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MARTIN HEAD-GORDON, MANABU OUMI and DAVID MAURICE

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

A family of quasidegenerate second-order perturbation theories that correct excitation energies from single-excitation configuration interaction (CIS) are introduced which generalize the earlier non-degenerate second-order method, CIS(D). The new methods are termed CIS(D_n), where n ranges from 0 to ∞, according to the number of terms retained in a doubles denominator expansion. Truncation at either $n = 0$ or $n = 1$ yields methods which involve the diagonalization of a dressed singles-only response matrix, where the dressing is state-independent. Hence CIS(D_0) and CIS(D_1) can be implemented efficiently using semidirect methods, which are discussed. Test calculations on formaldehyde, ethylene, chlorine nitrate, styrene, benzaldehyde, and chalcone are presented to assess the performance of these methods. CIS(D_0) and CIS(D_1) both show significant improvements relative to CIS(D) in cases of near-degeneracy.

1. Introduction

Single-reference *ab initio* excitation energy methods are becoming widely used, with the simplest useful scheme being single excitation configuration interaction (CIS) [1, 2]. CIS often provides a qualitatively correct description of low lying one-electron excited states in much the same sense that Hartree–Fock molecular orbital theory does for the ground state. CIS itself suffers from three general deficiencies: (1) neglect of dynamic correlation, which means that often transition energies are in error by roughly 1 eV, even if the CIS wavefunction is qualitatively correct; (2) near-degenerate CIS excited states of the same symmetry may be strongly mixed when electron correlation is included, causing the CIS wavefunctions to be suspect in such cases; and (3) CIS wavefunctions cannot describe excited states which contain significant double-excitation character, without specialized extensions [3].

One natural next step beyond CIS for excited states is to include electron correlation via perturbation theory through second order, akin to second-order Møller–Plesset theory for the ground state [4]. Using the CIS wavefunctions as a reference, the CIS(D) method is a non-degenerate second-order correction of this type [5, 6]. CIS(D) approximately accounts for differential dynamical correlation effects on electronic transitions, to correct the first deficiency noted above. We have recently introduced a 'theta diagnostic' [7], which indicates the stability of the CIS wavefunctions to mixing induced by near-degeneracies, thereby at least detecting potential breakdowns of CIS(D), and the corresponding reference CIS wavefunctions. This diagnostic requires essentially no additional computational cost relative to CIS(D) itself.

The purpose of this paper is to introduce a family of quasidegenerate generalizations of CIS(D) termed CIS(D_n), with the objective of obtaining reliable results even in the presence of near-degeneracies amongst the excited states. There have been several previous single-reference based methods for eletronic transitions which include second-order electron correlation effects in a way that treats near-degeneracies properly. The CC2 model [8, 9] iteratively determines the single and double substitutions as the poles of a true linear response function, which involves iteratively determining the second-order ground state double substitutions as well. The P-EOM-MBPT2 method [10] uses the ground state MP2 solution but iteratively determines both singles and doubles amplitudes via a truncation of the equation of motion coupled cluster equations. In terms of the perturbation expansion which is the basis for CIS(D), CC2 is a second-order theory, while P-EOM-MBPT2 accounts for part of a third-order term as well [11].

The CIS(D_n) methods introduced in this paper are similar in spirit to both CC2 and P-EOM-MBPT2, but when $n = 0$ or 1 they offer a critically important simplification. CC2 and P-EOM-MBPT2 both require explicit iteration of the singles and the doubles amplitudes together (or alternatively diagonalization of an extremely awkward state-dependent singles response matrix), which restricts their domain of applicability

relative to CIS(D), where only singles are required explicitly. We shall show that $CIS(D_0)$ and $CID(D_1)$ require only explicit iteration of the singles, with the effect of doubles being included by a simple state-independent dressing of the singles response matrix. The idea of defining a dressed singles response matrix has been elegantly pursued also in the similarity-transformed (ST)-EOM methods [12–14], which implicitly folds in the effects of not just doubles but also higher substitutions. Other methods involving intermediate Hamiltonians [15] are based on similar general ideas.

The theory is developed in section 2, and shows that the $CIS(D_n)$ methods are defined by a binomial expansion of a doubles denominator, where the index n indicates the order at which the series is truncated. Thus $CIS(D_\infty)$ is a full diagonalization of the response matrix through second order in the space of singles and doubles. It requires explicit iteration of double substitutions like CC2 and P-EOM-MBPT2, or a computationally awkward energy-dependent singles response matrix. The low order $CIS(D_0)$ and $CIS(D_1)$ methods have the unique feature of not requiring iteration of doubles amplitudes, so that efficient generalizations of semidirect MP2 methods [16, 17] can be employed, as described in section 3. Only cubic memory and disc storage is needed, so that $CIS(D_0)$ and $CIS(D_1)$ excitation energies are feasible for systems virtually as large as those which are feasible for ground state MP2 calculations. Indeed, the computational effort per state and per iteration is made essentially equal to evaluating the ground state MP2 energy and one-particle density matrix via semidirect methods.

Numerical tests of the performance of $CIS(D_0)$ and $CIS(D_1)$ are presented in section 4, for vertical excitation energies. We wish to compare against non-degenerate CIS(D) to assess the improvement, as well as against full diagonalization of the single-double response matrix through second order, which is $CIS(D_\infty)$. A variety of molecules are considered, and the results suggest that $CIS(D_0)$ and $CIS(D_1)$ perform satisfactorily. $CIS(D_1)$ yields results closer to $CIS(D_\infty)$, as expected, while $CIS(D_0)$ yields excitation energies that are systematically higher. $CIS(D_1)$ has been used to study the nature of low-lying excitations in the chalcone molecule Ph—CO—CH=CH—Ph, which permits assignment of the principal low-lying bands of its absorption spectrum [18].

2. Theory

Coupled cluster linear response theory [19] provides an ideal formulation for excitation energies, which is exact (equivalent to the full configuration interaction problem) if carried through cluster excitations $\hat{t}_\beta$ equal to the number of electrons. The coupled cluster equations for the ground state amplitudes, a_α (where the indices α and β run over all excitations) can be written symbolically as

$$\left\langle \Phi_\alpha \left| \hat{H} \right| \exp\left(\sum_\beta a_\beta \hat{t}_\beta\right) \Phi_0 \right\rangle_C = 0. \qquad (1\,a)$$

The coupled cluster response matrix **A**, in terms of the same notation, may be written as

$$A_{\alpha\beta} = \left\langle \Phi_\alpha \left| \hat{H} \right| \hat{t}_\beta \exp\left(\sum_\gamma a_\gamma \hat{t}_\gamma\right) \Phi_0 \right\rangle_C. \qquad (1\,b)$$

The eigenvalues of the response matrix **A** are the Bohr frequencies of the system:

$$\mathbf{Ab} = \omega\mathbf{b}. \qquad (1\,c)$$

Truncating the cluster expansion employed for the ground state, and therefore the corresponding response amplitudes for electronic transitions, yields a hierarchy of size-consistent approximations to equation (1a–c). Truncation at the singles and doubles level yields the widely used LR-CCSD [20] or EOM-CCSD [21] methods, for example. Approximations to the corresponding theories including triple excitations also have been proposed [22, 23], yielding improved results at great computational expense.

The perturbation expansion of the response matrix that we proposed to define the CIS(D) method is as follows. First, as in ground state Møller–Plesset theory, the Hamiltonian is partitioned into the (zero-order) mean-field Fock operator plus a (first-order) fluctuation potential, $\hat{H} = \hat{F}^{(0)} + \hat{V}^{(1)}$ which yields the Møller–Plesset expansion of the ground state cluster operators. In the response matrix, the zero-order part is the CIS problem in the singles-singles block (SS), plus matrix elements of the mean-field Fock operator in other blocks (diagonal in the canonical orbital basis). Thus the Møller–Plesset partition of the Hamiltonian is applied everywhere in the response matrix except the SS block.

With this construction, CIS solutions are obtained at zero order from eigenvectors of the SS block. At zero order the doubles and triples blocks are diagonal in the canonical basis (denoted as $\mathbf{D}^{(0)}$ in equation (2) below). First-order terms are matrix elements of the fluctuation potential (except in the SS block, where it was part of CIS itself). Higher-order terms enter because the exact response matrix depends on the ground state cluster amplitudes (which have their usual Møller–Plesset expansion), giving an expansion of the response matrix of the form:

$$
\mathbf{A} = \begin{bmatrix} \mathbf{A}_{SS}^{(0)} & \mathbf{0} & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{D}_{DD}^{(0)} & \mathbf{0} & \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_{TT}^{(0)} & \\ \vdots & & & \ddots \end{bmatrix}
$$

$$
+ \begin{bmatrix} \mathbf{0} & \mathbf{A}_{SD}^{(1)} & \mathbf{A}_{ST}^{(1)} & \cdots \\ \mathbf{A}_{DS}^{(1)} & \mathbf{A}_{DD}^{(1)} & \mathbf{A}_{DT}^{(1)} & \\ \mathbf{0} & \mathbf{A}_{TD}^{(1)} & \mathbf{A}_{TT}^{(1)} & \\ \vdots & & & \ddots \end{bmatrix}
$$

$$
+ \begin{bmatrix} \mathbf{A}_{SS}^{(2)} & \mathbf{A}_{SD}^{(2)} & \mathbf{0} & \cdots \\ \mathbf{A}_{DS}^{(2)} & \mathbf{A}_{DD}^{(2)} & \mathbf{A}_{DT}^{(2)} & \\ \mathbf{A}_{TS}^{(1)} & \mathbf{A}_{TD}^{(2)} & \mathbf{A}_{TT}^{(2)} & \\ \vdots & & & \ddots \end{bmatrix} + \cdots. \tag{2}
$$

CIS(D) is the result of applying non-degenerate perturbation theory through second order:

$$
\omega_i^{(2)} = \mathbf{b}_i^{(0)\dagger} \mathbf{A}_{SS}^{(2)} \mathbf{b}_i^{(0)} - \mathbf{b}_i^{(0)\dagger} \mathbf{A}_{SD}^{(1)} (\mathbf{D}_{DD}^{(0)} - \omega_i^{(0)})^{-1} \mathbf{A}_{DS}^{(1)} \mathbf{b}_i^{(0)}. \tag{3}
$$

The result is a correction to the CIS excitation energy of the ith excited state.

As stated in the introduction, CIS(D) is potentially ill-behaved when the reference CIS states exhibit near-degeneracies. In such cases, our objective should be to apply quasidegenerate perturbation theory through second order within a well defined manifold of near-degenerate states. Suppose, for example, a small number of CIS states are nearly degenerate, with eigenvalue $\omega_k^{(0)}$. We must diagonalize the response matrix constructed through second order in this small manifold, which is

$$
A_{ij}^{(0\to2)}(\omega_k) = \mathbf{b}_i^{(0)\dagger}(\mathbf{A}_{SS}^{(0)} + \mathbf{A}_{SS}^{(2)})\mathbf{b}_j^{(0)} - \mathbf{b}_i^{(0)\dagger}
$$

$$
\times \mathbf{A}_{SD}^{(1)}(\mathbf{D}_{DD}^{(0)} - \omega_k^{(0)})^{-1} \mathbf{A}_{DS}^{(1)} \mathbf{b}_j^{(0)}. \tag{4}
$$

Although this is physically reasonable, and clearly corrects the possibly large errors that would arise from employing non-degenerate perturbation theory, it is still not entirely satisfactory. The necessity to select an arbitrary energy threshold that defines near-degeneracy means that such an approach does not constitute an unambiguous theoretical model chemistry.

Instead, we prefer to view the entire manifold of reference CIS states as being potentially near-degenerate, and develop the second-order perturbation correction under this simple parameter-free assumption. We will therefore be rediagonalizing the entire singles block of the response matrix to allow for remixing induced by including electron correlation effects through second order in the fluctuation potential. The singles block is redefined analogously to equation (4):

$$
A_{SS}^{(0\to2)}(\omega) = (\mathbf{A}_{SS}^{(0)} + \mathbf{A}_{SS}^{(2)}) - \mathbf{A}_{SD}^{(1)}(\mathbf{D}_{DD}^{(0)} - \omega)^{-1}\mathbf{A}_{DS}^{(1)}, \tag{5}
$$

except that we cannot employ the zero-order CIS eigenvalues on the right hand side because they may span a large energy range. Hence this dressed Hamiltonian is excitation-energy dependent. It arises equivalently from diagonalization of the following truncated response matrix which is defined only in the singles and doubles blocks:

$$
\begin{bmatrix} \mathbf{A}_{SS}^{(0)} + \mathbf{A}_{SS}^{(2)} & \mathbf{A}_{SD}^{(1)} \\ \mathbf{A}_{DS}^{(1)} & \mathbf{D}_{DD}^{(0)} \end{bmatrix}
$$

$$
\equiv \begin{bmatrix} \langle \Phi_S | \hat{H} | \Phi_S \rangle + \langle \Phi_S | \hat{V} | T_2^{(1)} \Phi_S \rangle & \langle \Phi_S | \hat{V} | \Phi_D \rangle \\ \langle \Phi_D | \hat{V} | \Phi_S \rangle & \langle \Phi_D | \hat{F} | \Phi_D \rangle \end{bmatrix}. \tag{6}
$$

One eliminates the doubles from explicit consideration by inverting the diagonal zero-order DD block, leading to an energy-dependent dressed singles response matrix as given by equation (5). Diagonalizing either equation (6) or the energy-dependent equation (5) is a quaside-generate generalization of CIS(D), which is similar in spirit to the CC2 and P-EOM-MBPT2 methods, although slightly simpler.

A significant additional simplification is possible, which serves to define the CIS(D_n) family of methods. We observe that the diagonal elements defining $\mathbf{D}_{DD}^{(0)}$ (the doubles eigenvalue differences, $\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$) are bounded from below by twice the lowest ionization potential of the system (within the Koopman's approximation, assuming no bound virtual levels), and are generally much larger. Therefore such elements are much larger than the excitation energies ω to relatively low lying excited states that are of interest. Defining

$$
\Delta = \omega(\mathbf{D}_{DD}^{(0)})^{-1}, \tag{7}
$$

we can write a rapidly convergent binomial expansion:

$$
(\mathbf{D}_{DD}^{(0)} - \omega)^{-1} = (\mathbf{D}_{DD}^{(0)})^{-1}(1 - \Delta)^{-1}
$$

$$
= (\mathbf{D}_{DD}^{(0)})^{-1}(1 + \Delta + \Delta^2 + \cdots). \tag{8}
$$

We shall define CIS(D_n) as the method which results from truncating the series after the Δ^n-term. Thus

CIS(D_∞) involves finding exact eigenvalues and eigenvectors of equation (6).

In CIS(D_1) we retain just the first two terms of the binomial expansion (i.e., up to first order in Δ). This permits us to replace diagonalization of equation (5) by a generalized eigenvalue problem of the form

$$\mathbf{A}_{SS}^{eff}\mathbf{b}_S = \omega\mathbf{S}_{SS}^{eff}\mathbf{b}_S, \qquad (9\,a)$$

where the dressed response matrix is independent of excitation energy and state, and the metric is non-diagonal. In more detail, the effective singles response matrix and metric are defined by

$$(\mathbf{A}_{SS}^{(0)} + \mathbf{A}_{SS}^{(2)} - \mathbf{A}_{SD}^{(1)}(\mathbf{D}_{DD}^{(0)})^{-1}\mathbf{A}_{DS}^{(1)})\mathbf{b}_S$$

$$= \omega(\mathbf{1}_{SS} + \mathbf{A}_{SD}^{(1)}(\mathbf{D}_{DD}^{(0)})^{-2}\mathbf{A}_{DS}^{(1)})\mathbf{b}_S. \qquad (9\,b)$$

The solution of equation ($9a$, b) defines CIS(D_1).

The corresponding method in which only the zero-order term of equation (8) is retained would simply replace the metric of equation (9) by the unit matrix, defining CIS(D_0). If we were to retain higher terms, energy dependence would reappear in the eigenvalue problem, making it computationally intractable (except for the lowest excited state). Therefore the three most interesting members of the CIS(D_n) family are CIS(D_0), CIS(D_1) and CIS(D_∞). Our objective in the results section will be to compare CIS(D_0) and CIS(D_1), which yield energy-independent dressings of the singles response matrix, against CIS(D_∞), to assess the legitimacy of truncating the Δ expansion in equation (8).

We briefly summarize the CIS(D_1) (and implicitly also CIS(D_0)) spin–orbital expressions for the matrix–vector multiples which correspond to evaluating the left and right sides of equation (9) for a given trial vector $\mathbf{b}_S$. A close similarity to terms in the CIS(D) excitation energy will of course be evident. The leading term of equation ($9\,b$) is simply the singles-singles block of the Hamiltonian contracted with the trial vector:

$$(\mathbf{A}_{SS}^{(0)}\mathbf{b}_S)_i^a = \langle\Phi_i^a|\bar{H}|\Phi_j^b\rangle b_j^b = (\varepsilon_a - \varepsilon_i)b_i^a + \sum_{jb}(ja \parallel bi)b_j^b. \qquad (10)$$

The second term involves the same intermediate as the triples term of the CIS(D) energy:

$$(\mathbf{A}_{SS}^{(2)}\mathbf{b}_S)_i^a = \langle\Phi_i^a|\bar{H}|\hat{T}_2\Phi_j^b\rangle b_j^b$$

$$= \frac{1}{2}\sum_{jkbc}(jk \parallel bc)\{b_i^b a_{jk}^{ca} + b_j^a a_{ik}^{cb} + 2b_j^b a_{ik}^{ac}\}, \qquad (11)$$

where the doubles amplitudes are defined by the ground state first-order Møller–Plesset wavefunction:

$$\hat{T}_2|\Phi_0\rangle = \frac{1}{4}\sum_{ijab} a_{ij}^{ab}|\Phi_{ij}^{ab}\rangle$$

$$= -\frac{1}{4}\sum_{ijab}\frac{(ij \parallel ab)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}|\Phi_{ij}^{ab}\rangle. \qquad (12)$$

Note that this second term is the only part of the dressed response matrix of equation (9) which is not symmetric. Therefore the left and right eigenvectors are different. For some applications, such as nuclear forces, the left residual also must be evaluated. The left contraction of this asymmetric term is

$$(\mathbf{b}_S^\dagger\mathbf{A}_{SS}^{(2)})_i^a = \sum_{jb} b_j^b\langle\Phi_j^b|\bar{H}|\hat{T}_2\Phi_i^a\rangle$$

$$= \frac{1}{2}\sum_{jkbc} a_{jk}^{bc}\{b_i^b(jk \parallel ca) + b_j^a(ik \parallel cb)$$

$$+ 2b_j^b(ik \parallel ac)\}. \qquad (13)$$

The third term of equation ($9\,b$) is evaluated conveniently in terms of an effective set of doubles transition amplitudes:

$$\hat{U}_2|\Phi_0\rangle = \frac{1}{4}\sum_{ijab} b_{ij}^{ab}|\Phi_{ij}^{ab}\rangle = -\frac{1}{4}\sum_{ijab}\frac{\bar{u}_{ij}^{ab}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}|\Phi_{ij}^{ab}\rangle,$$

$$(14)$$

$$\bar{u}_{ij}^{ab} = \sum_c\{(ab \parallel cj)b_i^c - (ab \parallel ci)b_j^c\}$$

$$+ \sum_k\{(ka \parallel ij)b_k^b - (kb \parallel ij)b_k^a\}. \qquad (15)$$

The resulting expression for the third term is

$$l_i^a = (\mathbf{A}_{SD}^{(1)}(\mathbf{D}_{DD}^{(0)})^{-1}\mathbf{A}_{DS}^{(1)}\mathbf{b}_S)_i^a = \langle\Phi_i^a|\bar{H}|\hat{U}_2\Phi_0\rangle$$

$$= \frac{1}{2}\sum_{jbc}(ja \parallel bc)b_{ij}^{bc} + \frac{1}{2}\sum_{jkb}(jk \parallel ib)b_{jk}^{ab}. \qquad (16)$$

Finally, the second term on the right hand side (neglected in CIS(D_0)) is given by equation (16) also, but using doubles amplitudes which involve the eigenvalue differences squared in the denominator, according to:

$$b_{ij}^{ab} = \frac{\bar{u}_{ij}^{ab}}{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^2}. \qquad (17)$$

3. Implementation

The eigenvalue problem to be solved is equation (9). This is treated by Davidson's method [24] for asymmetric matrices [25], using expansion vectors which are

only single excitations. We begin with the converged CIS states as initial guesses, and the code employed for the iterative steps is quite similar to a CIS program. There are three noteworthy differences.

(a) Due to the asymmetric nature of the eigenvalue problem, the left and right eigenvectors are not identical. For excitation energy calculations, it suffices to have either one or the other, and this is our program's default. For properties such as forces on the excited state, it is necessary to simultaneously solve for both eigenvectors.

(b) The eigenvalue problem has a non-orthogonal metric given by the right hand side of equation (9), that must be respected in the iterative method. We evaluate the metric matrix within the expanding subspace of singles used for the Davidson method, and then solve the generalized eigenvalue problem within the subspace. The metric is ignored when converting residual vectors into new subspace vectors, which is accomplished exactly as in a CIS calculation (dividing by the CIS eigenvalue differences and orthogonalizing against the existing space for each state).

(c) The contraction of the response matrix against a trial singles vector is vastly more complicated than in the CIS method, as summarized in equations (10)–(17). While equation (10) corresponds to the CIS contraction, and is therefore performed using the same direct methods [2], the remaining terms are different and more demanding. The rest of this section describes the algorithm we have developed to perform this contraction efficiently, assuming we are given a set of $\mathbf{b}_S$ vectors.

The triples-like contributions summarized in equations (11)–(13) contain three terms, each of which involves a triple product between two-electron integrals, ground state doubles amplitudes, and the excited state singles vectors. It is convenient to define two state-independent matrices based on contractions between integrals and ground state doubles, which can be computed once and for all:

$$w_{ab} = \frac{1}{2}\sum_{jkc}(jk \parallel bc)a_{jk}^{ca}, \qquad (18)$$

$$w_{ij} = \frac{1}{2}\sum_{kbc}(jk \parallel bc)a_{ik}^{cb}. \qquad (19)$$

The evaluation of these terms can be performed as the ground state first-order Møller–Plesset doubles amplitudes are formed, exactly as in a direct [26] or semidirect MP2 gradient method [16, 17]. Thus only the cubic memory and disc of such methods are necessary. The fifth-order work associated with forming the ground state doubles amplitudes and evaluating equations (18)

and (19) is state-independent, and thus is very small in the context of a CIS(D_1) calculation involving many states and/or iterations.

Given the matrices defined by equations (18) and (19), equation (11) may now be expressed as

$$(\mathbf{A}_{SS}^{(2)}\mathbf{b}_S)_i^a = \sum_b w_{ab}b_i^b + \sum_j w_{ij}b_j^a$$

$$+ 2\sum_{kc} a_{ik}^{ac}\left\{\sum_{jb}(jk \parallel bc)b_j^b\right\}, \qquad (20)$$

where the final term is evaluated by forming a Fock-like matrix for each trial singles vector from the term in parentheses, which can be contracted with the ground state doubles amplitudes as they are constructed. A key point is that if we are dealing with many iterations and/ or many states, the cost of evaluating equation (20) approaches the cost of the Fock-like matrix and its contraction with the ground state doubles, which asymptotically scales only quadratically with molecule size. Finally, if we need the left-contraction, it may be evaluated analogously:

$$(\mathbf{b}_S^\dagger\mathbf{A}_{SS}^{(2)})_i^a = \sum_b w_{ba}b_i^b + \sum_j w_{ji}b_j^a$$

$$+ 2\sum_{kc}(ik \parallel ac)\left\{\sum_{jb}a_{jk}^{bc}b_j^b\right\}, \qquad (21)$$

except that here the Fock-like matrices are made from density-like matrices which are not the singles, but rather the contraction of ground state doubles with singles, as given in parentheses.

We consider the evaluation of the excited state doubles-like terms contained in equations (14)–(16). Our approach to these contributions will be analogous to the semidirect evaluation of the MP2 energy and gradient. The rate-determining step in the MP2 energy is simply a transformation of the AO basis two-electron integrals to the MO basis. Explicitly, this is performed in four step-wise quarter-transformations

$$(ia \mid jb)$$

$$= \sum_\sigma C_{\sigma b}\left\{\sum_\lambda C_{\lambda j}\left\{\sum_\nu C_{\nu a}\left\{\sum_\mu C_{\mu i}(\mu\nu \mid \lambda\sigma)\right\}\right\}\right\}, \qquad (22)$$

where Greek indices refer to atomic orbitals, and the MO coefficient matrix is $\mathbf{C}$. These single-bar (Mulliken notation) integrals can then be antisymmetrized: $(ij \parallel ab) = (ia \mid jb) - (ib \mid ja)$. The operation count for evaluating equation (22) is formally proportional to ON^4 (O and N are the numbers of occupied orbitals

and basis functions) from the first quarter-transformation. With the use of integral prescreening, this term reduces to roughly ON^2 with a large prefactor. The order of transformations implied by equation (22) is consistent with the order in which AO basis integrals are generated, as has been discussed previously [27]. The basis of direct and semidirect methods for the MP2 energy is to treat only a subset of the occupied orbitals (index i) at a time in the first quarter-transformation. All j, a, b are then handled at once, ensuring that no rate determining computations that scale with the fifth power of molecule size are repeated, while the fourth-order (or lower with integral cutoffs) effort of AO integral evaluation is repeated as many times as there are batches. Memory and disc requirements are not worse than cubic in molecule size, since the quartic number of double substitutions are not all needed at once.

While $\bar{u}_{ij}^{ab}$ could be evaluated by first forming MO basis integrals and then evaluating equation (15); this requires preparing the much larger three-virtual-index class of MO integrals in addition to the two-virtual-index class required for the MP2 energy. Furthermore, it is not possible to treat only a subset of the transformed integrals at a time because all indices must be available in order to transform with the CIS amplitudes via equation (15), and therefore direct and semidirect methods cannot be applied in the manner which is possible for the MP2 energy. For these reasons, we believe it is preferable to instead directly form $\bar{u}_{ij}^{ab}$ from AO basis integrals, just as the MO integrals are constructed in a direct method.

We accomplish the direct (or semidirect) formation of $\bar{u}_{ij}^{ab}$ by defining a set of modified MO coefficients, which are derived by transforming the original coefficients with the current vector of single substitutions:

$$\bar{C}_{\mu i} = \sum_a C_{\mu a} b_i^a, \qquad (23\,a)$$

$$\bar{C}_{\mu a} = -\sum_i C_{\mu i} b_i^a. \qquad (23\,b)$$

In terms of the original coefficients and the single-bar coefficients, the following set of modified quarter-transformations permits the $\bar{u}_{ij}^{ab}$ to be prepared at the same time as the $(ia|jb)$ are generated:

$$\overline{(i\nu \mid \lambda\sigma)} = \sum_\mu \bar{C}_{\mu i}(\mu\nu \mid \lambda\sigma), \qquad (24\,a)$$

$$\overline{(ia \mid \lambda\sigma)} = \sum_v [\bar{C}_{va}(i\nu \mid \lambda\sigma) + C_{va}\overline{(i\nu \mid \lambda\sigma)}], \qquad (24\,b)$$

$$\overline{(ia \mid j\sigma)} = \sum_\lambda [\bar{C}_{\lambda a}(ia \mid \lambda\sigma) + C_{\lambda a}\overline{(i\nu \mid \lambda\sigma)}], \qquad (24\,c)$$

$$\overline{(ia \mid jb)} = \sum_\sigma [\bar{C}_{\sigma b}(ia \mid j\sigma) + C_{\sigma b}\overline{(ia \mid j\sigma)}]. \qquad (24\,d)$$

The antisymmetrized form of the final single-bar integrals are the desired target quantities: $\bar{u}_{ij}^{ab} = \overline{(ia \mid jb)} - \overline{(ib \mid ja)}$. It is clear that the batching of occupied orbitals employed in direct and semidirect MP2 methods applies immediately to this method of evaluating equation (15). The computational cost per state is roughly equivalent to MP2 itself (if sufficient states are treated to amortize the cost of the ground state contributions).

After converting the $\bar{u}_{ij}^{ab}$ array (or the current piece of it) into doubles transition amplitudes based on equation (14), it remains to evaluate equation (16). Fortunately equation (16) has the same form as two of the terms defining the MP2 Lagrangian in gradient theory [26], and therefore standard semidirect MP2 gradient methods may be employed to perform this contraction also. We use our recently developed MP2 gradient formalism [17], which avoids the need for generation of three-virtual-index integrals by performing the contractions in a mixed AO–MO representation. In spin–orbital notation, the form of the resulting contractions is:

$$l_i^a = \sum_\mu l_i^\mu C_{\mu a} + \sum_\mu l_\mu^a C_{\mu i}, \qquad (25\,a)$$

$$l_\mu^a = \sum_{jkc} a_{kj}^{ab}(jb \mid k\mu), \qquad (25\,b)$$

$$l_i^\mu = \sum_{jb\nu} a_{ij}^{b\nu}(jb \mid \mu\nu). \qquad (25\,c)$$

If converged CIS eigenvectors are employed as initial guesses, then on the first iteration of this procedure, the CIS(D) energy can be generated readily, as well as the theta diagnostic. The cost per state for semidirect CIS(D) is approximately equal to the cost of an MP2 energy calculation for the ground state, while CIS(D₁) states are more expensive by a factor which is the number of matrix vector contractions required per state.

4. Excited state properties and transition properties

There are (at least) two levels at which excited state properties, such as charge distributions, dipole moments, etc., may be evaluated based on converged CIS(D_n) solutions. The highest, and most internally consistent level is to evaluate all properties of the excited state as analytical derivatives of the total CIS(D_n) energy, defined as the ground state MP2 energy plus the CIS(D_n) excitation energy. As analytical derivatives are responses of the CIS(D_n) energy, which is correct through second order in electron correlation, properties defined this way should be regarded as also including contributions through second order in electron correla-

tion. This requires the formulation and implementation of analytical gradients, which is a tractable problem, but one that we shall not address here. It requires significant effort beyond that needed for the excitation energies, and of course is essential for properties such as excited state geometries and vibrational frequencies.

For more qualitative purposes, such as characterizing the nature of excitations, and coarse features of excited state charge distributions, a simpler alternative also exists. The alternative is only zero order in electron correlation, but is an improvement over CIS because it incorporates the effects of *mixing* of the zero-order solutions due to correlation. $CIS(D_n)$, as a quasidegenerate perturbation theory, yields eigenvectors whose singles components are linear combinations of the CIS eigenvectors, due to the mixings associated with near degeneracies. If we consider just the $CIS(D_n)$ singles vectors, this defines corrected zero-order solutions. In particular, the so-called unrelaxed difference density matrix [28] associated with CIS theory may be generalized to

$$A_{ij}^{(0)} = -\sum_a (b_L)_i^a (b_R)_j^a, \qquad (26\,a),$$

$$A_{ab}^{(0)} = \sum_i (b_L)_i^a (b_R)_i^b, \qquad (26\,b)$$

where subscripts L and R refer to left and right eigenvectors. This matrix describes zero-order charge rearrangements associated with the excitation. It is particularly convenient to analyse this difference density matrix (which can of course be symmetrized since it is always contracted with symmetric quantities) via attachment–detachment density analysis [28]. The promotion number remains identically one within this corrected zero-order model.

$CIS(D_n)$ transition properties are not defined uniquely by the theory presented in section 2, which is one disadvantage of these models relative to the second-order CC2 method, which is a true linear response theory. However, the corrected zero-order model discussed above for charge distributions can also be applied straightforwardly to the evaluation of transition moments and in particular oscillator strengths, as an improvement relative to CIS. Left and right transition moments exist:

$$\mathbf{r}_L^{(0)} = \sum_{ia} (b_L)_i^a \langle a|\mathbf{r}|i\rangle, \qquad (27\,a)$$

$$\mathbf{r}_R^{(0)} = \sum_{ia} \langle i|\mathbf{r}|a\rangle (b_R)_i^a. \qquad (27\,b)$$

Observable properties such as oscillator strengths involve the product of the left and right moments:

$$f^{(0)} = \tfrac{2}{3}\omega(\mathbf{r}_L^{(0)} \cdot \mathbf{r}_R^{(0)}), \qquad (28)$$

where ω is the second-order excitation energy. Use of this corrected zero-order oscillator strength permits an assessment of the changes in CIS spectral intensities due to the remixing of CIS states associated with near-degeneracies. In the limit in which no such mixing occurs (i.e., CIS(D) is correct), no changes to the CIS properties will be found (apart from the rescaling of the excitation energy).

5. Results and discussion

We have implemented CIS(D), $CIS(D_0)$ and $CIS(D_1)$ via the methods described in section 3, as part of a development version of the Q-Chem program [29]. $CIS(D_\infty)$ was obtained from previously described modifications [11] to the Titan programs [30] for performing CCSD excited states [31]. The purpose of this section is to present test calculations to address the following five questions.

(a) Are deviations between CIS(D) and either experiment or a more accurate theory such as LR-CCSD reduced by employing $CIS(D_1)$? This will apply particularly to cases where near-degeneracies occur in either the CIS or CIS(D) results.

(b) How significantly is the character of excited states changed at the $CIS(D_1)$ level relative to CIS? We will report the overlap of the $CIS(D_1)$ singles vector with CIS reference states.

(c) How significant are the differences between solution of $CIS(D_1)$ equation (9), and full diagonalization of the response matrix of equation (6), which defines $CIS(D_\infty)$? This assesses how well the state-independent dressing employed in $CIS(D_1)$ approximates the energy-dependent response matrix of $CIS(D_\infty)$.

(d) How much additional error would be incurred if we did not include the metric in equation (9), as in $CIS(D_0)$? In other words, how much benefit do we gain from carrying the binomial expansion of equation (8) through first order versus zero order?

(e) Does the theta diagnostic [7] reliably predict the cases where CIS(D) performs poorly? If so then in cases where the diagnostic is small, cheaper CIS(D) calculations would suffice.

Initially let us consider some fairly small molecules where direct comparison both against the higher level LR-CCSD method, and against full diagonalization of equation (6) (i.e., $CIS(D_\infty)$) is possible. Since $CIS(D_1)$ and CIS(D) are quasidegenerate and non-degenerate second-order approximations to LR-CCSD, comparison against CCSD measures directly how successful such approximations are in practice. These results are summarized in table 1 for ethylene, formaldehyde, and

Table 1. Vertical excitation energies (in eV) of ethylene (C_2H_4), formaldehyde (CH_2O) and chlorine nitrate $(ClONO_2)$ evaluated at various levels of theory.[a]

	CIS	θ^b	%CIS[c]	CIS(D)	CIS(D_0)	CIS(D_1)	CIS(D_∞)	CCSD
C_2H_4								
1^1B_{3u}	7.13	0.0°	100%	7.20	7.50	7.24	7.20	7.31
1^1B_{1g}	7.71	1.2°	100%	7.84	8.14	7.88	7.83	7.96
1^1B_{2g}	7.86	0.0°	100%	7.84	8.19	7.91	7.84	7.99
1^1B_{1u}	7.74	2.4°	99%	8.04	8.25	8.04	8.00	8.14
1^1A_g	8.09	0.0°	100%	8.17	8.51	8.23	8.17	8.34
CH_2O								
1^1A_2	4.48	0.5°	99%	3.98	4.09	3.88	3.87	3.95
1^1B_2	8.63	3.7°	91%	6.44	6.86	6.36	6.29	7.06
2^1B_2	9.36	3.8°	92%	7.26	7.81	7.32	7.24	7.89
2^1A_1	9.66	18.6°	63%	8.12	7.86	7.32	7.23	8.00
2^1A_2	9.78	3.0°	96%	7.50	8.11	7.56	7.47	8.23
3^1B_2	10.61	6.0°	89%	8.21	8.91	8.30	8.18	9.07
1^1B_1	9.66	0.0°	98%	9.36	9.64	9.21	9.15	9.26
3^1A_1	10.88	17.7°	90%	8.53	9.19	8.59	8.46	9.27
4^1B_2	10.98	13.3°	93%	8.63	9.32	8.71	8.59	9.38
$ClONO_2$								
$1^1A''$	4.82	1.7°	99%	4.53	4.67	4.47	4.44	4.46
$2^1A''$	5.77	1.3°	99%	4.99	5.30	4.91	4.88	5.10
$1^1A'$	5.69	1.8°	85%	5.42	5.53	5.23	5.19	5.32
$3^1A''$	6.58	1.3°	98%	6.02	6.39	5.93	5.88	6.00

[a] Geometries and non-CIS(D_n) values for CH_2O and C_2H_4 from [11] and for $ClONO_2$ from [32].

[b] θ (the theta diagnostic [7]) is the largest mixing angle between the CIS state and any other CIS state due to second-order correlation effects. Large angles indicates CIS is potentially unreliable.

[c] The percentage similarity between the unit-normalized singles component of the CIS(D_1) response vector and the CIS vector describing the state, from their dot product.

chlorine nitrate, using geometries optimized at the MP2/6-31G* level. The basis sets are 6-311(2+,2+)G(d,p) for ethylene [11] and formaldehyde [11], and 6-31G* for chlorine nitrate [32]. The states are ordered according to the (benchmark) CCSD results.

Several general conclusions can be drawn from this table. First, based on the good agreement between CIS(D_1) and CIS(D_∞), it is clear that the denominator expansion through first order is quite close to the explicit representation. By contrast, retaining only the zero-order term in CIS(D_0) gives rise to results which are systematically too high relative to the explicit representation. This is due to the fact that the zero-order term systematically enlarges denominators in a term which is negative-definite in CIS(D) theory. As far as approximating CIS(D_∞) is concerned, it seems quite clear from table 1 that CIS(D_1) is significantly more accurate than CIS(D_0).

Of course the objective is to approximate the Schrödinger equation rather than CIS(D_∞). It is not clear from table 1 that CIS(D_1) accomplishes this better than CIS(D_0), based on taking the CCSD results as a benchmark. For valence states, CIS(D_1) is in general slightly too low, and CIS(D_0) is generally too high.

Table 2. CIS, CIS(D) and CIS(D_1) vertical excitation energy calculations on styrene, benzaldehyde and chalcone using the 6-31+G* basis set at HF/6-31G* optimized geometries (energies in eV).

State	CIS	θ^a	%CIS[a]	CIS(D)	CIS(D_1)	Experiment
Styrene[b]						
$2^1A'$	5.88	11.1°	85%	5.18	5.11	4.42
$3^1A'$	5.54	11.2°	81%	5.72	5.65	5.21
Benzaldehyde[b]						
$1^1A''$	4.92	0.0°	96%	4.11	3.94	3.34
$2^1A'$	5.88	12.7°	81%	5.29	5.12	4.51
$3^1A'$	5.93	12.7°	71%	5.97	5.90	5.34
Chalcone[c]						
$1^1A''$	4.92	0.0°	93%	3.67	3.49	3.17–3.45
$2^1A'$	5.01	12.0°	86%	4.92	4.82	3.97–4.16
$3^1A'$	5.79	12.8°	79%	5.01	5.03	
$4^1A'$	5.81	21.0°	46%	5.38	5.10	
$5^1A'$	5.88	21.1°	36%	5.45	5.53	4.77

[a] See table 1 for detailed definitions.

[b] Assignments of experimental data to CIS and CIS(D) states, and optimized ground state geometries from [7].

[c] Assignments of experimental data to calculated states, and optimized ground state geometry from [18].

For the Rydberg states of formaldehyde, where CIS(D) itself performs rather poorly, CIS(D_0) is significantly closer to full CCSD than either CIS(D), CIS(D_1) or CIS(D_∞). Further comparison of CIS(D_0) and CIS(D_1) is merited in the future. For present purposes, it is clear that either is substantially superior to CIS.

CIS(D) yields results which are fairly close to either CIS(D_1) or CIS(D_∞) except when the theta diagnostic is large, as in the A_1 excited states of formaldehyde, for example. In the latter cases the iterative methods (including CIS(D_0)) yield greatly improved results as assessed by comparison with LR-CCSD. Indeed, judging by the small overlaps between the CIS wavefunction and the singles component of CIS(D_1) for the A_1 states of formaldehyde, CIS fails to describe those states correctly, as we had suggested previously [11].

Table 2 contains the results of calculations on several larger molecules using the CIS, CIS(D) and CIS(D_1) methods. These systems are too large for our CCSD or CIS(D_∞) codes on workstations, and therefore we consider the results relative to approximate experimental band maxima in absorption. The molecules considered are styrene, benzaldehyde, and *trans*-chalcone, all of which were optimized at the HF/6-31G* level of theory. The excitation energy calculations were all performed with the 6-31+G* basis set, which is of moderate quality in the sense of approaching the complete basis set limit to within a few tenths of an eV for valence

excited states. It is not adequate for Rydberg states such as those of formaldehyde and ethylene discussed above, but the low-lying states of interest for the molecules of table 2 are all valence in character.

The results of table 2 generally mirror the behaviour seen in table 1. The two lowest A$'$ states of styrene and isoelectronic benzaldehyde exhibit moderately large diagnostic values, which place them at the borderline of validity of conventional CIS(D). This is reflected in the unspectacular degree of similarity between the CIS(D$_1$) and CIS states, which is as small as 71% for the 3^{1}A$'$ state of benzaldehyde. The lowest two states of chalcone exhibit small diagnostic values, the CIS(D$_1$) vectors are very similar to CIS states, and there is little difference between CIS(D) and CIS(D$_1$). As we proceed higher into the A$'$ manifold of chalcone, the diagnostic values increase, and the extent of similarity between CIS and CIS(D$_1$) decreases monotonically. These deviations have substantial energetic consequences, with the splitting between the final two A$'$ states shifting by about 0.5 eV between CIS(D) and CIS(D$_1$).

These A$'$ chalcone states reflect a type of behaviour of approximate theories of excitation energies which is likely to be the rule rather than the exception. The quality of a low level description such as CIS inevitably is best for the lowest excited state and will diminish, sometimes gradually and at other times rapidly, as we examine higher excited states. This reflects the fact that omitted terms, such as electron correlation, cause increasingly significant remixing of levels as we go higher in energy. This is both because such levels become closer spaced, and because deviations in the lower levels cause cumulatively larger changes in the character of higher levels. Thus when we compare CIS states against those computed at the higher CIS(D$_1$) level, we find that, for a given symmetry class, the extent of similarity generally decreases monotonically. By contrast, the diagnostic values generally do not exhibit such behaviour, and it is important to note that the presence of a large diagnostic for a single state in the manifold usually implies that all higher states must be presumed suspect.

These observations about similarity of states provide an excellent way of summarizing the general improvements obtained at the quasidegenerate CIS(D$_1$) level relative to the non-degenerate CIS(D) level. Since CIS(D) employs unmodified CIS excited states, it is valid only as far up in the spectrum as the CIS reference state itself. By contrast, CIS(D$_1$) iterates the singles in the presence of the correlation perturbation to yield states which are correct through somewhat higher excitation energies. It is hard to quantify exactly how much further, but the general argument is exactly the same. We regard the difference between the CIS(D$_1$) response

matrix and an exact theory such as FCI (or more precisely its coupled cluster response function equivalent) as a perturbation. Its effect means that the deviations between CIS(D$_1$) and the exact theory become cumulatively significant as one proceeds higher in energy. However, such deviations must occur later than those that arise relative to a less complete theory such as CIS, since the perturbation is smaller. By this argument, and the associated numerical examples, we see that even in cases where there are no obvious near-degeneracies (and hence immediate failures of CIS(D)), the new quasidegenerate CIS(D$_1$) theory still provides a significant advantage.

6. Conclusion

We have introduced the CIS(D$_n$) family of excitation energy methods, which are quasidegenerate second-order perturbation corrections to CIS, that generalize our previous non-degenerate CIS(D) correction. Relative to other methods which include second-order electron correlation effects on the transition in a way which respects near-degeneracies, the low-order CIS(D$_0$) and CIS(D$_1$) methods are novel in being expressible as the diagonalization of a singles-only response matrix which is dressed in a state-independent fashion. Therefore no explicit iteration of the doubles is required.

The computational requirements of either CIS(D$_0$) or CIS(D$_1$) are similar to those of CIS(D), multiplied by a factor which approaches the number of iterations necessary to diagonalize the dressed singles response matrix. Thus fifth-order computation and approximately cubic memory and disc resources are required, which per state per iteration is similar to the ground state MP2 method. We describe an efficient semidirect algorithm with these properties.

Test calculations are reported to assess the performance of CIS(D$_0$) and CIS(D$_1$) by comparison with full iterative CIS(D$_\infty$) calculations for studying vertical absorption spectra. The CIS(D$_1$) results better approximate CIS(D$_\infty$) than CIS(D$_0$), although comparison against CCSD benchmarks suggests that CIS(D$_0$) also has merit. Clearly both CIS(D$_0$) and CIS(D$_1$) improve cases where CIS(D) yields poor results due to near-degeneracies, and also offer improvement in higher excited states.

Further tests of CIS(D$_0$) and CIS(D$_1$) are necessary for other excited state properties, such as geometries and vibrational frequencies where CIS(D) itself appears to be somewhat erratic [33].

The binomial expansion which is employed to define the CIS(D$_n$) methods equally can well be applied to define quasidegenerate triples corrections which do not require explicit iteration of the triples amplitudes. For example, an excellent approximation to the CC3 method

[34] could be obtained by making a binomial expansion of the triples denominator through first order, which would be applicable to substantially larger systems by avoiding storage of the triples.

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