

Second-order perturbation corrections to singles and doubles coupled-cluster methods: General theory and application to the valence optimized doubles model

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(Received 4 February 2000; accepted 11 May 2000)

We present a general perturbative method for correcting a singles and doubles coupled-cluster energy. The coupled-cluster wave function is used to define a similarity-transformed Hamiltonian, which is partitioned into a zeroth-order part that the reference problem solves exactly plus a first-order perturbation. Standard perturbation theory through second-order provides the leading correction. Applied to the valence optimized doubles (VOD) approximation to the full-valence complete active space self-consistent field method, the second-order correction, which we call (2), captures dynamical correlation effects through external single, double, and semi-internal triple and quadruple substitutions. A factorization approximation reduces the cost of the quadruple substitutions to only sixth order in the size of the molecule. A series of numerical tests are presented showing that VOD(2) is stable and well-behaved provided that the VOD reference is also stable. The second-order correction is also general to standard unwidowed coupled-cluster energies such as the coupled-cluster singles and doubles (CCSD) method itself, and the equations presented here fully define the corresponding CCSD(2) energy. © 2000 American Institute of Physics.
[S0021-9606(00)30130-1]

I. INTRODUCTION

Methods for approximately solving for the electronic energy of a molecular system often exploit a partitioning of the energy into two terms. The first contribution solves a reference problem that contains the leading energetic contributions. In general this problem must be solved in an iterative, or self-consistent fashion. The second contribution, which is in general much smaller, is often approximately obtained as a noniterative (perturbative) correction to the reference problem. The simplified treatment of the correction makes the overall theory far more feasible than a full treatment of the entire problem. At the same time it should be more accurate than neglecting the correction entirely.

The standard example is the partitioning of the electronic energy into a mean-field part (typically 99% of the total energy), plus a correlation correction, which can be evaluated by perturbation theory (or other methods). Second-order perturbation theory (MP2)¹ is the simplest example of this type. A second standard example is to break the correlation correction itself into two pieces. The leading correlation contributions are treated self-consistently, such as by coupled-cluster theory, and the residual correction is then evaluated noniteratively. The QCISD(T)² and CCSD(T)³ methods are of this type: A reference problem is solved in the space of all single and double substitutions, and the residual contribution of triple substitutions is then obtained as a noniterative cor-

rection. This dramatically improves the accuracy relative to adding no such correction and at the same time dramatically reduces the cost relative to self-consistent treatment of the triple substitutions.

The third example of such a splitting is the one that relates to this work. It is conceptually and practically useful to split the correlation energy into a part associated with correlations that involve substitutions of valence occupied orbitals by valence unoccupied orbitals. The correlation energy in this limited full valence space is sufficient to describe the leading contributions to bond-breaking processes, as well as the structure of nonclosed shell species such as diradicals. This “nondynamical” correlation energy⁴⁻⁶ requires a much higher level of treatment than the remaining “dynamical” correlations, which are far more atomiclike in nature. A complete description of electron correlations within the full valence space is given by solution of the Schrödinger equation in this space. This is accomplished in the complete active space self-consistent field (CASSCF)⁷ method. However, the cost scales factorially with the number of atoms in the molecule. Therefore, approximations are necessary even for quite small systems.

We have recently shown that a very accurate approximation to full valence CASSCF can be obtained with a coupled-cluster wave function where the substitutions are restricted to lie in an active space whose orbitals are variationally optimized.⁸ The simplest version of this theory is to restrict the cluster substitutions to doubles, yielding the valence optimized-orbital coupled-cluster doubles (VOO-CCD)⁸ method. For conciseness we refer to this simply as valence

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optimized doubles (VOD). VOD provides a near quantitative approximation to full valence CASSCF for processes in which no more than one chemical bond is broken in a local spatial region. In addition, VOD reduces the factorial cost of full valence CASSCF to scaling with only the sixth power of molecule size (and indeed, it can be lower with local correlation approximations).

The question we seek to address in this work is how to define a perturbative correction to VOD that can account for the omitted dynamical correlation contributions without greatly increasing the computational cost. The methods used to perturbatively correct full valence CASSCF calculations (such as CASPT2,^{9,10} and alternatives) are not applicable because of the coupled-cluster nature of the VOD reference. Furthermore, because VOD as a reference function is significantly more flexible than an SCF reference, it is important that the correction should not be based on Möller–Plesset theory, as that perturbation theory fails when the SCF reference becomes poor.

This paper presents our solution to this problem. It is based on defining a similarity-transformation of the Hamiltonian using the truncated cluster amplitudes. This Hamiltonian is then partitioned into a zeroth-order part that the truncated coupled-cluster problem (VOD) solves exactly plus a first-order perturbation. Second-order perturbation theory is then employed to obtain the leading correction to the VOD energy. We term the resulting method VOD(2) for obvious reasons. As it depends only on the VOD reference (specifically it does not depend in any way upon mean-field Hartree–Fock theory), VOD(2) should be stable and well-behaved whenever the VOD reference itself is. VOD(2) contains four separate terms that involve single, double, triple, and quadruple substitutions. We consider these terms in detail, and force a factorization of the quadruple substitutions to ensure that the computational cost is reasonable. The final section of the paper presents a series of calculations that explore the performance of VOD(2) numerically.

It may be evident to the reader that the solution we are proposing is actually somewhat more general than the question we were originally asking. A second-order correction of this kind can, in fact, be directly applied to any cluster method based on single and double substitutions. As this correction is designed to be robust even in cases where the Hartree–Fock single reference is poor, it presents an interesting alternative to methods of the CCSD(T) and QCISD(T) type that are still dependent upon the single reference performing well. In a separate publication¹¹ we explore this approach in the context of the optimized-orbital coupled-cluster doubles method^{12–15} and show that significant improvements against the standard triples corrections are, in fact, obtained. Elsewhere we shall also report on the related problem of the second-order correction to the CCSD¹² and QCISD² methods.

II. THEORY

A. VOD

We will begin with a quick overview of VOD. The process of choosing an active space consists of dividing up the

orbital space into active and inactive occupied and virtual orbitals. We will use the letters i, j, k, l, \dots to refer to any spin-orbital occupied in the reference determinant, with I, J, K, L, \dots standing for active occupied spin-orbitals, and i', j', k', l', \dots standing for inactive occupied spin-orbitals. Similarly, a, b, c, d, \dots will refer to any spin-orbital unoccupied in the reference determinant, with A, B, C, D, \dots standing for active unoccupied spin-orbitals, and a', b', c', d', \dots standing for inactive unoccupied spin-orbitals. For spin-orbitals of unspecified occupancy we will use p, q, r, s, \dots , with capitals and primes carrying their same meaning. Later in this paper a recognition of the tensorial nature of the equations is essential. Therefore, we will also use the tensor nomenclature introduced in Ref. 16, with all quantities written in the mixed representation.

Using this notation, the VOD equations are^{8,14}

$$\langle 0 | e^{-T_2} H_N e^{T_2} | 0 \rangle = E_{cc}, \quad (1)$$

$$\langle \Phi_{\bullet\bullet}^{AB} | e^{-T_2} H_N e^{T_2} | 0 \rangle = \mathbf{0}, \quad (2)$$

$$\mathbf{C} = \mathbf{C}^0 \mathbf{U}(\theta), \quad (3)$$

$$\frac{\partial E}{\partial \mathbf{U}(\theta)} \frac{\partial \mathbf{U}(\theta)}{\partial \theta} = \mathbf{0}. \quad (4)$$

Here, $|0\rangle$ is the reference determinant determined by the optimization procedure,

$$H_N = H - \langle 0 | H | 0 \rangle = f_{\bullet q}^p \{ a_p^\dagger a^q \} + \frac{1}{4} W_{\bullet\bullet}^{pq} \{ a_p^\dagger a_q^\dagger a^s a^r \}, \quad (5)$$

is the normal-product Hamiltonian in second quantization, and

$$T_2 = \frac{1}{4} t_{\bullet\bullet}^{AB} \{ a_A^\dagger a^I a_B^\dagger a^J \}, \quad (6)$$

is the coupled-cluster excitation operator. In the VOD model, T_2 consists of only double excitations in the active space. The first equation defines the coupled-cluster energy, which in the VOD model is the nondynamical correlation energy. The total energy is then $E = E_{cc} + \langle 0 | H | 0 \rangle$. Solving the second equation gives the cluster amplitudes. Also, \mathbf{C} is the molecular orbital matrix. It is defined as the product of some set of guess orbitals \mathbf{C}^0 and a transformation matrix \mathbf{U} , parameterized by a set of orbital transformation angles θ .¹⁴ Together, Eqs. (3) and (4) define the variationally optimized molecular orbitals. Note that $e^{-T} H_N e^T = (H_N e^T)_c$, where the subscript c means that the equations must be connected.

For the current work it will be helpful to rewrite Eqs. (1) and (2) as

$$\langle 0 | (1 + \Lambda_2) e^{-T_2} H_N e^{T_2} | 0 \rangle = F, \quad (7)$$

where

$$\Lambda_2 = \frac{1}{4} \lambda_{\bullet\bullet}^{IJ} \{ a_I^\dagger a^A a_J^\dagger a^B \}, \quad (8)$$

is a double de-excitation operator which serves as the coupled-cluster form of the \mathbf{Z} vector from the Handy–Schaefer \mathbf{Z} -vector method.¹⁷ Equation (7) is known as the Lambda functional.¹⁸ The equations for T can be derived by taking the derivative of Eq. (7) with respect to the λ amplitudes and setting the resultant equations to zero. Doing so reproduces Eq. (2). Similarly, the Λ equations are derived by

setting to zero the derivatives of Eq. (7) with respect to the t amplitudes. Hence, the value of F in Eq. (7) is stationary with respect to variations of both the t and λ amplitudes, and at stationarity it has as its numerical value the coupled-cluster energy.

B. Partitioning technique

To derive the dynamical energy correction, we will start with a Löwdin-style partitioning¹⁹ of a similarity-transformed Hamiltonian \bar{H} . The definition of \bar{H} for VOD will be given later, but for now it is only necessary to note that \bar{H} is not Hermitian. Since it is not Hermitian, it has different right-hand (\mathcal{R}) and left-hand (\mathcal{L}) eigenvectors. However, the right- and left-hand eigenvalues are the same, and the eigenvectors form a biorthogonal set

$$\langle 0 | \mathcal{L}_i \mathcal{R}_j | 0 \rangle = C_{ij} \delta_{ij}. \quad (9)$$

The first step is to divide the space of all possible n -electron determinants ($|\mathbf{h}\rangle$) formed from our set of orbitals into a primary space ($|\mathbf{p}\rangle$) and a secondary space ($|\mathbf{q}\rangle$) such that $|\mathbf{p}\rangle \oplus |\mathbf{q}\rangle = |\mathbf{h}\rangle$. We will discuss the appropriate choice of $|\mathbf{p}\rangle$ and $|\mathbf{q}\rangle$ later.

Next, we will write the problem of finding the exact eigenvalues of \bar{H} , which are the same as the exact eigenvalues of the untransformed Hamiltonian, as

$$\begin{bmatrix} \bar{H}_{pp} & \bar{H}_{pq} \\ \bar{H}_{qp} & \bar{H}_{qq} \end{bmatrix} \begin{bmatrix} \mathbf{R}_p \\ \mathbf{R}_q \end{bmatrix} = E_{\text{exact}} \begin{bmatrix} \mathbf{R}_p \\ \mathbf{R}_q \end{bmatrix}, \quad (10)$$

where \mathbf{R}_p and \mathbf{R}_q are the projections of \mathcal{R} into the $|\mathbf{p}\rangle$ space and $|\mathbf{q}\rangle$ space, respectively. Expanding Eq. (10) gives

$$\bar{H}_{pp} \mathbf{R}_p + \bar{H}_{pq} \mathbf{R}_q = E_{\text{exact}} \mathbf{R}_p, \quad (11)$$

$$\bar{H}_{qp} \mathbf{R}_p + \bar{H}_{qq} \mathbf{R}_q = E_{\text{exact}} \mathbf{R}_q. \quad (12)$$

Solving for \mathbf{R}_q in Eq. (12) yields

$$\mathbf{R}_q = (E_{\text{exact}} \mathbf{1} - \bar{H}_{qq})^{-1} \bar{H}_{qp} \mathbf{R}_p, \quad (13)$$

where $\mathbf{1}$ is a unit matrix of dimension $|\mathbf{q}\rangle$ by $|\mathbf{q}\rangle$. Substituting for \mathbf{R}_q back into Eq. (11), we get an energy-dependent effective Hamiltonian only over the $|\mathbf{p}\rangle$ space, but whose eigenvalues are still exact,

$$\bar{H}_{pp}^{\text{eff}} \mathbf{R}_p = \{ \bar{H}_{pp} + \bar{H}_{pq} (E_{\text{exact}} \mathbf{1} - \bar{H}_{qq})^{-1} \bar{H}_{qp} \} \mathbf{R}_p = E_{\text{exact}} \mathbf{R}_p. \quad (14)$$

Although this eigenvalue equation is only over the reduced space, it is not computationally useful, since it involves the inverse of a huge matrix (in the $|\mathbf{q}\rangle$ space), and the energy appears on both sides.

If we multiply on the left by \mathbf{L}_p (the projection of \mathcal{L} onto the $|\mathbf{p}\rangle$ space) and integrate, we get an expression for the energy

$$E_{\text{exact}} \langle 0 | \mathbf{L}_p \mathbf{R}_p | 0 \rangle = \langle 0 | \mathbf{L}_p \{ \bar{H}_{pp} + \bar{H}_{pq} (E_{\text{exact}} \mathbf{1} - \bar{H}_{qq})^{-1} \bar{H}_{qp} \} \mathbf{R}_p | 0 \rangle. \quad (15)$$

To make this into a computationally useful formula, it is necessary to expand the inverse in some perturbation series. We will split \bar{H} into a zeroth-order part $\bar{H}^{[0]}$ and a first-order

part $\bar{H}^{[1]}$. Similarly, we will split E_{exact} into a zeroth-order part $E^{[0]}$ and higher order parts ($E^{[1]}, E^{[2]}, E^{[3]}, \dots$) referred to collectively as ΔE . We will choose $\bar{H}^{[0]}$ to consist of \bar{H}_{pp} and part of \bar{H}_{qq} . The rest of \bar{H} will be considered first order. Using these definitions and expanding the inverse in Eq. (15) gives

$$\begin{aligned} (E_{\text{exact}} \mathbf{1} - \bar{H}_{qq})^{-1} &= (E^{[0]} \mathbf{1} + \Delta E \mathbf{1} - \bar{H}_{qq}^{[0]} - \bar{H}_{qq}^{[1]})^{-1} \\ &= \{ (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]}) [\mathbf{1} - (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} \\ &\quad \times (\bar{H}_{qq}^{[1]} - \Delta E \mathbf{1})] \}^{-1} \\ &= (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} + (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} \\ &\quad \times (\bar{H}_{qq}^{[1]} - \Delta E \mathbf{1}) (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} \\ &\quad + (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} (\bar{H}_{qq}^{[1]} - \Delta E \mathbf{1}) \\ &\quad \times (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} (\bar{H}_{qq}^{[1]} - \Delta E \mathbf{1}) \\ &\quad \times (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} + \dots \end{aligned} \quad (16)$$

Finally, we need to expand \mathbf{R}_p and \mathbf{L}_p as

$$\mathbf{R}_p = \mathbf{R}_p^{[0]} + \mathbf{R}_p^{[2]} + \mathbf{R}_p^{[3]} + \mathbf{R}_p^{[4]} + \dots, \quad (17)$$

and

$$\mathbf{L}_p = \mathbf{L}_p^{[0]} + \mathbf{L}_p^{[2]} + \mathbf{L}_p^{[3]} + \mathbf{L}_p^{[4]} + \dots \quad (18)$$

Neither \mathbf{R}_p nor \mathbf{L}_p can have a first-order component, since $\bar{H}^{[1]}$ acting on a $|\mathbf{p}\rangle$ space function gives only a $|\mathbf{q}\rangle$ space contribution. Substituting Eqs. (16)–(18) into Eq. (15) and collecting orders yields

$$E^{[0]} \langle 0 | \mathbf{L}_p^{[0]} \mathbf{R}_p^{[0]} | 0 \rangle = \langle 0 | \mathbf{L}_p^{[0]} \bar{H}_{pp}^{[0]} \mathbf{R}_p^{[0]} | 0 \rangle, \quad (19)$$

$$E^{[1]} = 0, \quad (20)$$

$$\begin{aligned} E^{[2]} \langle 0 | \mathbf{L}_p^{[0]} \mathbf{R}_p^{[0]} | 0 \rangle &+ E^{[0]} \langle 0 | \mathbf{L}_p^{[2]} \mathbf{R}_p^{[0]} | 0 \rangle \\ &+ E^{[0]} \langle 0 | \mathbf{L}_p^{[0]} \mathbf{R}_p^{[2]} | 0 \rangle \\ &= \langle 0 | \mathbf{L}_p^{[0]} \bar{H}_{pq}^{[1]} (E^{[0]} \mathbf{1} - \bar{H}_{qq}^{[0]})^{-1} \bar{H}_{qp}^{[1]} \mathbf{R}_p^{[0]} | 0 \rangle \\ &+ \langle 0 | \mathbf{L}_p^{[2]} \bar{H}_{pp}^{[0]} \mathbf{R}_p^{[0]} | 0 \rangle + \langle 0 | \mathbf{L}_p^{[0]} \bar{H}_{pp}^{[0]} \mathbf{R}_p^{[2]} | 0 \rangle. \end{aligned} \quad (21)$$

C. VOD(2)

The above equations are general for any similarity-transformed Hamiltonian, but here we want to focus on a dynamical correlation correction to VOD. Therefore, we define the similarity-transformed Hamiltonian, \bar{H} , as

$$\begin{aligned} \bar{H} &= e^{-T} H_N e^T \\ &= (H_N e^T)_c \\ &= \bar{F}_{\bullet q}^p \{ a_p^\dagger a^q \} + \frac{1}{4} \bar{W}_{\bullet\bullet rs}^{pq} \{ a_p^\dagger a_q^\dagger a^r a^s \} \\ &\quad + \frac{1}{36} \bar{W}_{\bullet\bullet\bullet stu}^{pqr} \{ a_p^\dagger a_q^\dagger a_r^\dagger a^u a^t a^s \} \\ &\quad + \frac{1}{576} \bar{W}_{\bullet\bullet\bullet\bullet tuvw}^{pqrs} \{ a_p^\dagger a_q^\dagger a_r^\dagger a_s^\dagger a^w a^v a^u a^t \} + \dots \end{aligned} \quad (22)$$

Note that since T contains up to double excitations, \bar{H} contains up to six-body terms. However, only up to four-body terms appear in the VOD(2) equations. The one- and two-body terms in \bar{H} are

$$\bar{F}_{\bullet i}^a = f_{\bullet i}^a + t_{\bullet\bullet IM}^{AE} f_{\bullet E}^M + \frac{1}{2} t_{\bullet\bullet IM}^{EF} W_{\bullet\bullet EF}^{aM} - \frac{1}{2} t_{\bullet\bullet MN}^{AE} W_{\bullet\bullet iE}^{MN}, \quad (23)$$

$$\bar{F}_{\bullet b}^a = f_{\bullet b}^a - \frac{1}{2} t_{\bullet\bullet MN}^{AE} W_{\bullet\bullet bE}^{MN}, \quad (24)$$

$$\bar{F}_{\bullet j}^i = f_{\bullet j}^i + \frac{1}{2} t_{\bullet\bullet JM}^{EF} W_{\bullet\bullet EF}^{iM}, \quad (25)$$

$$\bar{F}_{\bullet a}^i = f_{\bullet a}^i, \quad (26)$$

$$\begin{aligned} \bar{W}_{\bullet\bullet ij}^{ab} = & W_{\bullet\bullet ij}^{ab} - P(ij)t_{\bullet\bullet MJ}^{AB} f_{\bullet i}^M + P(ab)t_{\bullet\bullet IJ}^{EB} f_{\bullet E}^a \\ & + \frac{1}{2} t_{\bullet\bullet IJ}^{EF} W_{\bullet\bullet EF}^{ab} + \frac{1}{2} t_{\bullet\bullet MN}^{AB} W_{\bullet\bullet ij}^{MN} \\ & - P(ab)P(ij)t_{\bullet\bullet IM}^{AE} W_{\bullet\bullet jE}^{Mb}, \end{aligned} \quad (27)$$

$$\bar{W}_{\bullet\bullet IJ}^{AB} = 0, \quad (28)$$

$$\begin{aligned} \bar{W}_{\bullet\bullet ci}^{ab} = & W_{\bullet\bullet ci}^{ab} - t_{\bullet\bullet MI}^{AB} f_{\bullet c}^M + \frac{1}{2} t_{\bullet\bullet MN}^{AB} W_{\bullet\bullet ic}^{NM} \\ & + P(ab)t_{\bullet\bullet MI}^{EB} W_{\bullet\bullet cE}^{aM}, \end{aligned} \quad (29)$$

$$\begin{aligned} \bar{W}_{\bullet\bullet jk}^{ia} = & W_{\bullet\bullet jk}^{ia} - t_{\bullet\bullet JK}^{EA} f_{\bullet E}^i + \frac{1}{2} t_{\bullet\bullet JK}^{EF} W_{\bullet\bullet FE}^{ai} \\ & + P(jk)t_{\bullet\bullet MK}^{EA} W_{\bullet\bullet jE}^{iM}, \end{aligned} \quad (30)$$

$$\bar{W}_{\bullet\bullet cd}^{ab} = W_{\bullet\bullet cd}^{ab} + \frac{1}{2} t_{\bullet\bullet MN}^{AB} W_{\bullet\bullet cd}^{MN}, \quad (31)$$

$$\bar{W}_{\bullet\bullet ij}^{kl} = W_{\bullet\bullet ij}^{kl} + \frac{1}{2} t_{\bullet\bullet IJ}^{EF} W_{\bullet\bullet EF}^{kl}, \quad (32)$$

$$\bar{W}_{\bullet\bullet jb}^{ia} = W_{\bullet\bullet jb}^{ia} - t_{\bullet\bullet JM}^{EA} W_{\bullet\bullet Eb}^{iM}, \quad (33)$$

$$\bar{W}_{\bullet\bullet bc}^{ai} = W_{\bullet\bullet bc}^{ai}, \quad (34)$$

$$\bar{W}_{\bullet\bullet ka}^{ij} = W_{\bullet\bullet ka}^{ij}, \quad (35)$$

$$\bar{W}_{\bullet\bullet ab}^{ij} = W_{\bullet\bullet ab}^{ij}, \quad (36)$$

Here and elsewhere, the Einstein summation convention is used. The symbol $P(pq)$ is a permutation operator defined by its operation on a generic operator $P(pq)X(\dots,p,\dots,q,\dots) = X(\dots,p,\dots,q,\dots) - X(\dots,q,\dots,p,\dots)$. Note that Eq. (28) is equivalent to Eq. (2). The three- and four-body terms which we will need will be given later.

Before we insert this definition of \bar{H} into Eqs. (19)–(21) we must choose definitions for $|\mathbf{p}\rangle$ and $\bar{H}^{[0]}$. If $|\mathbf{p}\rangle$ is restricted to just $|0\rangle$, H is used instead of \bar{H} , and $f_{\bullet j}^i$ and $f_{\bullet b}^a$ are assigned to be zeroth-order, with the rest of H being first order, we recover standard Møller–Plesset perturbation theory,¹ where a single determinant serves as the reference wave function.

However, here we want the VOD wave function to be the underlying reference wave function. Therefore, we will choose $|\mathbf{p}\rangle = |0\rangle \oplus |\mathbf{D}\rangle$, where $|\mathbf{D}\rangle$ is the set of all determinants formed from double excitations within the active space. This is the space over which Eq. (2) was solved. We will choose $\bar{H}^{[0]}$ to consist of $\bar{\mathbf{H}}_{\mathbf{pp}}$ augmented by $\bar{F}_{\bullet J}^I$, $\bar{F}_{\bullet j'}^{i'}$, $\bar{F}_{\bullet B}^A$, and $\bar{F}_{\bullet b'}^{a'}$ from $\bar{\mathbf{H}}_{\mathbf{qq}}$. The rest of \bar{H} is considered first order, regardless of its order in standard perturbation theory. For $\mathbf{R}_{\mathbf{p}}^{[0]}$ and $\mathbf{L}_{\mathbf{p}}^{[0]}$ we will choose the (normalized) eigenvectors of $\bar{\mathbf{H}}_{\mathbf{pp}}^{[0]}$ which represent the VOD solution. These are $\mathbf{R}_{\mathbf{p}}^{[0]} = 1$ and $\mathbf{L}_{\mathbf{p}}^{[0]} = 1 + \Lambda$.²⁰ With these definitions, Eqs. (19)–(21) become

$$E^{[0]} = \langle 0 | (1 + \Lambda) \bar{\mathbf{H}}_{\mathbf{pp}}^{[0]} | 0 \rangle = E_{cc}, \quad (37)$$

$$E^{[1]} = 0, \quad (38)$$

$$\begin{aligned} E^{[2]} = & \langle 0 | \bar{\mathbf{H}}_{\mathbf{pq}}^{[1]} (E^{[0]} \mathbf{1} - \bar{\mathbf{H}}_{\mathbf{qq}}^{[0]})^{-1} \bar{\mathbf{H}}_{\mathbf{qp}}^{[1]} | 0 \rangle \\ & + \langle 0 | \Lambda \bar{\mathbf{H}}_{\mathbf{pq}}^{[1]} (E^{[0]} \mathbf{1} - \bar{\mathbf{H}}_{\mathbf{qq}}^{[0]})^{-1} \bar{\mathbf{H}}_{\mathbf{qp}}^{[1]} | 0 \rangle. \end{aligned} \quad (39)$$

Equation (37) is the same as Eq. (7), which means that the zeroth-order energy in our scheme is the VOD energy. This is consistent with us treating VOD as the zeroth-order wave function. This also means that we have a well-defined total energy, in that we can add the dynamical correlation correction to the VOD energy. The terms, $\langle 0 | \mathbf{L}_{\mathbf{p}}^{[2]} \bar{\mathbf{H}}_{\mathbf{pp}}^{[0]} \mathbf{R}_{\mathbf{p}}^{[0]} | 0 \rangle = E_{cc} \langle 0 | \mathbf{L}_{\mathbf{p}}^{[2]} \mathbf{R}_{\mathbf{p}}^{[0]} | 0 \rangle$ and $\langle 0 | \mathbf{L}_{\mathbf{p}}^{[0]} \bar{\mathbf{H}}_{\mathbf{pp}}^{[0]} \mathbf{R}_{\mathbf{p}}^{[2]} | 0 \rangle = E_{cc} \langle 0 | \mathbf{L}_{\mathbf{p}}^{[0]} \mathbf{R}_{\mathbf{p}}^{[2]} | 0 \rangle$, which appeared in Eq. (21), cancel here.

The two terms in Eq. (39) will be discussed separately. The first, which we call MP2-like, consists of two terms that differ by the level of excitation in $|\mathbf{q}\rangle$. The two terms are

$$\text{MP2 singles} = \bar{F}_{\bullet a}^i (\bar{t}^{[1]})_{\bullet i}^a, \quad (40)$$

and

$$\text{MP2 doubles} = \frac{1}{4} \bar{W}_{\bullet\bullet ab}^{ij} (\bar{t}^{[1]})_{\bullet ij}^{ab}. \quad (41)$$

These are called MP2-like because in the limit of $|\mathbf{p}\rangle = |0\rangle$ these equations become MP2 for a non-Hartree–Fock reference.²¹

The second term in Eq. (39) we call the Lambda term, and it consists of four parts. They are the singles, doubles, triples, and quadruples terms, and they differ in the excitation level of the first-order amplitudes. The equations for the terms are as follows:

$$\begin{aligned} \Lambda \text{ singles} = & \lambda_{\bullet B}^I \bar{F}_{\bullet a'}^B (\bar{t}^{[1]})_{\bullet I}^{a'} - \lambda_{\bullet A}^J \bar{F}_{\bullet J}^{i'} (\bar{t}^{[1]})_{\bullet i'}^A + \lambda_{\bullet B}^J \bar{W}_{\bullet\bullet Ja}^{iB} (\bar{t}^{[1]})_{\bullet i}^a + \lambda_{\bullet AE}^{IM} \bar{F}_{\bullet M}^E (\bar{t}^{[1]})_{\bullet I}^A + \frac{1}{2} \lambda_{\bullet\bullet EF}^{IM} \bar{W}_{\bullet\bullet aM}^{EF} (\bar{t}^{[1]})_{\bullet i}^a \\ & - \frac{1}{2} \lambda_{\bullet\bullet AE}^{MN} \bar{W}_{\bullet\bullet MN}^{iE} (\bar{t}^{[1]})_{\bullet i}^A + \frac{1}{2} \lambda_{\bullet\bullet EF}^{MN} W_{\bullet\bullet Ga}^{Fi} t_{\bullet\bullet MN}^{EG} (\bar{t}^{[1]})_{\bullet i}^a - \frac{1}{2} \lambda_{\bullet\bullet EF}^{MN} W_{\bullet\bullet Na}^{iE} t_{\bullet\bullet MO}^{EF} (\bar{t}^{[1]})_{\bullet i}^a, \end{aligned} \quad (42)$$

$$\begin{aligned} \Lambda \text{ doubles} = & \lambda_{\bullet A}^I \bar{F}_{\bullet b}^j (\bar{t}^{[1]})_{\bullet ij}^{Ab} + \frac{1}{2} \lambda_{\bullet E}^I \bar{W}_{\bullet\bullet ab}^{Ej} (\bar{t}^{[1]})_{\bullet ij}^{ab} - \frac{1}{2} \lambda_{\bullet A}^M \bar{W}_{\bullet\bullet Mb}^{ij} (\bar{t}^{[1]})_{\bullet ij}^{Ab} + \frac{1}{2} \lambda_{\bullet\bullet AE}^{IJ} \bar{F}_{\bullet b'}^E (\bar{t}^{[1]})_{\bullet ij}^{Ab'} \\ & - \frac{1}{2} \lambda_{\bullet\bullet AB}^{IM} \bar{F}_{\bullet M}^{j'} (\bar{t}^{[1]})_{\bullet ij}^{AB} + \frac{1}{8} \lambda_{\bullet\bullet EF}^{IJ} \bar{W}_{\bullet\bullet ab}^{EF} (\bar{t}^{[1]})_{\bullet ij}^{ab} + \frac{1}{8} \lambda_{\bullet\bullet AB}^{MN} \bar{W}_{\bullet\bullet MN}^{ij} (\bar{t}^{[1]})_{\bullet ij}^{AB} \\ & - \lambda_{\bullet\bullet AE}^{MJ} \bar{W}_{\bullet\bullet Mb}^{iE} (\bar{t}^{[1]})_{\bullet ij}^{Ab} - \frac{1}{4} \lambda_{\bullet\bullet FE}^{MI} W_{\bullet\bullet ab}^{Nj} t_{\bullet\bullet MN}^{FE} (\bar{t}^{[1]})_{\bullet ij}^{ab} - \frac{1}{4} \lambda_{\bullet\bullet EA}^{NM} W_{\bullet\bullet Fb}^{ij} t_{\bullet\bullet NM}^{EF} (\bar{t}^{[1]})_{\bullet ij}^{Ab}, \end{aligned} \quad (43)$$

$$\Lambda \text{ triples} = \frac{1}{4}\lambda_{\bullet\bullet A}^I \bar{W}_{\bullet\bullet bc}^{jk} (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet jk}^{Abc} + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ} \bar{F}_{\bullet\bullet c}^k (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet IJk}^{ABc} + \frac{1}{4}\lambda_{\bullet\bullet AE}^{IJ} \bar{W}_{\bullet\bullet bc}^{Ek} (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet IJk}^{Abc} - \frac{1}{4}\lambda_{\bullet\bullet AB}^{IM} \bar{W}_{\bullet\bullet Mc}^{jk} (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet Ijk}^{ABc}, \quad (44)$$

$$\Lambda \text{ quadruples} = \frac{1}{16}\lambda_{\bullet\bullet AB}^{IJ} \bar{W}_{\bullet\bullet cd}^{kl} (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet IJkl}^{ABcd}. \quad (45)$$

The last two terms of Eqs. (42) and (43) arise from three-body terms in \bar{H} which have been expanded out. The first-order amplitudes, which appear in these equations, are given by

$$0 = (\bar{F}^{[0]})_{\bullet\bullet e}^a (\bar{t}^{[1]})_{\bullet\bullet i}^e - (\bar{F}^{[0]})_{\bullet\bullet i}^m (\bar{t}^{[1]})_{\bullet\bullet m}^a + \bar{F}_{\bullet\bullet i}^a, \quad (46)$$

$$0 = (\bar{F}^{[0]})_{\bullet\bullet e}^a (\bar{t}^{[1]})_{\bullet\bullet ij}^{eb} + (\bar{F}^{[0]})_{\bullet\bullet e}^b (\bar{t}^{[1]})_{\bullet\bullet ij}^{ae} - (\bar{F}^{[0]})_{\bullet\bullet i}^m (\bar{t}^{[1]})_{\bullet\bullet mj}^{ab} - (\bar{F}^{[0]})_{\bullet\bullet j}^m (\bar{t}^{[1]})_{\bullet\bullet im}^{ab} + \bar{W}_{\bullet\bullet ij}^{ab}, \quad (47)$$

$$0 = (\bar{F}^{[0]})_{\bullet\bullet e}^a (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijk}^{ebc} + (\bar{F}^{[0]})_{\bullet\bullet e}^b (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijk}^{aec} + (\bar{F}^{[0]})_{\bullet\bullet e}^c (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijk}^{abe} - (\bar{F}^{[0]})_{\bullet\bullet i}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet mjk}^{abc} - (\bar{F}^{[0]})_{\bullet\bullet j}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet imk}^{abc} - (\bar{F}^{[0]})_{\bullet\bullet k}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijm}^{abc} + \bar{W}_{\bullet\bullet\bullet\bullet ijk}^{abc}, \quad (48)$$

$$0 = (\bar{F}^{[0]})_{\bullet\bullet e}^a (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijkl}^{ebcd} + (\bar{F}^{[0]})_{\bullet\bullet e}^b (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijkl}^{aecd} + (\bar{F}^{[0]})_{\bullet\bullet e}^c (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijkl}^{abcd} + (\bar{F}^{[0]})_{\bullet\bullet e}^d (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijkl}^{abce} - (\bar{F}^{[0]})_{\bullet\bullet i}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet mjkl}^{abcd} - (\bar{F}^{[0]})_{\bullet\bullet j}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet imkl}^{abcd} - (\bar{F}^{[0]})_{\bullet\bullet k}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijml}^{abcd} - (\bar{F}^{[0]})_{\bullet\bullet l}^m (\bar{t}^{[1]})_{\bullet\bullet\bullet\bullet ijkm}^{abcd} + \bar{W}_{\bullet\bullet\bullet\bullet ijkl}^{abcd}, \quad (49)$$

where $(\bar{F}^{[0]})_{\bullet\bullet i}^j = \bar{F}_{\bullet\bullet i}^j + \bar{F}_{\bullet\bullet i'}^{j'}$, and $(\bar{F}^{[0]})_{\bullet\bullet b}^a = \bar{F}_{\bullet\bullet b}^a + \bar{F}_{\bullet\bullet b'}^{a'}$. The parts of \bar{F} that couple occupied and unoccupied indices and the parts that couple active and inactive indices are excluded since they are considered first order. The three-body term in Eq. (48) is

$$\bar{W}_{\bullet\bullet\bullet\bullet ijk}^{abc} = P(k|ij)P(a|bc)t_{\bullet\bullet\bullet\bullet IJ}^{AE}[W_{\bullet\bullet\bullet\bullet Ek}^{bc} - t_{\bullet\bullet\bullet\bullet MK}^{BC}f_{\bullet\bullet E}^M + \frac{1}{2}t_{\bullet\bullet\bullet\bullet MN}^{BC}W_{\bullet\bullet\bullet\bullet Ek}^{MN} + P(bc)t_{\bullet\bullet\bullet\bullet MK}^{FC}W_{\bullet\bullet\bullet\bullet EF}^{bM}] - P(i|jk)P(c|ab)t_{\bullet\bullet\bullet\bullet IM}^{AB}[W_{\bullet\bullet\bullet\bullet jk}^{Mc} + \frac{1}{2}t_{\bullet\bullet\bullet\bullet JK}^{EF}W_{\bullet\bullet\bullet\bullet EF}^{Mc} + P(jk)t_{\bullet\bullet\bullet\bullet NK}^{EC}W_{\bullet\bullet\bullet\bullet jE}^{MN}]. \quad (50)$$

The four-body term in Eq. (49) is

$$\bar{W}_{\bullet\bullet\bullet\bullet ijkl}^{abcd} = P(ij|kl)P(a|bc|d)t_{\bullet\bullet\bullet\bullet IJ}^{AE}t_{\bullet\bullet\bullet\bullet KL}^{FD}[W_{\bullet\bullet\bullet\bullet EF}^{bc} + \frac{1}{2}t_{\bullet\bullet\bullet\bullet MN}^{BC}W_{\bullet\bullet\bullet\bullet EF}^{MN}] + P(i|jk|l)P(ab|cd) \times t_{\bullet\bullet\bullet\bullet IM}^{AB}t_{\bullet\bullet\bullet\bullet NL}^{CD}[W_{\bullet\bullet\bullet\bullet jk}^{MN} + \frac{1}{2}t_{\bullet\bullet\bullet\bullet JK}^{EF}W_{\bullet\bullet\bullet\bullet EF}^{MN}] - P(i|j|kl)P(ab|c|d)t_{\bullet\bullet\bullet\bullet IM}^{AB}t_{\bullet\bullet\bullet\bullet KL}^{ED}[W_{\bullet\bullet\bullet\bullet jE}^{Mc} - t_{\bullet\bullet\bullet\bullet JN}^{FC}W_{\bullet\bullet\bullet\bullet FE}^{MN}]. \quad (51)$$

The permutation operator $P(p|qr)$ means to permute p with q and permute p with r but not permute q with r . The four-index permutation operators are defined similarly. Both Eqs. (50) and (51) can be simplified with careful use of two-body parts of \bar{W} as intermediates.

With the inclusion of λ_a^i terms, which do not appear in VOD(2), these equations have been generalized to describe methods including single excitations. Therefore, along with the appropriate choice of \bar{H} , these equations exactly define the (2) correction for any method based on coupled-cluster singles and doubles, such as CCSD, QCISD, or Brueckner orbital CCD.²²

Finally, we need to consider the choice of orbitals. The VOO-CC optimization procedure defines the inactive occupied, active occupied, active virtual, and inactive virtual spaces, but the VOO-CC model and the equations presented here are invariant to rotations within those spaces. These spaces form the diagonal blocks of \bar{F} and comprise $\bar{\mathbf{H}}_{\text{qq}}^{[0]}$. From a practical standpoint, we want these blocks to be diagonal, since that makes solving for the first-order amplitudes trivial. Therefore, the natural choice of orbitals would be a semicanonical set where the inactive occupied, active occupied, active virtual, and inactive virtual blocks of \bar{F} are

made diagonal. The problem is that, like \bar{H} , \bar{F} is not Hermitian, and so it has different right- and left-hand eigenvectors. Therefore, diagonalizing \bar{F} requires a biorthogonal transformation of the integrals and amplitudes, where the bra and ket indices of all the integrals and amplitudes get different transformation matrices. Because of the tensor nature of the equations,¹⁶ this poses no fundamental difficulties, but it does add to the computational complexity. The (2) equations in spin-orbital form for this semicanonical basis are presented in Appendix A.

D. Discussion of the theory

1. Significance of the terms

The derivation used here follows closely one^{23–25} used to justify CCSD(T). This derivation is also very close to the one used to derive an asymmetric CCSD(T)-type correction²⁶ which had been derived independently as CCSD(T)_Λ.²⁷ The primary difference between the current work and previous work is in the choice of order. Previously, \bar{H} had always been expanded in terms of order with respect to the bare Hamiltonian. However, our interest is to treat the entire VOD wave function as zeroth-order. This is especially important in

cases with strong nondynamical correlation, which have several determinants of close to equal importance. Such cases show up in a VOO-CC calculation as a t amplitude close to 1. By treating all of \bar{H} as either zeroth- or first-order, we are implicitly treating all other significant determinants on the same footing as the reference determinant.

VOD(2) is fundamentally a single determinant method, just as the underlying VOD is. This does have drawbacks in that it would be difficult for VOD(2) to handle cases, such as open-shell singlets, where two determinants need to have identical weights in the wave function. However, the single-determinantal nature of the method does have some major advantages. The first is that the method is unambiguously defined by the choice of the number and symmetry of the orbitals in the active occupied and active virtual spaces. Also, we have none of the problems associated with multi-reference methods, such as intruder states. Finally, since both VOD and the perturbative correction contain only linked diagrams, VOD(2) is fully size extensive. Coupled with VOD's ability to handle active spaces much larger than those possible with CASSCF, this makes VOD(2) potentially very useful for large systems.

The MP2 singles and Λ singles terms are almost always small. Furthermore, in almost all cases studied to date, they nearly cancel as well. Therefore, they are relatively unimportant, and we will not discuss them in detail.

As will be seen later, the MP2 doubles term is the dominant term in VOD(2). From the point of view of standard perturbation theory, this term is the leading-order correction. To a large extent it looks like MP2, but with any active-space contribution excluded. The exclusion of any contribution from the active space for both the MP2 doubles term and the Λ doubles term occurs because of Eq. (28). However, the MP2 doubles term tends to be too negative, and the Λ doubles term serves to dampen the effect.

In some ways the Λ doubles term can be thought of as a renormalization term. The VOD wave function is in intermediate normalization, which puts the coefficient for the reference determinant always as one. The importance of other determinants in the VOD wave function does not have a direct impact on the size of the MP2 doubles term. However, if other determinants are also significant, this will appear as large t and λ amplitudes. Ignoring the three-body terms, the Λ doubles term looks like an excitation of a pair of electrons to outside of the $|\mathbf{D}\rangle$ space, followed by a second excitation of the same electrons to an excited $|\mathbf{D}\rangle$ space determinant. This is multiplied by the weight of the excited $|\mathbf{D}\rangle$ space determinant in the left-hand eigenvector. Thus, the Λ doubles term appears to be correcting the over importance the MP2 doubles term is putting on the reference determinant by including a positive term whose magnitude is directly related to the size of the λ amplitudes.

The Λ triples term closely resembles the CCSD(T) $_{\Lambda}$ ²⁷ or a -CCSD(T)²⁶ method mentioned earlier. In fact, if bare integrals were used in Eqs. (44) and (50), we would almost recover CCSD(T) $_{\Lambda}$. The only difference is that CCSD(T) $_{\Lambda}$ has an extra Λ_1 term which we do not get, since we do not have any Λ_1 in VOD.

Qualitatively, the triples term acts to provide dynamical

correlation to the excited VOD determinants. Specifically, the triples describe the situation when one of the electrons in the excited pair is further excited to another virtual orbital, while simultaneously a third electron is promoted from an occupied to a virtual orbital. The other situation they describe is when an electron from an occupied orbital fills one of the newly created holes at the same time that the third electron is excited into a virtual orbital. Since at least three of the six indices must be active, only a subset of possible triple excitations are included. Thus, this term can be considered a type of semi-internal triples correction.

The Λ quadruples term is related to the $E_Q^{[5]}(\Lambda)$ term from the CC5SD(TQ) $_{\Lambda}$ method of Ref. 27. In this case the terms are identical, except for the use of transformed versus bare integrals. These quadruples describe the correlation of a doubly excited VOD determinant with independent double excitations. These correlations are of two types. The first type is when the second excitation also occurs within the active space. Such correlations are included in the VOD model from the T_2^2 term in the wavefunction. The quadruples term, then, describes the differential correlation that exists when the appropriate weight for the second electron pair is different for the reference determinant and the doubly excited determinant. The second role of the quadruples is to give a MP2-like description of the correlation of the VOD doubly excited determinant coming from the inactive space. However, no more than two of the indices in the quadruple can be inactive, giving us a semi-internal quadruples correction. Therefore only a part of the external-space correlation is included.

2. Computational considerations

An important consideration with any computational method is cost. For VOD(2), the calculation can be viewed as four separate steps. The first is the calculation of the underlying VOD wave function. The cost of a VOD calculation has steps that scale as $O_a^2V_a^4$, $O_a^3V_a^3$, and $O_a^4V_a^2$ that must be performed every iteration. Here, O , V , and N stand for the number of occupied orbitals, virtual orbitals, and total orbitals, respectively, while the subscript a means active and t means total. Normally, the number of virtual orbitals far outweighs the number of occupied orbitals. However, the number of active occupied and active virtual orbitals is usually about the same. A VOD calculation also involves an integral transformation which must be performed each iteration and that scales as $N_aN_t^4$. The size of the active space as a proportion of the size of the basis set will determine whether the n^6 or n^5 terms will dominate.

The second logical step in a VOD(2) calculation is the formation of \bar{H} . The most expensive step of the similarity transformation scales as $O_a^2V_a^2V_t^2$. The next step is then the transformation of the integrals to the semi-canonical basis. The leading term here transforms as V_t^5 .

The final step is the calculation of the various energy contributions. The costs of the MP2 terms are trivial. The singles term scales as O_tV_t , and the doubles terms scales as $O_t^2V_t^2$. The most expensive part of the Λ singles term scales

as $O_a^2 V_a^2 V_t$. In the Λ doubles term, the most expensive part is $O_a^2 V_a^2 V_t^2$. Because of the noniterative nature of the (2) correction, these terms should be about as expensive overall as the iterative VOD.

The Λ triples term, on the other hand, has two terms that scale as $O_t O_a^2 V_a^2 V_t^2$. Although the fourth power dependence on the size of the active space means that the triples term here will be significantly cheaper than the triples term in CCSD(T), the expense of the triples term could still limit the applicability of the method. Thus, applying some sort of local approximation to this term may be appropriate.²⁸

Finally, we come to the Λ quadruples term. As written in Eqs. (45) and (51) the cost of the quadruples scales as $O_a^4 V_a^3 V_t^2$. Clearly, this is cost-prohibitive for all but the smallest of cases. The extreme cost of the term arises because the presence of the eight index denominator necessitates the formation of the four body \bar{W} term. This type of term also arises in MP5.²⁹ However, there the n^9 step is avoided by using a factorization trick.²⁹ In MP5 the two left-most operators are identical, and by summing over all possible time orderings of the two operators, the denominator can be factorized into two four-index denominators multiplied together. Unfortunately, that does not apply here, since our two left-most operators, Λ and \bar{W}_{ijab} are not equivalent.

This same problem arises in some noniterative quadruples corrections to CCSD. One solution that has been suggested there^{27,30} is to approximate the n^9 step by forcing a factorization of the denominator. In tests^{27,30-32} the factorization approximation changed the energy at the micro-Hartree level. We are going to choose to use this factorization trick here to reduce the cost of the quadruples term. In fact, we define the VOD(2) method to include this factorization trick. Forcing the factorization means that Eq. (45) is replaced by

Λ quadruples (factorized)

$$= \frac{1}{32} \lambda_{\bullet\bullet AB}^{IJ} (\bar{W}_D)^{kl}_{\bullet\bullet cd} \bar{W}_{\bullet\bullet\bullet\bullet}^{ABcd} IJkl, \quad (52)$$

where

$$(\bar{W}_D)^{ij}_{\bullet\bullet ab} = (\bar{F}^{[0]})^i_{\bullet m} \bar{W}_{\bullet\bullet ab}^{mj} + (\bar{F}^{[0]})^j_{\bullet m} \bar{W}_{\bullet\bullet ab}^{im} - (\bar{F}^{[0]})^e_{\bullet a} \bar{W}_{\bullet\bullet eb}^{ij} - (\bar{F}^{[0]})^e_{\bullet b} \bar{W}_{\bullet\bullet ae}^{ij}. \quad (53)$$

The elimination of the eight-index denominator allows us to avoid explicitly forming $\bar{W}_{\bullet\bullet\bullet\bullet}^{abcd}$. Instead, we substitute Eq. (51) into Eq. (52). By regrouping terms we can reduce the cost of the Λ quadruples term to just $V_a^4 V_t^2$. Spin-orbital equations for the factorized quadruples term are given in Appendix B.

Finally, it should be noted that until Eq. (37), the derivation of the perturbative correction did not depend upon \mathcal{R} and \mathcal{L} being the ground state. In fact, a similar derivation has been used to generate a correction for ionized states.^{23,24,33} Also, the current derivation did not depend on the explicit form of \bar{H} . Therefore, this type of correction can be developed for any single-reference coupled-cluster based ground- or excited-state method.

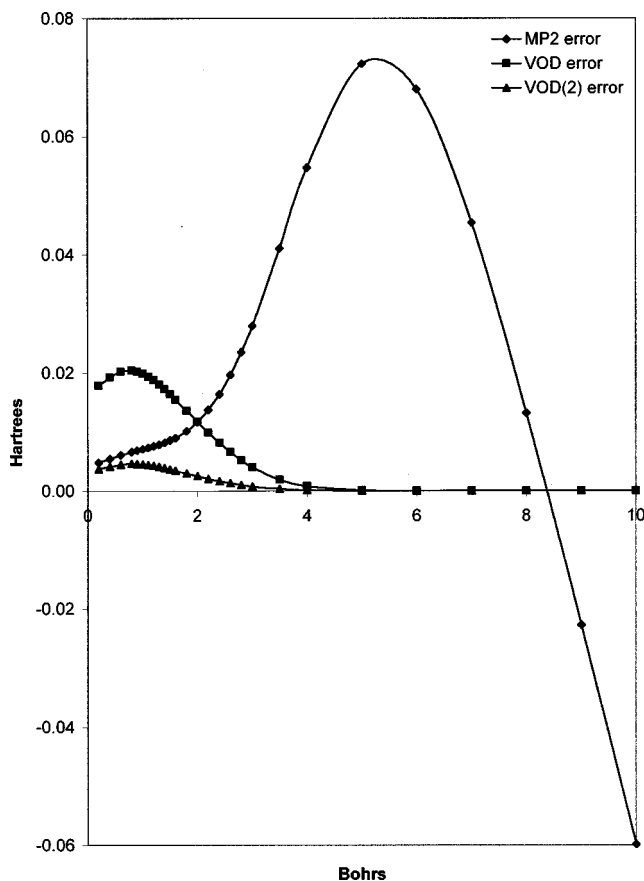


FIG. 1. MP2, VOD, and VOD(2) energy differences from OD (full CI) with a DZP basis for stretching H_2 .

III. RESULTS

We have implemented VOD(2) in both the Q-Chem³⁴ and PSI³⁵ quantum chemistry packages. In order to test the performance of the method we have studied potential curves for four model systems, stretching H_2 and F_2 , symmetrically stretching H_2O , and twisting ethylene.

A. H_2 stretch

Our first example is stretching H_2 . Since H_2 is a two electron problem, OD (VOD where all orbitals are active) is equivalent to full CI. In other words, it is exact within the chosen basis set. Also, VOD, which in this case is equivalent to two configuration SCF, is exact at the dissociation limit. Furthermore, the triples and quadruples terms are zero, as are the singles terms. Therefore, this system lets us isolate just the doubles terms and study their effects.

In Fig. 1 we compare the error in VOD(2) to the error in VOD and to the error in standard MP2.¹ Our baseline is OD. The basis set was Dunning's DZ basis,^{36,37} scaled by a factor of 1.2 and augmented with a p function with exponent 0.75. The data for this and all other figures in the paper are contained in the supplementary material.³⁸ At short bond distances and around equilibrium, where dynamical correlation dominates, both VOD(2) and MP2 have small errors. In contrast, VOD, which does not include dynamical correlation, has rather large errors. At longer bond distances, where non-dynamical correlation dominates, the error in MP2 blows up

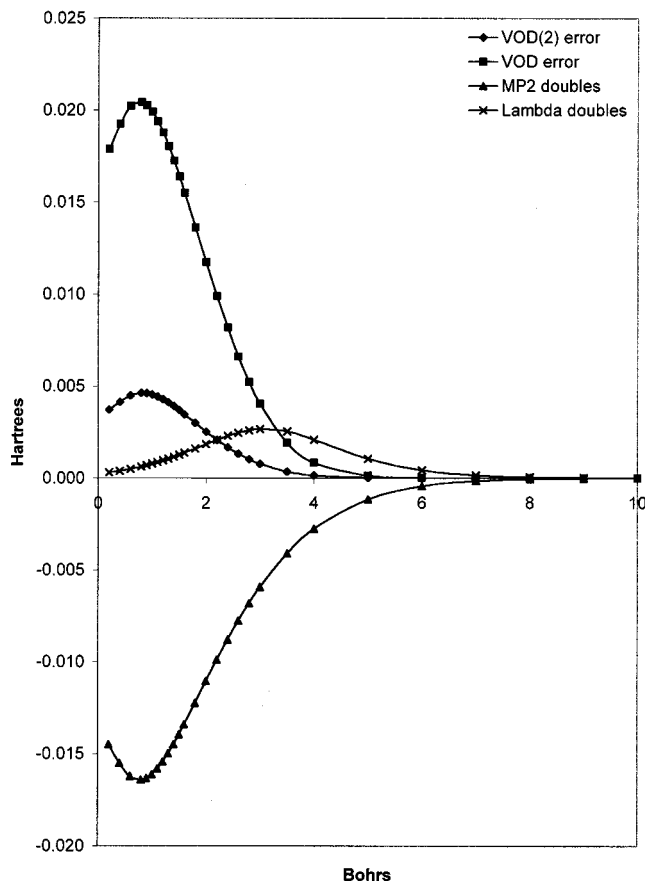


FIG. 2. A breakdown of the energy components of VOD(2) for stretching H_2 with a DZP basis.

and then turns negative in a dramatic failure. On the other hand, the VOD error decreases, ultimately going to zero at long bond distances. At all points, though, VOD(2) is the superior method. At short bond distances it beats MP2, and at long bond distances its error goes to zero much faster than the VOD error.

In Fig. 2 we break down VOD(2) into VOD, the MP2 doubles term, and the Λ doubles term. For the (2) correction the MP2 doubles term is dominant, but its size decreases with the decreasing role of dynamical correlation. As the second determinant in the two configuration description of dissociating H_2 becomes important, the Λ doubles term grows until it is nearly equal in magnitude to the MP2 doubles term. What is interesting is how both terms have significant magnitude for almost four Bohr after the VOD(2) error has gone to essentially zero. The VOD error is even zero well before the two terms die out. Clearly, these two terms serve to cancel out each other, and both must be included for a balanced treatment.

B. F_2 stretch

Our next test system will be stretching F_2 , which is a more realistic system. Since it is still a single bond being broken, we expect that VOD will be able to give a qualitatively correct description of the bond breaking. Figure 3 compares VOD and VOD(2) to OD(2). The OD(2) curve should have errors of about one milliHartree compared to

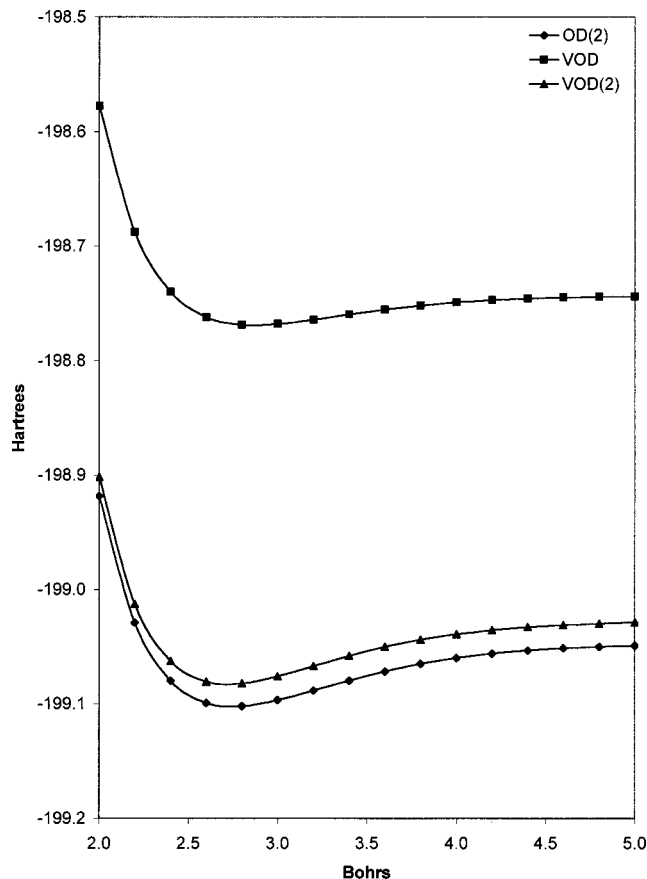


FIG. 3. VOD, VOD(2), and OD(2) energies with the cc-pVDZ basis set for stretching F_2 .

full CI.¹¹ Comparing OD(2) and VOD(2) also gives a direct measure of the effect of using an active space. The basis set used was cc-pVDZ,³⁹ and only the spherical harmonic components were kept.

In Fig. 3 the VOD(2) curve runs parallel to the OD(2), but with an offset. At 2.8 Bohr, the minimum calculated point on the curve, the VOD(2) curve lies 19.8 milliHartrees above the OD(2) curve. At 5 Bohr that difference is 20.3 milliHartrees. This leads to a discrepancy of 0.3 kcal/mol in the estimated dissociation energy, 33.3 kcal/mol for VOD(2) versus 33.0 kcal/mol for OD(2). On the other hand, the VOD curve is much too shallow, only giving a dissociation energy of 15.5 kcal/mol.

Another way to view the data is by looking at what percentage of the difference between OD(2) and VOD is recovered by VOD(2). At 2.8 Bohr the percentage is 94%, while at 5 Bohr it is 93%. This difference is indicative of the shallowness of the VOD curve. The important point, though, is that the (2) correction recovers over 90% of the dynamical correlation across the whole curve.

C. H_2O stretch

Our third test is symmetrically stretching both O–H bonds in water. Since we are now breaking two single bonds, only including doubles in the active space should not be sufficient; connected quadruples should also be needed. The CASSCF, CASPT2, MRSDCI (multireference singles and

TABLE I. Energy differences (in milliHartrees) from full CI^a for several approximate methods for H₂O at equilibrium and several stretched geometries using the cc-pVDZ basis set.

Method	1.0* R_e	1.5* R_e	2.0* R_e	2.5* R_e	3.0* R_e
VOD	164.128	150.974	128.962	96.140	81.703
VOD(2)	14.925	14.676	17.948	3.877	-12.302
CASSCF ^a	164.025	150.029	133.568	126.322	124.715
CASPT2 ^a	12.833	10.819	8.111	8.033	8.262
MRSDCI ^a	4.425	3.938	3.208	2.837	2.753

^aReference 40.

doubles configuration interaction), and full CI results from Olsen *et al.*⁴⁰ will be used for comparison. Again, Dunning's cc-pVDZ³⁹ basis set was used. The energy was calculated at 1.0* R_e , 1.5* R_e , 2.0* R_e , 2.5* R_e , and 3.0* R_e . For details of the calculations, see Ref. 40.

The results of the calculations are presented in Table I and Fig. 4. The CASSCF, CASPT2, and MRSDCI calculations all used the same full valence active space as the VOD and VOD(2) calculations. At the shorter bond distances, 1.0* R_e and 1.5* R_e , VOD and CASSCF differ by less than one milliHartree. In this same region VOD(2) is about four milliHartrees above CASPT2, which is about eight milliHartrees above the MRSDCI. By 2.0* R_e , however, the lack of higher excitations is causing VOD to have problems, as it turns below the CASSCF curve. As the VOD(2)'s reference wave function breaks down, VOD(2) also begins to break down. One positive note, though, is that the VOD(2) curve

dips far less than the VOD curve. The perturbative inclusion of connected higher excitations seems to be reducing the instability of the VOD(2) curve relative to the reference VOD.

D. Ethylene twist

Our final test is twisting ethylene. By varying the dihedral angle, we can adjust the problem from one totally dominated by dynamical correlation (zero degrees) to one where the nondynamical correlation is so strong that it is impossible for any single reference method to give a correct qualitative description of the wave function (ninety degrees). The problem at ninety degrees is that for the wave function to transform as an irrep of the D_{2d} point group as it should, the π^2 and π^{*2} determinants must have equal weight in the wave function. In a coupled-cluster method, where the reference determinant is one of the two, for the wave function to transform properly, the other determinant must have a coefficient of unity. Even in VOD, which is designed to handle nondynamical correlation, the coefficient of the π^{*2} determinant at ninety degrees is just over 0.9. Hence, the VOD wave function at ninety degrees only has D_2 symmetry. Although the VOD curve appears smooth⁸ despite the symmetry breaking, the symmetry breaking causes the VOD(2) curve to have a cusp. This should not be surprising. The question, then is how far into the twist curve can VOD(2) go before the symmetry breaking in the reference causes the method to break down.

We examine this question in Figs. 5 and 6. For all of the calculations the CC bond distance was 1.330 Å, the CH bond distance was 1.076 Å, and the HCC bond angle was 121.7°. These coordinates were kept fixed while the dihedral angle was varied. The basis set used was a DZP basis consisting of Dunning's DZ basis^{36,37} augmented by polarization functions with an exponent of 0.75 added to the carbons and hydrogens. All six Cartesian components of the carbon d functions were kept. Figure 5 presents the VOD and VOD(2) curves. On this scale, both curves appear smooth. However, when we plot just the (2) correction, we see that after 80° the (2) curve turns up. By fitting a sixth-order polynomial to the data from 15° to 80° and from 100° to 165°, we can estimate the error caused by the symmetry breaking. The curve fit estimate of the correction at 90° is -175.2 milliHartrees, while the calculated correction is -173.5 milliHartrees. Thus, we get an error of 1.1 kcal/mol. So, even though the (2) correction breaks down when the reference wave function breaks symmetry, the theory does work for situations with a large

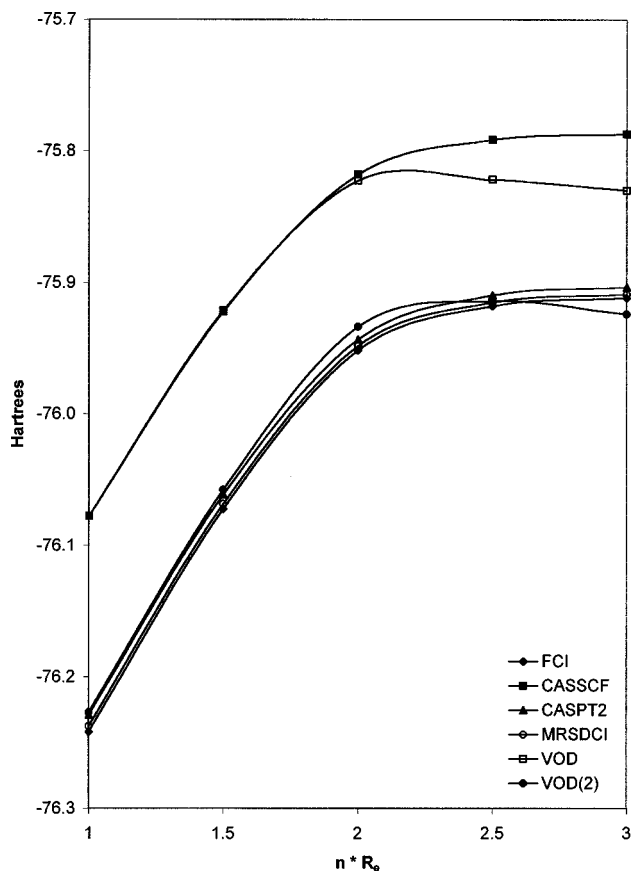


FIG. 4. Several approximate methods and full CI for the symmetric stretch of H₂O with the cc-pVDZ basis.

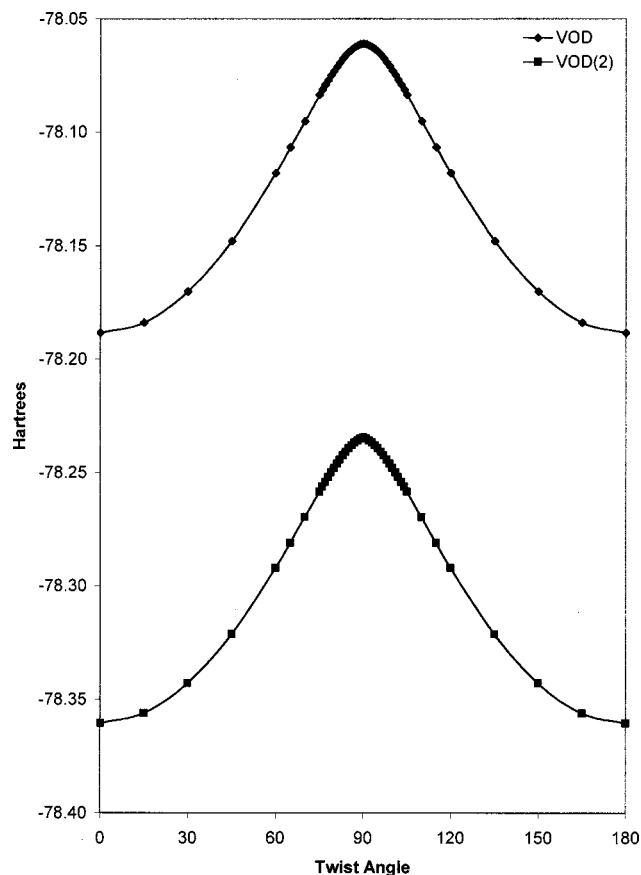


FIG. 5. VOD and VOD(2) energies with a DZP basis set as a function of twisting angle for ethylene.

amount of nondynamical correlation, as shown by the results up to 80° .

IV. CONCLUSIONS

In this paper we first develop a general theory for perturbative expansions of similarity-transformed matrices. This is accomplished via a Löwdin-style partitioning of the transformed matrix. The $\bar{\mathbf{H}}_{\mathbf{q}\mathbf{q}}$ block of the matrix and the right- and left-hand eigenvectors are then expanded in a perturbation series. As long as the zeroth-order right- and left-hand eigenvectors are chosen to be eigenvectors of $\bar{\mathbf{H}}_{\mathbf{p}\mathbf{p}}^{[0]}$, the zeroth-order energy is the energy of the unperturbed problem, and we have a consistent perturbation theory. Furthermore, the first-order correction to the energy is zero, meaning that the leading correction to the energy appears at second order.

Next, we applied this scheme to the problem of developing new perturbative corrections on top of coupled-cluster theory. Although we focused on VOD, we derived corrections for all methods which can be viewed as approximations to CCSD, including QCISD, BD, OD, and CCSD itself. This new type of correction, called (2), consists of, in general, single, double, triple, and quadruple excitation terms. By introducing a factorization approximation to the quadruple excitation term, the cost is reduced from n^9 to n^6 . The overall scaling of the method, as determined by the triples term, is then n^7 .

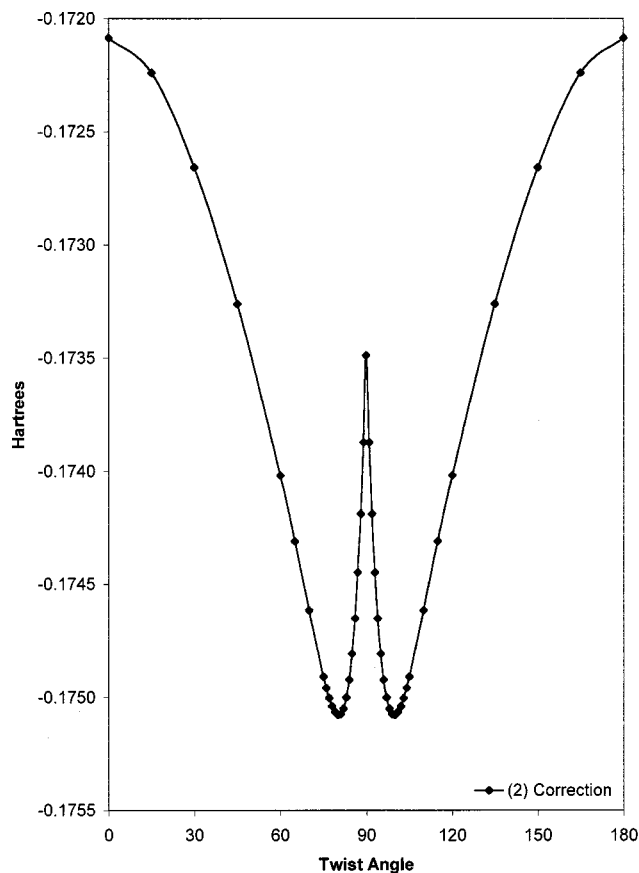


FIG. 6. The (2) correction as a function of twisting angle ethylene with a DZP basis.

Finally, we examined the effectiveness of the VOD(2) method for some examples of bond breaking and diradical formation, difficult problems for single-reference methods to describe properly. For those areas of the potential-energy surface where VOD provides a reasonable qualitative description of the wave function, VOD(2) does an excellent job of recovering the dynamical correlation. Clearly, more testing needs to be done, but it appears that this new method provides an inexpensive and robust way to describe the breaking of single bonds with quantitative accuracy.

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research SBIR Grant No. F49620-97-C-0049 and by Sandia National Laboratories through subcontract No. LS-5503. Additionally, this work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098. We thank Professor Stanisław Kucharski (Silesian University) for his help in debugging. We would also like to acknowledge Professor Rodney Bartlett (University of Florida) and Professor John Watts (Jackson State University) for enlightening conversations. M.H.G. gratefully acknowledges a Packard Fellowship (1995–2000). A.I.K. acknowledges support by the Petroleum Research Fund, administered by the American Chemical Society. The calculations presented in this paper were performed on an IBM RS/6000 SP provided through an IBM SUR grant.

APPENDIX A: SPIN-ORBITAL FORM OF THE (2) EQUATIONS

Equations (40)–(45) present the equations for the various terms in the (2) correction in their completely general,

tensor form. However, it is useful to present those equations in their spin-orbital form within the semicanonical basis. Therefore, in this Appendix we present spin-orbital forms of Eqs. (40)–(45). The MP2 terms are

$$\text{MP2 singles} = \sum_i \frac{\bar{F}_{\bullet a}^i \bar{F}_{\bullet i}^a}{\bar{\epsilon}_i - \bar{\epsilon}_a}, \quad (\text{A1})$$

$$\text{MP2 doubles} = \frac{1}{4} \sum_{i,j} \frac{\bar{W}_{\bullet ab}^{ij} \bar{W}_{\bullet ij}^{ab}}{\bar{\epsilon}_i + \bar{\epsilon}_j - \bar{\epsilon}_a - \bar{\epsilon}_b}, \quad (\text{A2})$$

where $\bar{\epsilon}_p$ stands for $\bar{F}_{\bullet p}^p$ in the semicanonical basis. The Λ terms are

$$\begin{aligned} \Lambda \text{ singles} = & \sum_{a',B} \frac{\lambda_{\bullet B}^I \bar{F}_{\bullet a'}^B \bar{F}_{\bullet I}^{a'}}{\bar{\epsilon}_I - \bar{\epsilon}_{a'}} - \sum_{i',J} \frac{\lambda_{\bullet A}^J \bar{F}_{\bullet i'}^J \bar{F}_{\bullet J}^{A'}}{\bar{\epsilon}_{i'} - \bar{\epsilon}_A} + \sum_{a,B} \frac{\lambda_{\bullet B}^J \bar{W}_{\bullet Ja}^{iB} \bar{F}_{\bullet i}^a}{\bar{\epsilon}_i - \bar{\epsilon}_a} \\ & + \sum_{\substack{A,E \\ I,M}} \frac{\lambda_{\bullet AE}^{IM} \bar{F}_{\bullet M}^E \bar{F}_{\bullet I}^A}{\bar{\epsilon}_I - \bar{\epsilon}_A} + \frac{1}{2} \sum_{\substack{A,E,F \\ I,M}} \frac{\lambda_{\bullet EF}^{IM} \bar{W}_{\bullet aM}^{EF} \bar{F}_{\bullet I}^a}{\bar{\epsilon}_I - \bar{\epsilon}_a} - \frac{1}{2} \sum_{\substack{A,E \\ i,M,N}} \frac{\lambda_{\bullet AE}^{MN} \bar{W}_{\bullet MN}^{iE} \bar{F}_{\bullet i}^A}{\bar{\epsilon}_i - \bar{\epsilon}_A} \\ & + \frac{1}{2} \sum_{\substack{a,E,F,G \\ i,M,N}} \frac{\lambda_{\bullet EF}^{MN} \bar{W}_{\bullet Ga}^{Fi} \bar{W}_{\bullet MN}^{EG} \bar{F}_{\bullet i}^a}{\bar{\epsilon}_i - \bar{\epsilon}_a} - \frac{1}{2} \sum_{\substack{a,E,F \\ i,M,N,O}} \frac{\lambda_{\bullet EF}^{MN} \bar{W}_{\bullet Na}^{Oi} \bar{W}_{\bullet MO}^{EF} \bar{F}_{\bullet i}^a}{\bar{\epsilon}_i - \bar{\epsilon}_a}, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \Lambda \text{ doubles} = & \sum_{\substack{A,b \\ I,j}} \frac{\lambda_{\bullet A}^I \bar{F}_{\bullet b}^j \bar{W}_{\bullet Ij}^{Ab}}{\bar{\epsilon}_I + \bar{\epsilon}_j - \bar{\epsilon}_A - \bar{\epsilon}_b} + \frac{1}{2} \sum_{a,b,E} \frac{\lambda_{\bullet E}^I \bar{W}_{\bullet ab}^{Ej} \bar{W}_{\bullet Ij}^{ab}}{\bar{\epsilon}_I + \bar{\epsilon}_j - \bar{\epsilon}_a - \bar{\epsilon}_b} - \frac{1}{2} \sum_{a,b,M} \frac{\lambda_{\bullet A}^M \bar{W}_{\bullet Mb}^{ij} \bar{W}_{\bullet Ij}^{Ab}}{\bar{\epsilon}_i + \bar{\epsilon}_j - \bar{\epsilon}_A - \bar{\epsilon}_b} \\ & + \frac{1}{2} \sum_{\substack{A,b',E \\ I,J}} \frac{\lambda_{\bullet AE}^{IJ} \bar{F}_{\bullet b'}^E \bar{W}_{\bullet IJ}^{Ab'}}{\bar{\epsilon}_I + \bar{\epsilon}_J - \bar{\epsilon}_A - \bar{\epsilon}_{b'}} - \frac{1}{2} \sum_{\substack{A,B \\ I,j',M}} \frac{\lambda_{\bullet AB}^{IJ} \bar{F}_{\bullet M}^{j'} \bar{W}_{\bullet Ij'}^{AB}}{\bar{\epsilon}_I + \bar{\epsilon}_{j'} - \bar{\epsilon}_A - \bar{\epsilon}_B} + \frac{1}{8} \sum_{a,b,E,F} \frac{\lambda_{\bullet EF}^{IJ} \bar{W}_{\bullet ab}^{EF} \bar{W}_{\bullet Ij}^{ab}}{\bar{\epsilon}_I + \bar{\epsilon}_J - \bar{\epsilon}_a - \bar{\epsilon}_b} \\ & + \frac{1}{8} \sum_{\substack{A,B \\ i,j,M,N}} \frac{\lambda_{\bullet AB}^{MN} \bar{W}_{\bullet MN}^{ij} \bar{W}_{\bullet Ij}^{AB}}{\bar{\epsilon}_i + \bar{\epsilon}_j - \bar{\epsilon}_A - \bar{\epsilon}_B} - \sum_{\substack{A,b,E \\ i,j,M}} \frac{\lambda_{\bullet AE}^{MJ} \bar{W}_{\bullet Mb}^{iE} \bar{W}_{\bullet Ij}^{Ab}}{\bar{\epsilon}_i + \bar{\epsilon}_j - \bar{\epsilon}_A - \bar{\epsilon}_b} - \frac{1}{4} \sum_{\substack{a,b,E,F \\ I,j,M,N}} \frac{\lambda_{\bullet FE}^{MI} \bar{W}_{\bullet ab}^{Nj} \bar{W}_{\bullet MN}^{FE} \bar{W}_{\bullet Ij}^{ab}}{\bar{\epsilon}_I + \bar{\epsilon}_J - \bar{\epsilon}_a - \bar{\epsilon}_b} \\ & - \frac{1}{4} \sum_{\substack{A,b,E,F \\ i,j,M,N}} \frac{\lambda_{\bullet EA}^{NM} \bar{W}_{\bullet Fb}^{ij} \bar{W}_{\bullet NM}^{EF} \bar{W}_{\bullet Ij}^{Ab}}{\bar{\epsilon}_i + \bar{\epsilon}_j - \bar{\epsilon}_A - \bar{\epsilon}_b}, \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} \Lambda \text{ triples} = & \frac{1}{4} \sum_{\substack{A,b,c \\ I,j,k}} \frac{\lambda_{\bullet A}^I \bar{W}_{\bullet bc}^{jk} \bar{W}_{\bullet Ijk}^{Abc}}{\bar{\epsilon}_I + \bar{\epsilon}_j + \bar{\epsilon}_k - \bar{\epsilon}_A - \bar{\epsilon}_b - \bar{\epsilon}_c} + \frac{1}{4} \sum_{\substack{A,B,c \\ I,J,k}} \frac{\lambda_{\bullet AB}^{IJ} \bar{F}_{\bullet c}^k \bar{W}_{\bullet IJk}^{ABc}}{\bar{\epsilon}_I + \bar{\epsilon}_J + \bar{\epsilon}_k - \bar{\epsilon}_A - \bar{\epsilon}_B - \bar{\epsilon}_c} + \frac{1}{4} \sum_{\substack{A,b,c,E \\ I,J,k}} \frac{\lambda_{\bullet AE}^{IJ} \bar{W}_{\bullet bc}^{Ek} \bar{W}_{\bullet IJk}^{Abc}}{\bar{\epsilon}_I + \bar{\epsilon}_J + \bar{\epsilon}_k - \bar{\epsilon}_A - \bar{\epsilon}_b - \bar{\epsilon}_c} \\ & - \frac{1}{4} \sum_{\substack{A,B,c \\ I,j,k,M}} \frac{\lambda_{\bullet AB}^{IM} \bar{W}_{\bullet M}^{jk} \bar{W}_{\bullet Ijk}^{ABc}}{\bar{\epsilon}_I + \bar{\epsilon}_j + \bar{\epsilon}_k - \bar{\epsilon}_A - \bar{\epsilon}_B - \bar{\epsilon}_c}, \end{aligned} \quad (\text{A5})$$

$$\Lambda \text{ quadruples} = \frac{1}{16} \sum_{\substack{A,B,c,d \\ I,J,k,l}} \frac{\lambda_{\bullet AB}^{IJ} \bar{W}_{\bullet cd}^{kl} \bar{W}_{\bullet IJkl}^{ABcd}}{\bar{\epsilon}_I + \bar{\epsilon}_J + \bar{\epsilon}_k + \bar{\epsilon}_l - \bar{\epsilon}_A - \bar{\epsilon}_B - \bar{\epsilon}_c - \bar{\epsilon}_d}. \quad (\text{A6})$$

APPENDIX B: FACTORIZED QUADRUPLES EQUATIONS

In this appendix we give the equations for the factorized quadruples approximation. The terms are broken up into four groups for manageability. Also, $\bar{W}_{\bullet\bullet cd}^{ab}$, $\bar{W}_{\bullet\bullet ij}^{kl}$, and $\bar{W}_{\bullet\bullet jb}^{ia}$ from Eqs. (31)–(33) and $(\bar{W}_D)^{kl}$ from Eq. (53) are used as convenient intermediates. The four groups are

$$\begin{aligned} \Lambda \text{ Quads}_f^1 = & \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{cdAE}\bar{t}_{\bullet\bullet IK}^{FB}t_{\bullet\bullet LJ}^{FB} + \frac{1}{8}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{cdAE}\bar{t}_{\bullet\bullet KL}^{FB}t_{\bullet\bullet IJ}^{FB} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{dA}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet IJ}^{FB} + \lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{dA}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet KI}^{FB}t_{\bullet\bullet LJ}^{FB} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{dA}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet IJ}^{FB}t_{\bullet\bullet KL}^{FB} + \frac{1}{8}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{AB}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet KL}^{FB}t_{\bullet\bullet IJ}^{FD} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{KL}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet EF}^{AB}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet KI}^{FD}t_{\bullet\bullet JL}^{FD}, \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} \Lambda \text{ Quads}_f^2 = & \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ki}^{MNAC}\bar{t}_{\bullet\bullet IM}^{DB}t_{\bullet\bullet NJ}^{DB} + \frac{1}{8}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ki}^{MN}\bar{t}_{\bullet\bullet IM}^{CD}t_{\bullet\bullet NJ}^{AB} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IJ}^{MN}\bar{t}_{\bullet\bullet KM}^{CD}t_{\bullet\bullet NJ}^{AB} + \lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IJ}^{MN}\bar{t}_{\bullet\bullet CA}^{CA}t_{\bullet\bullet KM}^{DB}t_{\bullet\bullet NJ}^{DB} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IJ}^{MN}\bar{t}_{\bullet\bullet KM}^{CD}t_{\bullet\bullet NJ}^{AB} + \frac{1}{8}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IJ}^{MN}\bar{t}_{\bullet\bullet KM}^{CD}t_{\bullet\bullet NJ}^{AB}t_{\bullet\bullet NL}^{AB} \\ & + \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IJ}^{MN}\bar{t}_{\bullet\bullet CA}^{CA}t_{\bullet\bullet KM}^{BD}t_{\bullet\bullet NL}^{BD}, \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} \Lambda \text{ Quads}_f^3 = & -\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet IE}^{Mc}\bar{t}_{\bullet\bullet IK}^{AE}t_{\bullet\bullet MJ}^{DB} - \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet ke}^{Md}\bar{t}_{\bullet\bullet IJ}^{CE}t_{\bullet\bullet ML}^{AB} \\ & - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet IE}^{Md}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet MJ}^{AB} - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet ke}^{Mc}\bar{t}_{\bullet\bullet IJ}^{AE}t_{\bullet\bullet ML}^{DB} \\ & - \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet IE}^{Md}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet MJ}^{AB} - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet ke}^{Md}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet IJ}^{AB}t_{\bullet\bullet ML}^{AB} \\ & - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet IE}^{Mc}\bar{t}_{\bullet\bullet CE}^{AE}t_{\bullet\bullet MJ}^{DB} - \lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet cd}\bar{W}_{\bullet\bullet ke}^{Mc}\bar{t}_{\bullet\bullet IJ}^{AE}t_{\bullet\bullet ML}^{BD}, \end{aligned} \quad (\text{B3})$$

$$\begin{aligned} \Lambda \text{ Quads}_f^4 = & -\frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ke}^{MB}\bar{t}_{\bullet\bullet IJ}^{AE}t_{\bullet\bullet ML}^{CD} - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ke}^{MA}\bar{t}_{\bullet\bullet IJ}^{CE}t_{\bullet\bullet ML}^{BD} \\ & - \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IE}^{MB}\bar{t}_{\bullet\bullet IK}^{AE}t_{\bullet\bullet MJ}^{CD} - \lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IE}^{MA}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet MJ}^{DB} \\ & + \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IE}^{MA}\bar{t}_{\bullet\bullet CE}^{CE}t_{\bullet\bullet MJ}^{DB} - \lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ke}^{MA}\bar{t}_{\bullet\bullet IJ}^{CE}t_{\bullet\bullet ML}^{BD} \\ & - \frac{1}{4}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet IE}^{MB}\bar{t}_{\bullet\bullet CE}^{AE}t_{\bullet\bullet MJ}^{CD} + \frac{1}{2}\lambda_{\bullet\bullet AB}^{IJ}(\bar{W}_D)^{kl}_{\bullet\bullet CD}\bar{W}_{\bullet\bullet ke}^{MB}\bar{t}_{\bullet\bullet IK}^{AE}t_{\bullet\bullet ML}^{CD}. \end{aligned} \quad (\text{B4})$$

Finally,

$$\Lambda \text{ quadruples (factorized)} = \frac{1}{2}(\Lambda \text{ Quads}_f^1 + \Lambda \text{ Quads}_f^2 + \Lambda \text{ Quads}_f^3 + \Lambda \text{ Quads}_f^4). \quad (\text{B5})$$

The overall factor of one-half arises from the factorization approximation.²⁷

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- ¹C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
²J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).
³K. Raghavachari, G. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
⁴O. Sinanoğlu, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience, London, 1964), Vol. VI, pp. 315–412.
⁵B. O. Roos, in *Lecture Notes in Quantum Chemistry: European Summer School in Quantum Chemistry*, Vol. 58 of Lecture notes in Chemistry, edited by B. O. Roos (Springer-Verlag, Berlin, 1992), pp. 177–254.
⁶D. K. W. Mok, R. Neumann, and N. C. Handy, J. Phys. Chem. **100**, 6225 (1996).
⁷B. O. Roos, in *Ab Initio Methods in Quantum Chemistry, Part II*, Vol. 69 of *Advances in Chemical Physics*, edited by K. P. Lawley (Wiley, Chichester, 1987), pp. 399–445.
⁸A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 10669 (1998).
⁹K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Phys. Chem. **94**, 5483 (1990).
¹⁰K. Andersson, P.-Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).
¹¹S. R. Gwaltney and M. Head-Gordon, Chem. Phys. Lett. **323**, 21 (2000).
¹²G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
¹³G. E. Scuseria and H. F. Schaefer III, Chem. Phys. Lett. **142**, 354 (1987).
¹⁴C. D. Sherrill, A. I. Krylov, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 4171 (1998).
¹⁵T. B. Pederson, H. Koch, and C. Hättig, J. Chem. Phys. **110**, 8318 (1999).
¹⁶M. Head-Gordon, P. E. Maslen, and C. A. White, J. Chem. Phys. **108**, 616 (1998).
¹⁷N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).
¹⁸R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, Vol. 166 of NATO ASI series C, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986), pp. 35–61.
¹⁹P.-O. Löwdin, J. Math. Phys. **3**, 969 (1962).
²⁰J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
²¹W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **187**, 21 (1991).
²²N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari, and G. W. Trucks, Chem. Phys. Lett. **164**, 185 (1989).
²³J. F. Stanton and J. Gauss, Theor. Chim. Acta **93**, 303 (1996).
²⁴J. F. Stanton and J. Gauss, Theor. Chim. Acta **95**, 97(E) (1997).
²⁵J. F. Stanton, Chem. Phys. Lett. **281**, 130 (1997).
²⁶T. D. Crawford and J. F. Stanton, Int. J. Quantum Chem. **70**, 601 (1998).
²⁷S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **108**, 5243 (1998).
²⁸P. E. Maslen, M. S. Lee, and M. Head-Gordon, Chem. Phys. Lett. **319**, 205 (2000).
²⁹S. A. Kucharski and R. J. Bartlett, in *Advances in Quantum Chemistry*,

- edited by P.-O. Löwdin (Academic, Orlando, 1986), Vol. 18, pp. 281–344.
- ³⁰S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 9221 (1998).
- ³¹S. A. Kucharski, J. D. Watts, and R. J. Bartlett, *Chem. Phys. Lett.* **302**, 295 (1999).
- ³²S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **110**, 8233 (1999).
- ³³J. C. Saeh and J. F. Stanton, *J. Chem. Phys.* **111**, 8275 (1999).
- ³⁴C. A. White, J. Kong, D. R. Maurice, T. R. Adams, J. Baker, M. Challacombe, E. Schwegler, J. P. Dombroski, C. Ochsenfeld, M. Oumi, T. R. Furlani, J. Florian, R. D. Adamson, N. Nair, A. M. Lee, N. Ishikawa, R. L. Graham, A. Warshel, B. G. Johnson, P. M. W. Gill, and M. Head-Gordon, *Q-Chem, Version 1.2*, Q-Chem, Inc., Pittsburgh, PA (1998).
- ³⁵T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, M. L. Leininger, R. A. King, S. T. Brown, C. L. Janssen, E. T. Seidl, Y. Yamaguchi, W. D. Allen, Y. Xie, G. Vacek, T. P. Hamilton, C. B. Kellogg, R. B. Remington, and H. F. Schaefer III, *PSI 3.0*, development version, PSITECH, Inc., Watkinsville, GA 30677, U.S.A., 2000.
- ³⁶S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ³⁷T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).
- ³⁸See EPAPS Document No. E-JCPSA6-113-301030 for Tables II–VI. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory `/epaps/`. See the EPAPS homepage for more information.
- ³⁹T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ⁴⁰J. Olsen, P. Jørgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).