in terms of IP-EOM-CCSD and EA-EOM-CCSD eigenvectors. These equations are[66]

$$\begin{aligned} s_{i'}^{m} &= -\sum_{\lambda} r_{i'}(\lambda) r^{-1}_{\lambda m}, \\ s_{e}^{a'} &= \sum_{\lambda} r^{a'}(\lambda) r^{-1}_{\lambda e}, \\ s_{ji}^{bm} &= -\sum_{\lambda} r_{ji}^{b}(\lambda) r^{-1}_{\lambda m}, \\ s_{je}^{ba} &= \sum_{\lambda} r_{j}^{ba}(\lambda) r^{-1}_{\lambda e}. \end{aligned} \tag{4–13}$$

The λ's stand for the set of IP- and EA-EOM-CCSD eigenvectors. There is one eigenvector per active orbital. The terms $r_{\lambda p}^{-1}$ stand for the coefficients in the inverse of matrix constructed from the active components of the eigenvectors λ.[66]

After the S coefficients are determined, the problem remains of how to determine the *G* coefficients. Since the inverse of the normal ordered exponential is not known,[69] Eq. (4–9) cannot be used directly. Instead the equation

$$\left\{e^S\right\}G = \bar{H}\left\{e^S\right\} \tag{4–14}$$

is used. It has been shown[69] that this equation is equivalent to

$$\left(\left\{e^S\right\}G\right)_c = \left(\bar{H}\left\{e^S\right\}\right)_c \tag{4–15}$$

or

$$G = \left(\bar{H}\left\{e^S\right\}\right)_c - \left(\left\{e^S - 1\right\}G\right)_c, \tag{4–16}$$

where the *c* means that the equations must be connected.

In practice, all terms involving S_1 are dropped.[66] Since S_1 does not change the net excitation level, it is not involved in the decoupling of excitation blocks. Ignoring all of the S_1 terms is equivalent to a simple rotation of the eigenvector, and since the *G* matrix is diagonalized over all singly excited determinants this "rotation" is automatically compensated for in the diagonalization. Therefore, including the S_1 terms does not change the final answer, and for convenience they are left out. Leaving out S_1 also simplifies Eq. (4–16). Since only the singles-singles block of *G* is needed, the second term does not contribute,[66] leaving straightforward, linear equations for *G* in terms of $\bar{H}$ and S. The *G* equations in orbital form can be found in Ref. 66.

Finally, the *G* matrix is diagonalized over the space of single excitations to get the excited states. This is actually the fastest step in the process, since the final matrix to be diagonalized is so small. Afterwards, excited state and transition properties can be calculated, subject to certain approximations.[66]

Discussion About STEOM-CC

Formally, the introduction of active and inactive orbitals is not needed in STEOM-CC. All orbitals could be considered active. It would simply mean that S would have no one-body component and that an IP-EOM-CCSD eigenvector would need to be found for each occupied orbital and an EA-EOM-CCSD eigenvector would be needed for each virtual orbital. In practice, this would never work, except for trivial cases. For example, there is normally a one-to-one relation between IP-EOM-CCSD states and high lying occupied orbitals, but as the spectrum moves into the inner valence region, shake-up states appear.[13] At that point, many states appear per orbital, and even the concept of principal ionization potential becomes unclear. The same will happen for EA-EOM-CCSD. Eventually, the iterative diagonalization procedure[99] will have trouble converging.

Even if it were possible to find an IP-EOM-CCSD or EA-EOM-CCSD eigenvector for every orbital, it would not be desirable. The cost of each IP-EOM-CCSD state is $n_{occ}^3 N_{virt}^2$ times the number of iterations needed for the diagonalization. The cost of each EA-EOM-CCSD state is $n_{occ}^2 N_{virt}^3$ per iteration. If the number of states equals the number of orbitals, then the cost of calculating S becomes as large as the cost of calculating *T*. It is not necessary to include all of the orbitals in the active space, anyway. The second similarity transformation serves to describe the differential dynamic correlation between the ground and excited states. But relatively few orbitals actually are involved in the excitation, and it is only those orbitals involved in the excitation that need to be in the active space.

The relationship of STEOM-CCSD to both Fock space coupled-cluster (FSCCSD) theory[32–45] and EOM-CCSD[58, 59] have been discussed at some length.[66] Only the highlights will be reviewed here. If the active space includes all orbitals, then STEOM-CCSD and FSCCSD are numerically identical for singly excited states.[66] For doubly excited or higher states, the two remain quite different. If the active space does not include all orbitals, then the two are different for singly excited states. The first difference is that STEOM-CCSD can be viewed as a series of successive similarity transformations, whereas FSCCSD has just one transformation. The second difference is that in STEOM-CCSD the final diagonalization is over all singly excited determinants, while the final diagonalization in FSCC is over those determinants where only the active orbitals change occupation.

To consider the difference between STEOM-CCSD and EOM-CCSD, it is useful to fully expand out the STEOM-CCSD wavefunction. It is

$$\begin{aligned} |\Psi_x\rangle &= e^T\left\{e^S\right\}R_1|0\rangle + e^T|0\rangle r_0 \\ &= e^T\left(1 + S + \frac{1}{2}S^2\right)R_1\left|0\right\rangle + e^T\left|0\right\rangle r_0, \end{aligned} \tag{4–17}$$

where R_1 is the single excitation part of the STEOM-CCSD eigenvector and r_0 is the contribution of the reference determinant. This should be compared to the EOM-CCSD wavefunction, which is

$$|\Psi_x\rangle = e^T(\mathcal{R}_1 + \mathcal{R}_2)|0\rangle + e^T|0\rangle r_0. \tag{4–18}$$

Since S_1 does not change the excitation level, and is not included in the calculation anyway, it can be ignored in this discussion. It is possible to directly equate terms in Eqs. (4–17) and (4–18). They match up as follows:

$$\begin{aligned} e^T|0\rangle r_0 &\Leftrightarrow e^T|0\rangle r_0 \\ e^T R_1|0\rangle &\Leftrightarrow e^T\mathcal{R}_1|0\rangle \\ e^T S_2 R_1|0\rangle &\Leftrightarrow e^T\mathcal{R}_2|0\rangle \\ \frac{1}{2}e^T S_2^2 R_1|0\rangle &\Leftrightarrow \end{aligned} \tag{4–19}$$

The STEOM-CCSD term is on the left and the EOM-CCSD term is on the right. The primary differences between the two methods are therefore that the doubles term in EOM-CCSD has the flexibility to determine its optimum weight, while the doubles term in STEOM-CCSD is a product of a fixed R_1 and a fixed S_2. On the other hand, the only triple excitations included in the EOM-CCSD wavefunction are of the form $e^T\mathcal{R}$, while the STEOM-CCSD also includes a $\frac{1}{2}S_2^2R_1$ term. Thus STEOM-CCSD has a more complete description of triple excitations but gives up some flexibility in describing the doubles.[66]

The cost of a STEOM-CC calculation in almost dominated by the cost of calculating the ground state CCSD solution and the ground state left hand state, lambda.[107] Lambda is needed for transition properties.[66] Both of these are iterative $n_{occ}^2N_{virt}^4$ steps. The next most expensive step is the formation of $\bar{H}$, which also scales as $n_{occ}^2N_{virt}^4$ but is done only once. The costs of the IP-EOM-CCSD and EA-EOM-CCSD calculations were discussed above. Calculating the S coefficients will scale as $n_{occ}N_{virt}^2N_{virt,act}^2$, where $N_{virt,act}$ is the number of active virtual orbitals. Forming G will scale as $n_{occ}N_{virt}^4N_{virt,act}$. The final diagonalization is only an iterative N_{virt}^4 step.

What all of these scalings imply is that the cost of the calculation is effectively independent of the number of excited states desired. In fact, the only practical effect that the number of states has on the cost is that as higher lying excited states are calculated, more orbitals will need to be included in the active space. This independence of the cost of the calculation to the number of excited states is in contrast to almost every other excited state method in use today, and it makes STEOM-CC well suited to calculating large numbers of excited states.

However, STEOM-CC does have some drawbacks. The primary one is that the method is only suitable for states dominated by single excitations. It would be possible to derive a STEOM-CC variant whereby the final diagonalization takes place over the space of both singles and doubles. This would allow the description of both doubly excited states and states which are mixed singles and doubles. The problem is that the equations become much more complicated. For example, the second term in Eq. (4–16) would contribute. It would also be at least as expensive as an EOM-CCSD calculation.

STEOM-CC also has strong and poorly understood dependencies on the size and the nature of the active space. It is known that the component of the excited state vector which lies within the active space should be at least 95–99%. But it is not clear how the error in the energy and properties depends on that percentage. This is an area that will require much more practical experience before it becomes clear how best to choose the active space.

Finally, the calculation of excited state and transition properties in STEOM-CC is unsatisfactory. Several approximations[66] are currently made in the properties calculations. There is some hope, at least for the excited state properties, in that the advent of gradients for STEOM-CC will give a way to calculate one electron excited state properties rigorously.

CHAPTER 5
THE SPECTRUM OF FREE BASE PORPHIN

Introduction

Because of their importance in such biological processes as photosynthesis, electron transfer, and oxygen absorption and transport, the porphyrins have been extensively studied.[148] As the base molecule for the porphyrins, the electronic spectrum of free base porphin has received much attention, both with semiemperical (see, for example, Ref. 149) and *ab initio* methods.[150, 75, 151–153, 65] The interesting part of the spectrum consists of, in order, two visible peaks known as the Q bands, a very intense peak known as the B (or Soret) band, a shoulder on the B band, called the N band, and two other small peaks, the L and M bands. The spectrum can be found in Ref. 154 and Ref. 153.

The traditional interpretation of the spectrum is that, with the molecule in the *xy* plane and with the two internal hydrogens along the *x* axis, the lowest energy band, the Q_x band, comes from exciting to the 1^1B_{3u} state. The Q_y band then comes from the 1^1B_{2u}, with the B band assigned to the 2^1B_{3u} and 2^1B_{2u} states.[150] Nakatsuji *et al.*,[153] based on their SAC-CI (symmetry adapted cluster–configuration interaction) calculations,[155] reassigned the spectrum. They agreed with the assignments of the Q bands, but they claimed that the B band should be assigned to only the 2^1B_{3u} state, with the N band being the 2^1B_{2u} state.

However, their results have three significant weaknesses. The first is the method used. In principle SAC-CI energies (but not oscillator strengths) could be equivalent to EOM-CCSD (equation-of-motion coupled-cluster singles and doubles) [58] and coupled-cluster singles and doubles linear response[53] energies. In practice, though, some non-linear terms in the underlying ground state coupled-cluster result are always omitted. Also, in these calculations many double excitations were omitted based on a perturbation selection.[153] For complex organic molecules even the untruncated EOM-CCSD may not be sufficient. In a study of benzene and the azabenzenes, EOM-CCSD had an average error of 0.32 eV for the $\pi \rightarrow \pi^*$ states.[156] SAC-CI should do no better than this, unless it has some fortuitous error cancellations.

The second criticism is the basis set used. Nakatsuji *et al.*[153] discuss the importance of σ rearrangement to the excitation energies, yet their basis set only had 2*s* type and 2*p* type functions on the carbons and nitrogens, giving it no flexibility to describe the 2*s* orbitals. They also dropped some of the occupied and virtual orbitals corresponding to the 2*s* orbitals, along with all of the 1*s* orbitals on the carbons and nitrogens. The result is that the basis set had limited flexibility, no polarization functions, and no diffuse functions. The lack of diffuse and polarization functions corresponds to the conventional viewpoint that, for at least the lowest states of free base porphin, polarization and diffuse functions are not needed.[152]

Finally, there is a problem with the oscillator strengths. The N band appears as a shoulder to the B band, but Nakatsuji *et al.*[153] calculate the excitation to the 2^1B_{2u} state to have an oscillator strength sixty-eight percent larger than the excitation to the 2^1B_{3u} state. They argue that the N band is actually quite broad, with the B band being a narrow peak on top of it. But if that is true, then the splitting between the vertical excitation energies for the B and N bands would be less than the 0.32 eV reported.[154] To answer some of these questions, a series of STEOM-CCSD (similarity transformed equation-of-motion coupled-cluster singles and doubles)[64] excited state calculations have been performed.

Computational Details

STEOM-CC

In a STEOM-CCSD[64, 66] calculation (i.e. a STEOM-CC calculation[64] based on a CCSD[9] ground state), two similarity transformations are applied to the second quantized Hamiltonian, such that the one- and two-body terms in the Hamiltonian that increase the excitation level are set to zero. This effectively blocks the Hamiltonian matrix by excitation level, so that the single excitations can be accurately calculated with a diagonalization over just the singles-singles block. The higher excitation parts of the excited state wavefunction are then implicitly included through the similarity transformations. In this way, STEOM-CC has the same conceptual appeal as CI singles, but now in a fully correlated structure. The STEOM-CCSD method has been implemented within ACES II.

The first similarity transformation, the same as in EOM-CCSD,[58] involves the T amplitudes from a ground state CCSD[9] calculation. The new Hamiltonian is then

$$\bar{H} = e^{-T} H e^{T}. \tag{5–1}$$

The next step is to solve for a set of states with one electron removed and one electron added by means of the IP-EOM-CCSD (ionization potential EOM-CCSD)[67] and the EA-EOM-CCSD (electron attachment EOM-CCSD)[68] methods. These involve diagonalizing $\bar{H}$ over the space of $1h$–$2h1p$ and $1p$–$2p1h$ determinants, respectively. These eigenvectors are used to determine the S coefficients in the second similarity transformation

$$G = \left\{e^{S}\right\}^{-1} \bar{H} \left\{e^{S}\right\}. \tag{5–2}$$

The final double similarity transformed Hamiltonian G is then diagonalized over the space of single excitations. For a detailed description of the method, see Ref. 66.

In the current implementation the final wavefunction in terms of *G* has only single excitations, limiting the method to only singly excited states, but in terms of the normal Hamiltonian, the wavefunction actually includes all possible excited determinants (with only the singles having optimized coefficients). Specifically, the wavefunction contains double excitations in the form of S_2R_1 and T_1R_1, and triple excitations in the form of $S_2^2R_1$, T_2R_1, and $T_1S_2R_1$, where R_1 is the STEOM-CC single excitation eigenvector.

Since the higher excitations and the differential correlation between the ground and excited states are described via the S operator, it is critical that the excitation be described within the set of active orbitals chosen for the IP-EOM-CC and EA-EOM-CC calculations and included in S. In the calculations presented here, the active components of the excitations are almost always above 99% and in all singlets are above 98%. In test calculations the energy seems to be converged to within 0.05 eV when the active component is 98%.[64]

Basis Set and Geometry

The basis set used for the calculations presented here come from the large ANO basis set of Widmark, Malmqvist, and Roos.[157] This is a very large, generally contracted basis set. It has 14*s*9*p*4*d*3*f* primitives for carbon and nitrogen and 8*s*4*p*3*d* primitives for hydrogen. From this set, the first 3*s* and 2*p* contractions were used for C and N and the first *s* contraction was selected for H. This basis set, consisting of 230 functions, was the same as used by Merchán *et al.*[152] It is the same number of contracted functions as that used by Nooijen and Bartlett,[65] but their basis set had a much smaller set of primitives. This set is also significantly larger than the one used by Nakatsuji *et al.*[153]

This basis set was then extended in two different ways. First, to gauge the effect of polarization functions on the excitation energies, the first *d* contraction from the ANO set was added on the carbon and nitrogen atoms, while the second *s* function was added to the hydrogens. This gave a [3*s*2*p*1*d*] set on C and N and a [2*s*] set on H, with a total of 364 contracted functions. In other calculations, to gauge the effect of diffuse functions on the excited states, a set of 2*s* and 2*p* uncontracted functions were added to the center of the molecule and to the geometrical center of each ring. The diffuse exponents were taken from Ref. 158, and have been used for naphthalene[158] and biphenyl,[159] where they were placed at the center of the molecule. Since two functions of each type were used, the exact exponent chosen should not matter significantly. In all calculations the first 24 occupied orbitals, corresponding to the 1*s* orbitals on carbon and nitrogen, were left uncorrelated.

Two different geometries were used in this study. The first is an idealized x-ray structure,[160] where the molecule, without the two internal hydrogens, would be of D_{4h} symmetry. The hydrogens make the structure D_{2h}. It was used in several of the previous studies[153, 65] and will be referred to as "D_{4h}". With the [3*s*2*p*/1*s*] basis set, this geometry had a SCF energy of –982.955034 Hartrees and a CCSD energy of –985.154443 Hartrees. The [3*s*2*p*1*d*/2*s*] basis set gave a SCF energy of –983.416854 Hartrees and a CCSD energy of –986.676253 Hartrees. The basis with the diffuse functions gave a SCF energy of –982.967070 Hartrees and a CCSD energy of –985.182042 Hartrees.

The other geometry is a B3PW91/6–31G* optimized geometry,[161] which will be referred to as "Opt". It also has D_{2h} symmetry. This geometry gave a SCF energy of –982.964858 Hartrees and a CCSD energy of –985.163441 Hartrees with the [3*s*2*p*/1*s*] basis set. The diffuse basis gave a SCF energy of –982.977085 Hartrees and a CCSD energy of –985.191231 Hartrees. The [3*s*2*p*1*d*/2*s*] basis gave a SCF energy of –983.430681 Hartrees and a CCSD energy of –986.688179 Hartrees, putting this geometry 7.5 kcal/mol below the D_{4h} geometry.

Results

Ionized and Electron Attached States

In all of the current calculations, the occupied part of the active space consisted of eleven orbitals. Therefore, eleven IP-EOM-CCSD states were calculated. In Table 5–1 the current results, with the three basis sets, are compared with the SAC-CI results,[153] with the previous STEOM-CC results,[65] and with experiment.[162] Because of the low resolution of the experimental spectrum, it is very difficult to relate the measured peaks to the calculated states. Therefore, the assignments given should be considered tentative.

While adding the diffuse functions does little to change the ionization potentials, every other time that the basis set was enlarged, from the previous STEOM-CC results,[65] to the DZ (the [3*s*2*p*/1*s*] basis) results, to the polarized (the [3*s*2*p*1*d*/2*s*] basis) results, the electron became more bound. Adding the polarization functions had the most dramatic effect. It caused the first two states to switch and the sixth and seventh states to switch. However, the differences are close to an order of magnitude smaller than the errors in the calculations, so nothing can be said definitively. Going from the "D_{4h}" geometry to the "Opt" geometry had effects of less than 0.2 eV. The "Opt" geometry typically had larger IP's.

Twenty-three virtual orbitals (4 a_g, 2 b_{1g}, 3 b_{2g}, 3 b_{3g}, 3 a_u, 2 b_{1u}, 3 b_{2u}, and 3 b_{3u}) were included in the active space for the DZ and the polarized basis sets. For the diffuse basis set several more orbitals had to be included. The diffuse basis added forty Rydberg orbitals, and most of them had orbital eigenvalues very close to zero. Therefore, to include all of the equivalent orbitals that were included for the DZ basis, the active space needed to consist of fifty-nine virtual orbitals. But that many orbitals caused convergence problems. The final set included in the active space consisted of fifty-one virtual orbitals (10 a_g, 4 b_{1g}, 5 b_{2g}, 5 b_{3g}, 3 a_u, 8 b_{1u}, 5 b_{2u}, and 5 b_{3u}). If an IP-EOM-CC or an EA-EOM-CC eigenvector is less than 70% singles, the code automatically excludes it from the second similarity transformation. For the diffuse basis, one of the B_{3g} states was excluded, leaving fifty states for the similarity transformation.

In each of the calculations two positive electron affinities were predicted. They are listed in Table 5–2. The other electron attached states, even though they do not correspond to stable states, are still essential for the calculation of the excited states. They go into the second similarity transformation and help describe the differential correlation between the ground and excited states.

Excited States

The singlet excited states of free base porphin are listed in Tables 5–3 to 5–7, and the triplet excited states are in Tables 5–8 to 5–12. The important states will be discussed later, but some general comments can be made. The first is that the Rydberg states start about 4.5 eV, which is right in the region of most interest. The second is that the addition of the diffuse functions never changes the energy of the valence states by more than 0.02 eV. This has several consequences. It implies that the DZ basis set has diffuse enough tails that the diffuse functions are not needed to describe the valence region. It also means that there is essentially no mixing between Rydberg and valence excited states. Finally, it suggests that adding diffuse functions to the polarized basis would not significantly change the energetics. Adding diffuse functions might, however, have an effect on the oscillator strengths. Those tend to change a little with the addition of the diffuse functions.

In general, going from the "D_{4h}" geometry to the "Opt" geometry has little effect on the spectrum. The excitation energy typically increases by about 0.1 eV. The important exceptions are the $^1B_{2u}$ state which drops from 5.22 eV to 5.07 eV and the $^1B_{3u}$ state which drops from 5.33 eV to 5.23 eV.

A note should be made about the oscillator strengths. The oscillator strengths are calculated as

$$f = \frac{2}{3}\omega_x \langle\tilde{\Psi}_g|\mu|\Psi_x\rangle\langle\tilde{\Psi}_x|\mu|\Psi_g\rangle, \tag{5–3}$$

where ω is the excitation energy. The right-hand ground state is the coupled-cluster wavefunction, the left-hand ground state is the lambda solution from coupled-cluster theory,[107] and the right-hand excited state is the STEOM-CC state. Currently, several approximations are introduced when calculating the left-hand excited state.[64] These sometimes can cause numerical problems with the properties calculated. When the oscillator strength is listed as (—), it means that the approximations are too severe, and the calculated oscillator strength is unreliable. Since the energies are calculated with the right hand excited state wavefunction, they are still correct. For the polarized basis results, another approximation is made. Because the cost of calculating the ground state lambda vector is prohibitive for that large a basis set, the left-hand ground state is estimated with the same approximations as the excited state left-hand wavefunction. In a test calculation with the DZ basis, this makes a difference in the oscillator strengths of less than 20% in every case.

The "D_{4h}" geometry, polarized basis results for the singlet valence states from Tables 5–3 to 5–7 are listed in Table 5–13, along with CASPT2,[152] SAC-CI, [153] previous STEOM-CC,[65] and EOM-CCSD results. The EOM-CCSD calculation is at the "D_{4h}" geometry with the DZ basis. The valence states are numbered for convenience, but these numbers are only accurate through 3^1B_{1g}. After that the Rydberg states should enter into the numbering.

The energy of the first triplet state has been measured in a solvent/ethyl iodide mixture at 77K.[163] The phosphorescence peak is at 1.58 eV, well above the STEOM-CC polarized basis result of 1.26 eV. The CASPT2 result is between the two at 1.37 eV.[152]

Discussion

The recent controversy over the assignment of the spectrum centers around how to assign the N band. The argument of Nakatsuji *et al.*,[153] essentially, is that they calculated no other optically allowed states in the 3–4 eV range, and therefore, by default, the N band must be 2^1B_{2u}. Table 5–13 shows the poor quality of their results. Had they used a decent basis set and had they not made the approximations that are always used in their SAC-CI calculations,[153] their calculated energies would have approached the EOM-CCSD excitation energies, meaning that they all would have increased. At that point, it becomes impossible to draw any meaningful conclusions about the assignment of the spectrum.

The CASPT2[152] results for the B band are too low. This could have been caused by the size of their active space. It has been shown several times[164, 151, 153, 65] that for the 2^1B_{3u} and 2^1B_{2u} states, Gouterman's four orbital model[165–167] is not sufficient; the $4b_{1u}$

orbital must also be included. Merchan *et al.*[152] did not include it in their active space. More CASPT2 calculations, with a larger active space and with *d* functions, would be very informative.

The Q_x and Q_y bands belong to the 1^1B_{3u} and 1^1B_{2u} states. The current results show fortuitously good agreement with the Q_y band. For the Q_x band all of the methods predict too low an excitation energy. A fluorescence spectrum of free base porphin taken in a supersonic jet expansion[168] placed the 0–0 transition for the Q_x band at 2.0234 eV and the 0–0 transition for the Q_y band at 2.4653 eV, slightly higher than the vertical excitation energies reported by Edwards *et al.*[154] The addition of polarization functions increased the Q_x excitation energy by 0.05 eV, so the use of much larger basis sets may further increase the calculated excitation energy, moving it towards the experimental number.

The current results strongly support the original assignment for the B band being both the 2^1B_{3u} and 2^1B_{2u} states. The N band is then assigned to the 3^1B_{3u} state. If the assignments of Nakatsuji *et al.* were correct, it would mean that the polarized basis STEOM-CC energies would have to be 0.19 eV too low for the first L peak and 0.32 eV too low for the second L peak. It is highly unlikely that the STEOM-CC would consistently underestimate the excitation energy like that. Instead, this assignment puts 2^1B_{3u} 0.14 eV above the B peak and 2^1B_{2u} 0.29 eV above the B peak. The 3^1B_{3u} state is 0.41 eV above the N peak. This error is uncomfortably large. However, the energies of all of these states dropped substantially when the polarizations functions were added. Larger basis set calculations should further decrease these gaps.

The intensities still present a problem. The experimental oscillator strength of the N band is less than 0.1, and the calculated oscillator strength is 0.93. Edwards *et al.*[154]

mention that the shape of the B and N bands would be consistent with the two states of the B bands being split by 1500 cm^{-1} and an intense N band donating intensity into the B band. These calculations give a splitting of 1200 cm^{-1} between the $2^1\mathrm{B}_{3\mathrm{u}}$ and $2^1\mathrm{B}_{2\mathrm{u}}$ states. Thus these calculations agree with the possible interpretation given by Edwards *et al.*[154] A B band splitting of 240 cm^{-1} was measured in a low temperature crystal spectrum and assigned to the energy difference between the two electronic states,[169] but this assignment has been disputed.[170]

These assignments then leave the two peaks of the L band assigned to the $3^1\mathrm{B}_{2\mathrm{u}}$ and $4^1\mathrm{B}_{2\mathrm{u}}$ states. The diffuse basis energy for the $3^1\mathrm{B}_{2\mathrm{u}}$ state agrees well with the first L peak, but the $4^1\mathrm{B}_{2\mathrm{u}}$ state is 0.33 eV higher than the second L peak. This difference should also be reduced with larger basis sets. The experimental oscillator strength for the two states combined is about 0.1. The calculated oscillator strengths are well above that. The $1^1\mathrm{B}_{1\mathrm{u}}$ state sits under the L peak, but its intensity is so small that it is not visible.

The one remaining problem with this assignment is the M peak. The calculated excitation energy for the $4^1\mathrm{B}_{3\mathrm{u}}$ state is 5.17 eV, 0.33 eV lower than the M band maximum. The intensities match well, though, and there is no other assignment that makes sense. To say that $4^1\mathrm{B}_{3\mathrm{u}}$ is part of the L band would require that the excitation energy to drop by 0.5 eV, and it would cause problems assigning the other states. Still, it is not clear why the calculated excitation energy would be so low.

Finally, a point should be made about the cost of these calculations. For the polarized basis calculation there are 57 occupied and 283 virtual functions. This gave 2479 T_1 and 34 170 895 T_2 amplitudes. The time taken for each step on a Cray C90 is listed in Table 5–14. It took only 36 seconds per excited state to calculate the energies and properties.

Most of that time was used calculating the properties. The energies took 1.4 seconds each. This is a very important advantage of the STEOM-CC method. The total time for the calculation is effectively independent of the number of excited states calculated. That makes it possible to study entire spectra instead of just a few selected states.

Conclusions

STEOM-CCSD[64] calculation on free base porphin using a [3*s*2*p*1*d*/2*s*] basis set are presented. These are the first reported calculations on excited states above the lowest that use polarization functions. For the important optically allowed excited states, the polarization functions have a significant effect. These calculations strongly support the traditional interpretation of the spectrum, in that the intense B band is assigned to both the 2^1B_{3u} and 2^1B_{2u} states.

This study is possible only because the second similarity transformation in STEOM-CCSD means that the excited states can be represented in terms of single excitations with respect to a highly modified Hamiltonian. Thus it is possible to efficiently calculate many excited states at once.

Table 5–1: Ionization potentials (in eV) for free base porphin.

			"D_{4h}"			"Opt"		
	SAC-CI[a]	STEOM-CC[a]	DZ	diffuse	polarized	DZ	diffuse	Expt.[c]
$1^2A_u(\pi)$	6.35	6.34	6.65	6.63	6.66	6.71	6.69	6.9
$1^2B_{1u}(\pi)$	6.09	6.16	6.46	6.43	6.68	6.48	6.46	7.2
$1^2B_{3g}(\pi)$	7.98	7.84	8.11	8.09	8.19	8.29	8.27	8.4
$2^2B_{1u}(\pi)$	8.21	8.11	8.38	8.36	8.43	8.53	8.51	8.8
$1^2A_g(n)$	8.65	8.50	8.78	8.76	9.18	8.96	8.94	9.1
$1^2B_{2g}(\pi)$	9.10	8.79	9.08	9.06	9.20	9.01	8.99	
$1^2B_{2u}(n)$	8.79	8.57	8.84	8.82	9.23	8.99	8.96	
$3^2B_{1u}(\pi)$	9.34	9.10	9.37	9.36	9.47	9.22	9.20	
$2^2B_{2g}(\pi)$	9.42	9.22	9.50	9.47	9.55	9.43	9.41	
$2^2B_{3g}(\pi)$	9.54	9.31	9.59	9.57	9.64	9.66	9.63	
$2^2A_u(\pi)$	10.85	10.43	10.71	10.69	10.72	10.76	10.74	

a)Ref. 153.

b)Ref. 65.

c)Ref. 162.

Table 5–2: Electron affinities (in eV) for free base porphin.

		"D_{4h}"			"Opt"	
	IP-EOM-CC[a]	DZ	diffuse	polarized	DZ	diffuse
1^2B_{2g}	0.50	0.83	0.81	1.07	0.80	0.78
1^2B_{3g}	0.37	0.70	0.67	0.99	0.78	0.76

a)Ref. 65.

Table 5–3: Singlet excited states of free base porphin through 4.89 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^1B_{3u}$ (V)	1.70 (—)	1.70 (—)	1.75 (0.0007)	1.71 (0.0003)	1.71 (0.0004)
$^1B_{2u}$ (V)	2.59 (0.018)	2.59 (0.017)	2.40 (0.013)	2.65 (0.007)	2.65 (0.006)
$^1B_{1g}$ (V)	3.57	3.56	3.44	3.77	3.78
$^1B_{3u}$ (V)	3.64 (0.982)	3.63 (0.981)	3.47 (0.693)	3.71 (1.21)	3.71 (1.23)
$^1B_{2u}$ (V)	3.74 (1.36)	3.74 (1.37)	3.62 (1.20)	3.78 (1.46)	3.77 (1.48)
^1A_g (V)	4.04	4.04	3.95	4.09	4.10
$^1B_{2g}$ (V)	4.05	4.05	4.21	4.25	4.25
^1A_u (V)	4.09	4.09	4.24	4.26	4.26
$^1B_{3u}$ (V)	4.22 (0.721)	4.22 (0.741)	4.06 (0.931)	4.34 (0.494)	4.35 (0.501)
$^1B_{3g}$ (V)	4.43	4.41	4.51	4.55	4.54
$^1B_{1g}$ (V)	4.44	4.44	4.53	4.41	4.41
$^1B_{1u}$ (V)	4.50 (0.004)	4.48 (0.003)	4.56 (0.002)	4.59 (0.004)	4.58 (0.005)
$^1B_{1u}$ (R)	7.18 (0.008)	4.51 (0.006)	5.48 (0.013)	7.23 (0.006)	4.54 (0.004)
$^1B_{2u}$ (V)	4.63 (0.441)	4.63 (0.444)	4.35 (0.422)	4.65 (0.239)	4.66 (0.241)
^1A_g (V)	4.67	4.66	4.46	4.72	4.72
^1A_u (R)	7.33	4.72	5.52	7.40	4.78
$^1B_{2g}$ (R)	6.63	4.74	5.89	6.63	4.78
$^1B_{1g}$ (V)	4.79	4.78	4.66	4.67	4.67
$^1B_{3g}$ (R)	6.78	4.82	6.04	6.80	4.84
^1A_g (R)		4.89			4.94

Table 5–4: Singlet excited states of free base porphin from 4.94 eV to 5.50 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^1B_{3g}$ (R)	6.83	4.94	5.91	6.87	5.01
^1A_g (V)	5.00	4.99	4.87	5.01	5.02
$^1B_{2g}$ (R)	6.97	5.01	6.08	7.03	5.06
^1A_u (R)	7.14	5.07	6.62	7.14	5.09
$^1B_{1g}$ (R)		5.13			5.19
$^1B_{1u}$ (R)		5.14 (0.0006)	6.89 (0.000003)	7.93 (0.002)	5.17 (0.0005)
$^1B_{1u}$ (R)		5.20 (0.001)			5.22 (0.0008)
$^1B_{2u}$ (V)	5.22 (0.172)	5.22 (0.182)	5.00 (0.153)	5.06 (0.290)	5.07 (0.312)
$^1B_{3u}$ (R)		5.23 (0.007)			5.28 (0.010)
^1A_g (V)	5.28	5.25	5.12	5.26	5.27
$^1B_{1g}$ (V)	5.26	5.26	5.04	5.25	5.25
$^1B_{1u}$ (R)		5.28 (0.000008)		7.37 (0.00002)	5.33 (0.00002)
$^1B_{2u}$ (R)		5.31 (—)		6.65 (0.075)	5.32 (0.002)
^1A_u (R)	8.19	5.33	6.78	8.22	5.40
$^1B_{3u}$ (V)	5.33 (0.400)	5.33 (0.387)	5.17 (0.272)	5.22 (0.471)	5.23 (0.476)
^1A_u (R)		5.39			5.45
$^1B_{2u}$ (R)		5.45 (0.002)			5.52 (0.001)
$^1B_{2g}$ (R)	7.84	5.46	7.43	7.90	5.48
$^1B_{3g}$ (R)		5.47		7.91	5.50
$^1B_{3u}$ (R)		5.50 (—)			5.55 (—)

Table 5–5: Singlet excited states of free base porphin from 5.51 eV to 5.80 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^1B_{1u}$ (R)		5.51 (0.001)			5.54 (0.001)
$^1B_{2g}$ (R)		5.53			5.55
$^1B_{3g}$ (R)		5.56			5.58
^1A_g (R)		5.57			5.60
^1A_g (R)		5.61			5.64
$^1B_{3g}$ (R)		5.65	7.50		5.71
$^1B_{2g}$ (R)		5.66			5.68
$^1B_{2g}$ (R)		5.66			5.72
$^1B_{3g}$ (R)		5.68			5.70
^1A_g (R)		5.69			5.72
^1A_u (R)		5.71			5.77
$^1B_{3g}$ (R)		5.72			5.78
$^1B_{1u}$ (R)		5.72 (0.00004)			5.74 (0.00007)
^1A_g (R)	5.71	5.72	5.51	5.68	5.68
^1A_u (R)		5.73			5.75
$^1B_{1u}$ (R)		5.75 (0.001)			5.78 (0.0007)
$^1B_{2g}$ (R)		5.75			5.81
$^1B_{3u}$ (R)		5.76 (0.002)			5.80 (0.0005)
$^1B_{1g}$ (R)		5.78			5.84
$^1B_{2u}$ (R)		5.80 (0.002)			5.82 (0.002)

Table 5–6: Singlet excited states of free base porphin from 5.80 eV to 6.01 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^1B_{1g}$ (R)		5.80			5.85
^1A_u (R)		5.82			5.84
$^1B_{3g}$ (R)		5.85			5.92
$^1B_{2g}$ (R)		5.87			5.93
$^1B_{1g}$ (R)	5.88	5.88	5.59	5.88	5.90
$^1B_{2g}$ (R)		5.90			5.92
$^1B_{1g}$ (R)		5.90			5.96
$^1B_{3g}$ (R)		5.91			5.93
$^1B_{3g}$ (R)		5.91			5.95
$^1B_{2g}$ (R)		5.92			5.94
^1A_u (R)		5.92			5.99
$^1B_{1u}$ (R)		5.93 (0.00005)			5.99 (0.000002)
^1A_u (R)		5.94			6.00
^1A_g (R)		5.95			5.98
$^1B_{2u}$ (R)		5.97 (0.001)			6.03 (0.0008)
$^1B_{3g}$ (R)	7.89	5.99	6.73		6.10
$^1B_{3u}$ (R)		5.99 (—)			6.05 (—)
$^1B_{1u}$ (R)	7.94 (0.091)	6.00 (0.006)	6.70 (0.021)		6.07 (0.001)
^1A_g (R)		6.01			6.03
$^1B_{1u}$ (R)	7.81 (0.003)	6.01 (0.006)	6.72 (0.020)		6.39 (0.006)

Table 5–7: Singlet excited states of free base porphin from 6.04 eV to 6.23 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^1B_{1u}$ (R)		6.04 (0.001)			6.06 (0.005)
$^1B_{2g}$ (R)		6.05			6.08
$^1B_{3g}$ (R)		6.08			
$^1B_{3g}$ (R)					6.11
$^1B_{1u}$ (R)					6.15 (0.018)
$^1B_{3g}$ (R)		6.09			6.16
$^1B_{2g}$ (R)		6.10			6.16
$^1B_{1u}$ (R)		6.10 (0.0003)			6.12 (0.005)
$^1B_{2g}$ (R)		6.13			6.19
^1A_u (R)		6.14			6.17
$^1B_{1g}$ (R)		6.17			6.24
$^1B_{1u}$ (R)		6.19 (0.022)			6.21 (0.023)
^1A_g (R)		6.19			6.28
$^1B_{1g}$ (R)		6.20			6.25
$^1B_{3u}$ (V)	6.20 (0.166)	6.20 (0.160)	6.07 (0.182)		6.33 (0.110)
^1A_u (R)		6.23			6.29

Table 5–8: Triplet excited states of free base porphin through 4.73 eV. Energies are in eV.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^3B_{2u}$ (V)	1.19	1.19	1.26	1.15	1.15
$^3B_{3u}$ (V)	1.82	1.83	1.80	1.87	1.88
$^3B_{2u}$ (V)	2.02	2.02	1.85	2.07	2.07
$^3B_{3u}$ (V)	2.29	2.28	1.98	2.31	2.31
$^3B_{1g}$ (V)	2.96	2.97	2.87	3.09	3.10
$^3B_{3u}$ (V)	3.10	3.11	2.98	3.21	3.21
^3A_g (V)	3.49	3.48	3.33	3.61	3.61
$^3B_{1g}$ (V)	3.50	3.50	3.45	3.47	3.47
^3A_g (V)	3.81	3.81	3.64	3.82	3.82
$^3B_{1g}$ (V)	4.02	4.02	3.93	3.83	3.84
$^3B_{2g}$ (V)	4.04	4.04	4.19	4.24	4.24
$^3B_{2u}$ (V)	4.08	4.08	3.85	3.90	3.90
^3A_u (V)	4.10	4.10	4.23	4.27	4.27
$^3B_{3g}$ (V)	4.15	4.14	4.29	4.27	4.26
$^3B_{1u}$ (V)	4.20	4.18	4.33	4.28	4.27
$^3B_{2u}$ (V)	4.23	4.24	4.07	4.29	4.31
^3A_g (V)	4.48	4.47	4.31	4.47	4.47
$^3B_{1u}$ (R)	7.17	4.50	5.43	7.22	4.52
^3A_u (R)	7.29	4.71	5.49	7.36	4.77
$^3B_{2g}$ (R)	6.57	4.73	5.85	6.58	4.77

Table 5–9: Triplet excited states of free base porphin from 4.74 eV to 5.47 eV. Energies are in eV.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^3B_{1g}$ (V)	4.76	4.74	4.57	4.82	4.82
$^3B_{3g}$ (R)	6.71	4.81	5.98	6.72	4.83
^3A_g (R)		4.90			4.94
$^3B_{3u}$ (V)	4.92	4.92	4.74	4.83	4.83
$^3B_{3g}$ (R)	6.80	4.93	5.89	6.84	5.01
^3A_g (V)	4.98	4.97	4.76	4.97	4.97
$^3B_{2g}$ (R)	6.50	5.01	6.05	7.00	5.06
^3A_u (R)	7.02	5.06	6.53	7.02	5.08
$^3B_{1g}$ (R)		5.10			5.18
$^3B_{1u}$ (R)		5.13	6.87	7.79	5.17
$^3B_{1u}$ (R)		5.20			5.22
$^3B_{1g}$ (V)	5.24	5.24			5.23
$^3B_{3u}$ (R)		5.24	5.27		5.28
$^3B_{1u}$ (R)	7.34	5.28	6.70	7.37	5.33
$^3B_{2u}$ (R)		5.30			5.32
^3A_u (R)		5.32	6.76	8.19	5.39
$^3B_{2u}$ (R)		5.39	5.28		5.50
^3A_u (R)		5.39			5.45
$^3B_{2g}$ (R)	7.74	5.45		7.80	5.48
$^3B_{3g}$ (R)		5.47			5.49

Table 5–10: Triplet excited states of free base porphin from 5.49 eV to 5.75 eV. Energies are in eV.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^3B_{3u}$ (R)		5.49			5.55
$^3B_{3u}$ (R)	5.51	5.51		5.57	5.63
$^3B_{1u}$ (R)		5.51			5.53
$^3B_{2g}$ (R)		5.52			5.55
$^3B_{3g}$ (R)		5.55			5.57
$^3B_{2u}$ (R)	5.52	5.56		5.59	5.66
^3A_g (R/V)		5.56	5.26	5.59	5.57
^3A_g (R)		5.57			5.60
^3A_g (R)		5.64			5.66
$^3B_{3g}$ (R)		5.65		8.09	5.71
$^3B_{2g}$ (R)		5.66			5.68
$^3B_{2g}$ (R)		5.66			5.72
$^3B_{3g}$ (R)		5.68			5.70
^3A_g (R)		5.70			5.72
^3A_u (R)		5.71			5.77
$^3B_{3g}$ (R)		5.71			5.78
$^3B_{1u}$ (R)		5.71			5.74
^3A_u (R)		5.72			5.75
$^3B_{2g}$ (R)		5.75			5.80
$^3B_{1u}$ (R)		5.75			5.78

Table 5–11: Triplet excited states of free base porphin from 5.77 eV to 5.97 eV. Energies are in eV.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^3B_{3u}$ (R)		5.77			5.80
$^3B_{1g}$ (R)		5.77			5.84
$^3B_{2u}$ (R)		5.80			5.82
$^3B_{1g}$ (R)		5.80			5.87
^3A_u (R)		5.82			5.84
$^3B_{3g}$ (R)		5.85			5.92
$^3B_{2g}$ (R)		5.87			5.93
$^3B_{1g}$ (R)		5.88			5.95
$^3B_{3g}$ (R)		5.89			6.07
$^3B_{2g}$ (R)		5.89	6.64		5.92
$^3B_{3g}$ (R)		5.91			5.93
$^3B_{2g}$ (R)		5.92			5.94
^3A_u (R)		5.92			5.98
$^3B_{1u}$ (R)		5.93			5.99
^3A_u (R)		5.94			6.00
$^3B_{1u}$ (R)	7.75	5.96	6.63		6.09
$^3B_{1g}$ (R)		5.96			6.06
$^3B_{2u}$ (R)		5.96			6.03
$^3B_{3g}$ (R)		5.96			5.94
^3A_g (R)		5.97			5.99

Table 5–12: Triplet excited states of free base porphin from 5.97 eV to 6.11 eV. Energies are in eV.

	"D_{4h}"			"Opt"	
	DZ	diffuse	polarized	DZ	diffuse
$^3B_{3u}$ (R)	5.97	5.97	5.77	6.05	6.07
$^3B_{3u}$ (R)		6.00			6.04
^3A_g (R)		6.00			6.03
$^3B_{1u}$ (R)		6.01			6.06
$^3B_{1u}$ (R)		6.04			6.06
$^3B_{2g}$ (R)		6.05			6.08
$^3B_{3g}$ (R)		6.08			6.11
$^3B_{3g}$ (R)		6.09			6.15
$^3B_{2g}$ (R)		6.10			6.16
$^3B_{1u}$ (R)		6.10			6.13
$^3B_{3g}$ (R)		6.11			6.31

Table 5–13: Singlet valence excited states for free base porphin. Energies are in eV. Oscillator strengths given in parentheses below the excitation energies.

	CASPT2[a]	SAC-CI[b]	EOM-CCSD	STEOM-CC[c]	"D_{4h}" polarized	Expt.[d]
1^1B_{3u}	1.70 (0.001)	1.75 (0.0001)	2.15 (0.0007)	1.72 (—)	1.75 (0.0007)	1.98 Q_x (0.01)
1^1B_{2u}	2.26 (0.016)	2.23 (0.0006)	2.76 (0.007)	2.61 (0.016)	2.40 (0.013)	2.42 Q_y (0.06)
1^1B_{1g}		3.55		3.63	3.44	
2^1B_{3u}	2.91 (1.66)	3.56 (1.03)	3.89 (1.00)	3.66 (1.03)	3.47 (0.693)	3.33 B (1.15)
2^1B_{2u}	3.04 (1.54)	3.75 (1.73)	4.05 (1.56)	3.77 (1.42)	3.62 (1.20)	
2^1A_g		4.25		4.08	3.95	
3^1B_{3u}		4.24 (0.976)	4.51 (0.812)	4.28 (0.71)	4.06 (0.931)	3.65 N (<0.1)
1^1B_{2g}		4.05		4.08	4.21	
1^1A_u		4.18		4.14	4.24	
3^1B_{2u}		4.52 (0.350)	4.83 (0.313)	4.67 (0.44)	4.35 (0.422)	4.25 L (˜0.1)
1^1B_{3g}		4.37		4.45	4.51	
2^1B_{1g}		4.62		4.50	4.53	
1^1B_{1u}		4.51 (0.0005)	4.82 (0.004)	4.54 (0.004)	4.56 (0.002)	
3^1A_g		4.74		4.72	4.46	
3^1B_{1g}		5.13		4.82	4.66	
4^1A_g		5.28		5.06	4.87	
4^1B_{2u}		5.31 (0.280)		5.26 (0.20)	5.00 (0.153)	4.67 L (˜0.1)
5^1A_g				5.32	5.12	
4^1B_{1g}				5.31	5.04	

Table 5–13: (Continued) Singlet valence excited states for free base porphin. Energies are in eV. Oscillator strengths given in parentheses below the excitation energies.

	CASPT2[a]	SAC-CI[b]	EOM-CCSD	STEOM-CC[c]	"D_{4h}" polarized	Expt.[d]
4^1B_{3u}		5.45 (0.351)		5.38 (0.41)	5.17 (0.272)	5.50 M (˜0.3)
5^1B_{3u}				6.26 (0.19)	6.07 (0.182)	
5^1B_{2u}				6.57 (0.002)	6.21 (0.004)	

a)Ref. 152.

b)Ref. 153.

c)Ref. 65.

d)Ref. 154

Table 5–14: User CPU time needed for the steps
in the STEOM-CCSD calculation with the polarized basis.

Step	User CPU Time in Seconds
Integrals	29229
Property Integrals	136
SCF	166
Integral Transformation	2491
Integral Reordering	2744
CCSD	56405
Forming Hbar	3937
11 IP-EOM-CCSD States	243
23 EA-EOM-CCSD States	9873
Forming G	789
84 STEOM-CC States	3016

CHAPTER 6
GRADIENTS FOR THE SIMILARITY TRANSFORMED EQUATION-OF-MOTION COUPLED-CLUSTER METHOD

Theory

As described in Chapter 4, the similarity transformed equation-of-motion coupled-cluster singles and doubles (STEOM-CCSD)[64–66] energy for an excited state is an eigenvector of the double similarity transformed Hamiltonian

$$\begin{aligned} G &= \left\{e^{S}\right\}^{-1} \bar{H} \left\{e^{S}\right\} \\ &= \left\{e^{S}\right\}^{-1} e^{-T} H e^{T} \left\{e^{S}\right\}. \end{aligned} \tag{6–1}$$

Since *G* is not Hermitian, it has different right and left hand eigenvectors. Given a right and left hand eigenvector for a specific state, the energy of the state can be represented as

$$E = \langle 0|LGR|0\rangle, \tag{6–2}$$

where the defining equations for L and R are

$$\langle \mathbf{p}|GR|0\rangle = E\langle \mathbf{p}|R|0\rangle, \tag{6–3}$$

and

$$\langle 0|LG|\mathbf{p}\rangle = E\langle 0|L|\mathbf{p}\rangle. \tag{6–4}$$

The notation here is that the space of all possible determinants is divided into $|\mathbf{h}\rangle = |\mathbf{p}\rangle \oplus |\mathbf{q}\rangle$, as was done by Stanton for equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) gradients.[90–92] The difference is that since the STEOM-CCSD eigenvector only consists of the reference determinant and single excitations, $|\mathbf{p}\rangle$ only includes the reference determinant ($|0\rangle$) and single excitations ($|\mathbf{s}\rangle$). The double ($|\mathbf{d}\rangle$) excitations are a part of $|\mathbf{q}\rangle$.

It is possible to write down an energy functional[94] and take the derivatives of the appropriate quantities in order to derive expressions for the derivative of the STEOM-CCSD energy with respect to a general external perturbation. However, care must be taken since the STEOM-CCSD functional is much more complicated than the EOM-CCSD functional.[94] For EOM-CCSD gradients[90] the quantity Zeta (Z) was introduced in order to guarantee the solution of the ground state coupled-cluster equations and to make the ground state *T* amplitudes stationary with respect to the perturbation, i.e. the role of Lambda (Λ) for ground state coupled-cluster theory.[107] This Z is still needed for STEOM-CCSD, but now two more Z like quantities are needed in order to make the $S^{\pm}$ coefficients stationary with respect to the perturbation. These will be called Z^{+} and Z^{-}, and they have the form

$$\begin{aligned}
\mathrm{Z}^{+} &= \mathrm{Z}_1^{+} + \mathrm{Z}_2^{+} = \sum_{a',e} \zeta^{e}_{a'} \left\{ e^{\dagger} a' \right\} + \frac{1}{2} \sum_{\substack{a,b\\ e,j}} \zeta^{ej}_{ab} \left\{ e^{\dagger} a j^{\dagger} b \right\}, \\
\mathrm{Z}^{-} &= \mathrm{Z}_1^{-} + \mathrm{Z}_2^{-} = \sum_{i',m} \zeta^{i'}_{m} \left\{ i'^{\dagger} m \right\} + \frac{1}{2} \sum_{\substack{m,b\\ i,j}} \zeta^{ij}_{mb} \left\{ i^{\dagger} m j^{\dagger} b \right\}.
\end{aligned} \tag{6–5}$$

Even though $S_1^{\pm}$ are not used in the final diagonalization over singly excited states, they appear in the equations for $S_2^{\pm}$[66] and therefore must appear in the functional. Since $S_1^{\pm}$ appear, Z must also contain one-body components. The forms of $\mathrm{Z}^{\pm}$ can be compared to S^{+} and S^{-}, which are

$$\begin{aligned}
S^{+} &= S_1^{+} + S_2^{+} = \sum_{a',e} s^{a'}_{e} \left\{ a'^{\dagger} e \right\} + \frac{1}{2} \sum_{\substack{a,b\\ e,j}} s^{ab}_{ej} \left\{ a^{\dagger} e b^{\dagger} j \right\}, \\
S^{-} &= S_1^{-} + S_2^{-} = \sum_{i',m} s^{m}_{i'} \left\{ m^{\dagger} i' \right\} + \frac{1}{2} \sum_{\substack{m,b\\ i,j}} s^{mb}_{ij} \left\{ m^{\dagger} i b^{\dagger} j \right\}.
\end{aligned} \tag{6–6}$$

Of course, *T* is the same as previously, namely

$$T = \sum_{i,a} t_i^a \left\{a^\dagger i\right\} + \frac{1}{4} \sum_{\substack{i,j\\a,b}} t_{ij}^{ab} \left\{a^\dagger i b^\dagger j\right\}. \tag{6–7}$$

In order to be consistent with ground state coupled-cluster theory,[107] what was called Z for EOM-CCSD gradients[90] will be called Λ. It has the form

$$\Lambda = \sum_{a,i} \lambda_a^i \left\{i^\dagger a\right\} + \frac{1}{4} \sum_{\substack{a,b\\i,j}} \lambda_{ab}^{ij} \left\{i^\dagger a j^\dagger b\right\}. \tag{6–8}$$

While this notation can be confusing, it should be clear from context what is meant.

The STEOM-CCSD functional is

$$\begin{aligned} F =& \langle 0|LGR|0\rangle + \sum_e \langle \Phi^e|\mathrm{Z}^+ G|\Phi^e\rangle + \sum_m \langle \Phi_m|\mathrm{Z}^- G|\Phi_m\rangle \\ &+ \langle 0|\Lambda \bar{H}|0\rangle + E(1 - \langle 0|LR|0\rangle). \end{aligned} \tag{6–9}$$

The $|\Phi^e\rangle$ and $|\Phi_m\rangle$ are the determinants where an electron has been added to an active virtual orbital and where an electron has been removed from an active occupied orbital, respectively.

The procedure for deriving gradient equations from the functional is the same as that used in Chapter 3; the derivative of the functional with respect to each operator in the formula will be taken and set to zero. What taking the derivative with respect to an operator means is that the derivative with respect to each coefficient within the operator is taken, and the annihilation and creation part of the operator remains. By inspection it can be seen that taking the derivative of *F* with respect to L and R and setting them equal to zero give Eqs. (6–3) and (6–4) respectively. It also can be seen by inspection that taking the derivative with respect to Λ yields the ground state coupled-cluster equations. The derivative with respect to *E* gives the normalization condition for L and R. Therefore, L,R, Λ, and *E* are all stationary with respect to the perturbation.

The result of taking the derivative with respect to Z^+ and Z^- is more difficult to see. For this two new spaces must be introduced. They are $|Q^+\rangle$ and $|Q^-\rangle$, and they are defined as the spaces into which $S^\pm$ project when acting on $|P^+\rangle$ and $|P^-\rangle$ respectively, and where $|P^\pm\rangle$ are the space of all determinants with one electron added to an active virtual orbital or with one electron removed from an active occupied orbital.[66]

Using this notation, the result of taking the derivative of the functional with respect to Z^+ is

$$0 = \frac{\partial F}{\partial Z^+} = \langle Q^+|G|\Phi^e\rangle, \tag{6–10}$$

or equivalently

$$\begin{aligned} 0 &= \langle \Phi_{i'}|G|\Phi^e\rangle, \\ 0 &= \langle \Phi_j^{ba}|G|\Phi^e\rangle. \end{aligned} \tag{6–11}$$

The derivative with respect to Z^- is, for all m

$$0 = \frac{\partial F}{\partial Z^-} = \langle Q^-|G|\Phi_m\rangle, \tag{6–12}$$

or

$$\begin{aligned} 0 &= \langle \Phi_{i'}|G|\Phi_m\rangle, \\ 0 &= \langle \Phi_{ji}^{b}|G|\Phi_m\rangle. \end{aligned} \tag{6–13}$$

These are the equations for the parts of G set to zero in the second similarity transformation,[66] and these equations can be used as the defining equations for S. The fact that, in practice, S is calculated in a different manner does not matter. It is sufficient that these equations are equivalent to the ones used.

Before continuing, it is necessary to introduce another piece of notation. The term connected has been introduced previously, along with its symbol c. Algebraically it means that the two operators share at least one index. Operators which are not connected are disconnected; they share no indices. The symbol *disc* will be used to indicate when operators that potentially could be connected are explicitly disconnected. Disconnected operators containing an even number of annihilation and creation operators commute.[171] Therefore, for the generic operators A and B with an even number of annihilation and creation operators,

$$(AB)_{disc} = (BA)_{disc}. \tag{6–14}$$

By definition,

$$AB = (AB)_c + (AB)_{disc} = (AB)_c + (BA)_{disc}. \tag{6–15}$$

For a discussion about connectedness, see Ref. 116.

In order to continue, it is necessary to expand out G in Eq. (6–9). It has been shown[66] that

$$G = \left(\bar{H}\left\{e^{S}\right\}\right)_c - \left(\left\{e^{S} - 1\right\}G\right)_c. \tag{6–16}$$

For the first term in Eq. (6–9), $\left\{e^{S_1}\right\}$ is not used, and therefore the second term of Eq. (6–16) does not contribute. Breaking the commutator in the first term gives

$$G_2 = \bar{H}\left\{e^{S_2}\right\} - \left(\left\{e^{S_2} - 1\right\}\bar{H}\right)_{disc}, \tag{6–17}$$

where G_2 is used to show that this Hamiltonian was built using $\left\{e^{S_2}\right\}$ only, and the (-1) in the second term is to show that the constant part of the exponential is implicitly connected and is in Eq. (6–16). Substituting Eq. (6–17) into the first term of Eq. (6–9) gives

$$\langle 0|LGR|0\rangle = \langle 0|L\bar{H}\left\{e^{S_2}\right\}R|0\rangle - \langle 0|L\left(\left\{e^{S_2} - 1\right\}\bar{H}\right)_{disc}R|0\rangle. \tag{6–18}$$

The second term is zero, since $\left\{e^{S_2}-1\right\}$ excites into the $|\mathbf{q}\rangle$ space, and L can only connect $\langle 0|$ to $|\mathbf{p}\rangle$.

It has also been shown[66] that

$$\begin{aligned}\langle Q^{\pm}|G|P^{\pm}\rangle =&\langle Q^{\pm}|\bar{H}+\left(\bar{H}S^{\pm}\right)_c|P^{\pm}\rangle\\ &-\langle Q^{\pm}|S^{\pm}|P^{\pm}\rangle\langle P^{\pm}|\bar{H}+\left(\bar{H}S^{\pm}\right)_c-E_{CC}|P^{\pm}\rangle,\end{aligned} \tag{6–19}$$

where E_{CC} stands for the ground state coupled-cluster energy. The connectedness in the second term on the right is redundant; $S^{\pm}$ must be connected to $\bar{H}$ to give an nonzero contribution.

Substituting Eqs. (6–18) and (6–19) into Eq. (6–9) gives

$$\begin{aligned}F =&\langle 0|L\bar{H}\left\{e^{S_2}\right\}R|0\rangle\\ &+\sum_e\langle\Phi^e|\mathrm{Z}^+\left(\bar{H}+\left(\bar{H}S^+\right)_c\right)|\Phi^e\rangle\\ &-\sum_e\langle\Phi^e|Z^+S^+|P^+\rangle\langle P^+|\left(\bar{H}\left(1+S^+\right)-E_{CC}\right)|\Phi^e\rangle\\ &+\sum_m\langle\Phi_m|\mathrm{Z}^-\left(\bar{H}+\left(\bar{H}S^-\right)_c\right)|\Phi^m\rangle\\ &-\sum_m\langle\Phi_m|Z^-S^-|P^-\rangle\langle P^-|\left(\bar{H}\left(1+S^-\right)-E_{CC}\right)|\Phi_m\rangle\\ &+\langle 0|\Lambda\bar{H}|0\rangle+E(1-\langle 0|LR|0\rangle).\end{aligned} \tag{6–20}$$

It is now possible to continue taking derivatives of the functional with respect to the operators it contains. Since, L, R, Λ, E, and $\mathrm{Z}^{\pm}$ have been considered, only S^+, S^-, and T remain. The annihilation and creation portions of these operators will be called Ω_{S^+}, Ω_{S^-}, and Ω_T, respectively. Remember, these are the parts of the operators remaining after the derivative with respect to the operator has been taken.

The first term to consider is S^{+}. Taking the derivative of the functional with respect to it gives for all *f* and κ, where κ is a generic $|Q\rangle$ space determinant,

$$\begin{aligned}
0 =& \frac{\partial F}{\partial S^{+}} = \frac{\partial F}{\partial S_f^{\kappa}} \\
=& \langle 0|L\bar{H}\Big\{e^{S_2}\Omega_{S_2^{+}}\Big\}R|0\rangle \\
&+ \sum_e \langle \Phi^e|\mathrm{Z}^{+}\Big(\bar{H}\Omega_{S_f^{\kappa}}\Big)_c|\Phi^e\rangle\delta_{ef} \\
&- \sum_e \langle \Phi^e|\mathrm{Z}^{+}\Omega_{S_f^{\kappa}}|\Phi^f\rangle\langle\Phi^f|\big(\bar{H}\big(1+S^{+}\big)-E_{CC}\big)|\Phi^e\rangle \\
&- \sum_e \langle \Phi^e|\mathrm{Z}^{+}S^{+}|P^{+}\rangle\langle P^{+}|\bar{H}\Omega_{S_f^{\kappa}}|\Phi^e\rangle\delta_{ef},
\end{aligned} \tag{6–21}$$

or

$$\begin{aligned}
0 =& \langle 0|L\bar{H}\Big\{e^{S_2}\Omega_{S_2^{+}}\Big\}R|0\rangle \\
&+ \langle \Phi^f|\mathrm{Z}^{+}\Big(\bar{H}\Omega_{S_f^{\kappa}}\Big)_c|\Phi^f\rangle - \langle\Phi^f|\mathrm{Z}^{+}S^{+}|P^{+}\rangle\langle P^{+}|\bar{H}|\Phi^{\kappa}\rangle \\
&- \sum_e \langle \Phi^e|\mathrm{Z}^{+}|\Phi^{\kappa}\rangle\langle\Phi^f|\big(\bar{H}\big(1+S^{+}\big)-E_{CC}\big)|\Phi^e\rangle.
\end{aligned} \tag{6–22}$$

Inserting a resolution of the $|Q\rangle$ space into the second and third terms yields for all *f* and κ

$$\begin{aligned}
0 =& \langle 0|L\bar{H}\Big\{e^{S_2}\Omega_{S_2^{+}}\Big\}R|0\rangle \\
&+ \sum_\eta \langle \Phi^f|\mathrm{Z}^{+}|\Phi^{\eta}\rangle\langle\Phi^{\eta}|\Big(\bar{H}\Omega_{S_f^{\kappa}}\Big)|\Phi^f\rangle \\
&- \sum_\eta \langle \Phi^f|\mathrm{Z}^{+}|\Phi^{\eta}\rangle\langle\Phi^{\eta}|S^{+}|P^{+}\rangle\langle P^{+}|\bar{H}|\Phi^{\kappa}\rangle \\
&- \sum_e \langle \Phi^f|\big(\bar{H}\big(1+S^{+}\big)-E_{CC}\big)|\Phi^e\rangle\langle\Phi^e|\mathrm{Z}^{+}|\Phi^{\kappa}\rangle,
\end{aligned} \tag{6–23}$$

where η is another generic $|Q\rangle$ space determinant. In matrix form, Eq. (6–23) is

$$\begin{aligned}
\langle 0|L\bar{H}\Big\{e^{S_2}\Omega_{S_2^{+}}\Big\}R|0\rangle =& \langle P^{+}|\big(\bar{H}\big(1+S^{+}\big)-E_{CC}\big)|P^{+}\rangle\langle P^{+}|\mathrm{Z}^{+}|Q^{+}\rangle \\
&+ \langle P^{+}|\mathrm{Z}^{+}|Q^{+}\rangle\langle Q^{+}|S^{+}|P^{+}\rangle\langle P^{+}|\bar{H}|Q^{+}\rangle \\
&- \langle P^{+}|\mathrm{Z}^{+}|Q^{+}\rangle\langle Q^{+}|\big(\bar{H}\Omega_{S^{+}}\big)_c|P^{+}\rangle.
\end{aligned} \tag{6–24}$$

Taking the derivative with respect to S^- and following the same procedure as above gives

$$\begin{aligned}\langle 0|L\bar{H}\Big\{e^{S_2}\Omega_{S_2^-}\Big\}R|0\rangle =&\langle P^-|\big(\bar{H}\big(1+S^-\big)-E_{CC}\big)|P^-\rangle\langle P^-|\mathrm{Z}^-|Q^-\rangle\\ &+\langle P^-|\mathrm{Z}^-|Q^-\rangle\langle Q^-|S^-|P^-\rangle\langle P^-|\bar{H}|Q^-\rangle\\ &-\langle P^-|\mathrm{Z}^-|Q^-\rangle\langle Q^-|\big(\bar{H}\Omega_{S^-}\big)_c|P^-\rangle.\end{aligned} \tag{6–25}$$

Equations (6–24) and (6–25) can be solved iteratively to calculate Z$^\pm$.

Before taking the derivative of the functional with respect to *T*, it will be useful to remember that

$$\frac{\partial\bar{H}}{\partial T}=\frac{\partial}{\partial T}\Big(e^{-T}He^{T}\Big)=e^{-T}He^{T}\Omega_T-\Omega_T e^{-T}He^{T}=\big[\bar{H},\Omega_T\big]. \tag{6–26}$$

The derivative of Eq. (6–20) with respect to *T* is then

$$\begin{aligned}0=\frac{\partial F}{\partial T}=&\langle 0|L\big[\bar{H},\Omega_T\big]\Big\{e^{S_2}\Big\}R|0\rangle\\ &+\sum_e\langle\Phi^e|\mathrm{Z}^+\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^+\big)_c\big)|\Phi^e\rangle\\ &-\sum_e\langle\Phi^e|\mathrm{Z}^+S^+|P^+\rangle\langle P^+|\big[\bar{H},\Omega_T\big]\big(1+S^+\big)|\Phi^e\rangle\\ &+\sum_m\langle\Phi_m|\mathrm{Z}^-\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^-\big)_c\big)|\Phi_m\rangle\\ &-\sum_m\langle\Phi_m|\mathrm{Z}^-S^-|P^-\rangle\langle P^-|\big[\bar{H},\Omega_T\big]\big(1+S^-\big)|\Phi_m\rangle\\ &+\langle 0|\Lambda\big[\bar{H},\Omega_T\big]|0\rangle.\end{aligned} \tag{6–27}$$

Focusing on the last term,

$$\begin{aligned}\langle 0|\Lambda\big[\bar{H},\Omega_T\big]|0\rangle&=\langle 0|\Lambda\bar{H}\Omega_T|0\rangle-\langle 0|\Lambda\Omega_T\bar{H}|0\rangle\\ &=\langle 0|\Lambda\bar{H}|\mathbf{s}+\mathbf{d}\rangle-\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle\langle 0|\bar{H}|0\rangle\\ &=\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle\langle\mathbf{s}+\mathbf{d}|\big(\bar{H}-\mathbf{1}E_{CC}\big)|\mathbf{s}+\mathbf{d}\rangle,\end{aligned} \tag{6–28}$$

where **1** is a unit matrix of the appropriate rank. Inserting Eq. (6–28) into Eq. (6–27) gives

$$\begin{aligned}
0 = &\langle 0|L\big[\bar{H},\Omega_T\big]\Big\{e^{S_2}\Big\}R|0\rangle \\
&+\sum_e \langle\Phi^e|\mathrm{Z}^+\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^+\big)_c\big)|\Phi^e\rangle \\
&-\sum_e \langle\Phi^e|\mathrm{Z}^+S^+|P^+\rangle\langle P^+|\big[\bar{H},\Omega_T\big]\big(1+S^+\big)|\Phi^e\rangle \\
&+\sum_m \langle\Phi_m|\mathrm{Z}^-\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^-\big)_c\big)|\Phi_m\rangle \\
&-\sum_m \langle\Phi_m|\mathrm{Z}^-S^-|P^-\rangle\langle P^-|\big[\bar{H},\Omega_T\big]\big(1+S^-\big)|\Phi_m\rangle \\
&+\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle\langle\mathbf{s}+\mathbf{d}|\big(\bar{H}-\mathbf{1}E_{CC}\big)|\mathbf{s}+\mathbf{d}\rangle,
\end{aligned} \tag{6–29}$$

and solving for Λ yields

$$\begin{aligned}
\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle = -[&\langle 0|L\big[\bar{H},\Omega_T\big]\Big\{e^{S_2}\Big\}R|0\rangle \\
&+\sum_e \langle\Phi^e|\mathrm{Z}^+\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^+\big)_c\big)|\Phi^e\rangle \\
&-\sum_e \langle\Phi^e|\mathrm{Z}^+S^+|P^+\rangle\langle P^+|\big[\bar{H},\Omega_T\big]\big(1+S^+\big)|\Phi^e\rangle \\
&+\sum_m \langle\Phi_m|\mathrm{Z}^-\big(\big[\bar{H},\Omega_T\big]+\big(\big[\bar{H},\Omega_T\big]S^-\big)_c\big)|\Phi_m\rangle \\
&-\sum_m \langle\Phi_m|\mathrm{Z}^-S^-|P^-\rangle\langle P^-|\big[\bar{H},\Omega_T\big]\big(1+S^-\big)|\Phi_m\rangle] \\
\times[&\langle\mathbf{s}+\mathbf{d}|\big(\bar{H}-\mathbf{1}E_{CCSD}\big)|\mathbf{s}+\mathbf{d}\rangle]^{-1}.
\end{aligned} \tag{6–30}$$

With these definitions of $\mathrm{Z}^{\pm}$ and Λ, the derivative the functional with respect to all of the terms which appear in it is zero, and the generalized Hellmann-Feynmann theorem[117, 118] can be applied. Therefore, the derivative of the STEOM-CCSD energy with respect to any perturbation χ is

$$\begin{aligned}\frac{\partial E}{\partial \chi} = \frac{\partial F}{\partial \chi} =& \langle 0|L\bar{H}\left\{e^{S_2}\right\}R|0\rangle \\ &+ \sum_e \langle \Phi^e|\mathrm{Z}^+\big(\bar{H}^\chi + \big(\bar{H}^\chi S^+\big)_c\big)|\Phi^e\rangle \\ &- \sum_e \langle \Phi^e|Z^+ S^+|P^+\rangle\langle P^+|\bar{H}^\chi\big(1+S^+\big)|\Phi^e\rangle \\ &+ \sum_m \langle \Phi_m|\mathrm{Z}^-\big(\bar{H}^\chi + \big(\bar{H}^\chi S^-\big)_c\big)|\Phi^m\rangle \\ &- \sum_m \langle \Phi_m|Z^- S^-|P^-\rangle\langle P^-|\bar{H}^\chi\big(1+S^-\big)|\Phi_m\rangle \\ &+ \langle 0|\Lambda\bar{H}^\chi|0\rangle.\end{aligned} \tag{6–31}$$

with

$$\bar{H}^\chi = e^{-T}\frac{\partial H}{\partial \chi}e^T. \tag{6–32}$$

So far, the derivation has been for excitation energy STEOM-CCSD (EE-STEOM-CCSD)[64] gradients, but their extension to double ionization potential STEOM-CCSD (DIP-STEOM-CCSD)[66] or double electron attachment STEOM-CCSD (DEA-STEOM-CCSD)[66] is straightforward. The only difference in the algebraic equations is that for DIP-STEOM-CC, S^+ does not appear,[66] and therefore Z^+ will not appear in the functional. Likewise, for DEA-STEOM-CC, S^- does not appear,[66] which leads to Z^- not being in the functional.

One extra consideration arises with STEOM-CC gradients. In normal coupled-cluster gradients, the equations for the response of the orbitals to the perturbation are simplified by using the fact that the method is invariant to rotation among the occupied orbitals and among the virtual orbitals.[109] In STEOM-CC, because of the splitting of the orbitals into an active set and an inactive set, this invariance to orbital rotations does not hold. The solution is simple, though. In the derivation of gradients for the case that some orbitals are not correlated,[172] the extra terms that arise have already been included, and the same code can be used here.

Applications

In order to test how well STEOM-CCSD describes excited state potential energy surfaces, the diatomic molecule examples[93] from Chapter 3 were tested. The STEOM-CCSD gradients are an iterative $n_{occ}^2 N_{virt}^4$ method, both from the ground state CCSD and from the calculation of the excited state Λ. Therefore, the only fair comparison for STEOM-CCSD is EOM-CCSD. The STEOM-CCSD gradients will be about half as expensive as EOM-CCSD gradients. Gradients for the STEOM-PT2 method[64] should have roughly the same cost as P-EOM-MBPT(2)[114] gradients.

The active space used for H_2 consisted of the 1–4σ_g^+, 1–3σ_u^-, $1\pi_u$, $1\pi_g$, and $1\delta_g$ orbitals, giving a percent active space of 99.7% for the $1^1\Sigma_u^-$ state at the excited state minimum geometry. The active space for BH was 1–7σ and 1–3π, giving a 98.2% active space component for the $1^1\Pi$ state at its minimum. For CO the active space was 4–10σ, 1–4π, and 1δ, giving a 98.7% active space component for the $1^1\Pi$ state at its minimum. For N_2 the active space was 3–6σ_g^+, 2–5σ_u^-, 1–2π_u, 1–2π_g, and $1\delta_g$, giving a 99.2% active space component for the $1^1\Pi_g$ state at its minimum. For BF the active space was 4–10σ, 2–4π and 1δ, giving a 98.9% active space component for the $1^1\Pi$ state at its minimum. Finally, the active state for C_2 was 3–5σ_g^+, 2–3σ_u^-, 1–2π_u, 1–2π_g, and $1\delta_g$, giving a 99.8% active space component for the $1^1\Pi_u$state at its minimum.

The active spaces were chosen by including all orbitals for which the corresponding IP-EOM-CCSD[67] or EA-EOM-CCSD[68] state could be converged and for which the state consisted of greater than seventy percent single excitation character. Since the decoupling caused by the second similarity transformation depends on the S_2 coefficients being small, any IP-EOM-CCSD or EA-EOM-CCSD states with less than seventy percent single excitation character are automatically excluded from the transformation.

The vertical excitation energies for each molecule are listed in Table 6–1. The aug-cc-pVTZ basis set[121] was used for all of the calculations, and only the spherical components of the *d* and *f* functions were kept. The ground state geometries used were the aug-cc-pVTZ CCSD geometries from Table 3–3. Except for N_2. the EOM-CCSD and STEOM-CCSD vertical excitation energies agree pretty well.

The adiabatic excitation energies are given in Table 6–2. The EOM-CCSD and STEOM-CCSD are very close for BH, BF, and C_2. For H_2 the EOM-CCSD and STEOM-CCSD straddle the experiment, with the EOM-CCSD being a little closer. For CO the STEOM-CCSD is 0.15 eV lower than the EOM-CCSD, and for N_2 the STEOM-CCSD is 0.28 eV lower. In both cases the STEOM-CCSD agrees better with the experimental adiabatic excitation energy.[122] Presumably, for excitations out of the triple bond, the better description of higher excitations given by STEOM-CCSD is important.

The equilibrium distances for the excited states are given in Table 6–3. Except for H_2, the EOM-CCSD and STEOM-CCSD geometries are quite close. It is not clear why H_2 shows such a big discrepancy. EOM-CCSD for H_2 is exact within a basis set, so the difference must be attributed to a shortcoming in the STEOM-CCSD. The fact that the rest of the equilibrium bond lengths agree well with the EOM-CCSD and with the experiment gives confidence that the problem with H_2 is an anomaly.

That the H_2 excited state vibrational frequency, as given in Table 6–4, does not agree with the EOM-CCSD frequency should be attributed to the problem with the bond length.

Even still, its agreement with the experimental vibrational frequency is satisfactory. For all of the molecules, the error in the vibrational frequency is about the same for the two methods.

One final note should be made about the dependence of the STEOM-CCSD results on the choice of active space. Conspicuous by their absence in the active space for BF are the (occupied) 1π orbitals. They are not included because at the ground state minimum geometry, the EA-EOM-CCSD state which corresponds to them is only about fifty percent single excitations. However, at the excited state minimum, the percentage is just over seventy percent. Some test calculations were run to determine the effect of including them in the active space. When that was done, the adiabatic excitation energy dropped to 6.331 eV, in better agreement with the experimental adiabatic excitation energy. On the other hand the excited state bond length decreased to 1.291 Å, and the vibrational frequency decreased to 1183 cm^{-1}, both in noticeably worse agreement with experiment. The strangest part, though, was that adding the functions to the active space decreased the percent active space component to 97.8% from 98.9%. It is not clear why adding functions to the active space would decrease the percent active space component. But this does show that the issue of active spaces in STEOM-CCSD needs further study.

Table 6–1: Vertical excitation energies (in eV) for the excited singlet states

	EOM-CCSD[a]	STEOM-CCSD
H_2	12.717	12.723
BH	2.914	2.934
CO	8.666	8.552
N_2	9.514	9.302
BF	6.454	6.469
C_2	1.308	1.285

a)Ref. 93.

Table 6–2: Adiabatic excitation energies (in eV) for the excited singlet states

	EOM-CCSD[a]	STEOM-CCSD	Expt.[b]
H_2	11.353	11.422	11.3694
BH	2.913	2.934	2.8685
CO	8.256	8.107	8.0684
N_2	8.839	8.560	8.5900
BF	6.417	6.425	6.3427
C_2	1.103	1.098	1.0404

a)Ref. 93.

b)Ref. 122.

Table 6–3: Equilibrium distances (in Å) for the excited singlet states

	EOM-CCSD[a]	STEOM-CCSD	Expt.[b]
H_2	1.283	1.258	1.2928
BH	1.211	1.214	1.2186
CO	1.224	1.232	1.2353
N_2	1.202	1.208	1.2203
BF	1.304	1.308	1.3038
C_2	1.318	1.314	1.3184

a)Ref. 93.

b)Ref. 122.

Table 6–4: Harmonic vibrational frequencies (in cm^{-1}) for the excited singlet states

	EOM-CCSD[a]	STEOM-CCSD	Expt.[b]
H_2	1368	1344	1358.09
BH	2372	2371	2251.0
CO	1592	1586	1518.2
N_2	1854	1837	1694.21
BF	1279	1248	1264.9
C_2	1630	1652	1608.35

a)Ref. 93.

b)Ref. 122.

CHAPTER 7
A FINAL WORD

In this dissertation two new methods were presented for calculating excitation energies of atoms and molecules. The new methods are the partitioned equation-of-motion coupled-cluster singles and doubles (P-EOM-CCSD) method and the partitioned equation-of-motion second order many-body perturbation theory (P-EOM-MBPT(2)) method.[114] These methods were shown to have great promise for calculating vertical excitation energies, but they consistently were a little worse for valence excited states than for Rydberg excited states.

Gradients for the P-EOM-MBPT(2) method were developed. Being able to analytically calculate the derivative of the energy with respect to an external perturbation (such introducing an electric field or moving an atom) not only allows for the efficient and accurate calculation of one electron properties for the state of interest, but also it makes possible efficient searches of potential energy surfaces for extrema, such as minima or transition states. Ultimately, if a computational method is going to be useful for describing a variety of chemistry, it must have gradients available.

Being able to search potential energy surfaces also provides more demanding tests for a computational method. If structures are to be determined, it is not sufficient to be able to accurately describe just one region of the potential energy surface. Any method that can only accurately describe a small region of the surface is of limited use, since it may be difficult to know *a priori* whether or not the structures of interest lie within the well-described region.

In the end, the performance of the P-EOM-MBPT(2) method for excited state surfaces was mixed. The method was almost always qualitatively correct, but only sometimes quantitatively correct. Because of its reduced cost relative to EOM-CCSD gradients,[90] the method is still useful as a relatively simple and inexpensive way to account for electron correlation in excited state energies and structures and as a way to generate a good initial guess for an EOM-CCSD structure search.

Since an inexpensive method that gives consistently reliable results for excited state structures is still needed, focus shifts to the new similarity transformed equation-of-motion coupled-cluster singles and doubles (STEOM-CCSD) method.[64] As an example of the power of the STEOM-CCSD method, the vertical excited state spectrum of free base porphin was studied. This study shows how accurate calculations, even without including the effects of geometry relaxation, can be used to interpret complicated spectra. The ability of STEOM-CCSD to calculate many excited states quickly was important in that it allowed the calculation of essentially the entire spectrum in the energy range of interest. These calculations also showed the importance of care in choosing the details of the calculation, such as the basis set and the active space.

Finally, gradients for STEOM-CCSD were developed. Because of the complicated structure of the STEOM-CC method, the gradient equations are tedious. But eventually the equations take on a very nice structure. Initial tests on very simple molecules look promising, but it is clear that many issues involving the role of the active space in STEOM-CC remain to be explored.

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BIOGRAPHICAL SKETCH

Steven Ray Gwaltney was born on July 21, 1970, in Indianapolis, Indiana to Charles and Catherine Gwaltney. Steven has one brother, David Gwaltney. His father was a high school science teacher (now retired) and his mother is an elementary school reading teacher who took several years off before her sons went to school.

Growing up in a family of teachers meant that Steven knew he had to work hard at school. He was still quite strong willed, though. Some very caring teachers encouraged him, but at the same time they showed him that he had to do the necessary work, even if he felt it was not needed.

In junior high school, Steven started wrestling and playing football. However, after his freshman year, he dropped both for more academic pursuits. He got involved in high school choir, musicals, and many math and science contests. In May of 1988, Steven graduated seventh out of a class of 742 at Warren Central High School in Indianapolis, Indiana. He received many academic awards, including being a National Merit finalist.

In the fall of 1988 Steven matriculated at Indiana University in Bloomington, Indiana, to major in chemistry. In his junior year, he started doing undergraduate research with Prof. Ernest Davidson. This continued through the Summer of 1991, in which he did research full time, until he graduated in May of 1992. Steven graduated with highest distinction and received several academic awards and honors, including being named the Outstanding Senior B.S. Chemistry major by the Chemistry Department and being inducted into Phi Beta Kappa.

Growing up, Steven had always been very active in his church. When he went away to college, he found a church in Bloomington and got involved in the Baptist Student Union. It was through the Baptist Student Union that he spent the summer of 1990 as a missionary in the suburbs of Chicago. It was also through the Baptist Student Union that he met Charity Altman. Steven and Charity were married July 25, 1992.

Less than two weeks later, Steven and Charity moved to Gainesville, Florida, where Steven started graduate school at the University of Florida. Steven is now in his sixth year as a graduate student in the Department of Chemistry. His research advisor is Prof. Rodney Bartlett. This has also been a fertile learning experience, with the interaction within the Quantum Theory Project and with the interaction with other scientists at various conferences. These years have also been a good experience for Steven and Charity as a family. Charity gave birth to their first child, Caleb Steven Gwaltney, on May 5, 1997.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Rodney J. Bartlett, Chair
Graduate Research Professor of
Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

N. Yngve Öhrn
Professor of Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Philip J. Brucat
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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