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# Excitation energies from the coupled cluster singles and doubles linear response function (CCSDLR). Applications to Be, CH<sup>+</sup>, CO, and H<sub>2</sub>O

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The linear response function for a coupled cluster singles and doubles wave function is used to calculate vertical electronic energies for the closed shell system Be, CH<sup>+</sup>, CO, and H<sub>2</sub>O. It is shown that excitations of single electron replacement character can be described accurately in such an approach. Improved convergence is obtained using a preconditioned form of the coupled cluster linear response matrix.

## I. INTRODUCTION

In the coupled cluster (CC) model<sup>1</sup> excitation energies may be calculated by subtracting total energies of single- or multireference CC calculations for the separate states.<sup>2-5</sup> Note that CC calculations on excited states have, however, proven difficult due to the complexity of the CC equations and problems in converging them.<sup>3</sup> Furthermore, the excitation energies obtained in this way suffer from the fact the CC states are nonorthogonal and interacting. It is difficult to make the states orthogonal and noninteracting, as the truncation of the commutator expressions that simplifies matrix element evaluation in CC theory cannot be applied to expressions containing the adjoint of a CC state. The evaluation of transition matrix elements becomes difficult for the same reason.

Alternatively, excitation energies can be calculated from the coupled cluster linear response (CCLR) function.<sup>6,7</sup> The excitation energies occur at the poles of the CCLR function and can be determined as eigenvalues of the CCLR matrix. The excitation process described in the CCLR approach corresponds to excitations between states, which may be interpreted as both orthogonal and noninteracting. The expressions for the transition matrix elements between these states are determined from the residues of the CCLR function as described in Ref. 8.

The CCLR function was first derived by Monkhorst<sup>6</sup> and Dalgaard and Monkhorst<sup>7</sup> by analyzing the time evolution of the phase factor. The generalization by Helgaker and Jørgensen<sup>9</sup> of the Hellmann–Feynman theorem to CC transition expectation values was then used by Koch and Jørgensen<sup>8</sup> to simplify the derivation of the CCLR function and to derive the CC quadratic response function. The linear response function for the extended coupled cluster method has been derived by Arponen *et al.*<sup>10</sup> based on a generalization of the Hellmann–Feynman theorem. Excitation energies have also been calculated using CC theory by applying the

equation of motion technique<sup>11,12</sup> and using the Fock space multireference coupled cluster technique.<sup>13,14</sup> The CC wave function has been used by Geertsens and Oddershede<sup>15</sup> to calculate excitation energies in the coupled cluster polarization propagator approach.

In this communication, we consider coupled cluster wave functions constructed from single and double excitations<sup>1</sup> (CCSD) and demonstrate how excitation energies may be calculated from the CCSDLR eigenvalue equation. The numerical examples include Be and CH<sup>+</sup>, which are compared with full configuration interaction (FCI) results, and CO and H<sub>2</sub>O where comparison is made with experiment. The calculations demonstrate that excitation energies are obtained accurately for excitations of single electron replacement character. Excitations of double electron replacement character are difficult to describe in the CCLR approach using a CCSD reference wave function.

The coupled cluster electronic energy is size extensive, i.e., if a CC calculation is carried out on a system consisting of subsystems *A* and *B* at infinite separation then the total energy is equal to the sum of the energies for subsystem *A* and system *B*. Similarly, the excitation energies of the CCLR calculations are size intensive, i.e., the excitation energies of the subsystems are also obtained as excitation energies of the combined system.

The advantages of using the CCSDLR response function to calculate excitation energies are the “black box” nature of the CC approach, its size extensivity, and its accurate description of dynamical correlation. The main deficiency is the single determinant nature of the approach with the consequent limitation on its application range.

## II. THEORY

### A. Excitation energies in the coupled cluster model

The CCLR eigenvalues equation is

$$(\mathbf{A} - \omega_j \mathbf{S})\mathbf{X}_j = 0, \quad (1)$$

where  $\omega_j$  and  $\mathbf{X}_j$  and the *j*th eigenvector of the CCLR eigen-

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value equation. The CC Jacobian is given in Eq. (33) of Ref. 8,

$$A_{\mu\nu} = \langle \mu | \exp(-T) [H, \tau_\nu] | CC \rangle, \quad (2)$$

and the CC metric is given in Eq. (21) of Ref. 8,

$$S_{\mu\nu} = \langle \mu | \exp(-T) \tau_\nu | CC \rangle = \langle \mu | \tau_\nu | HF \rangle. \quad (3)$$

$H$  is the nonrelativistic electronic Hamiltonian and  $|CC\rangle$  the coupled cluster reference state

$$|CC\rangle = \exp(T) |HF\rangle, \quad (4)$$

where  $|HF\rangle$  is the Hartree-Fock reference state and  $T$  the cluster operator

$$T = \sum_{\nu} T_{\nu} = \sum_{\nu} t_{\nu} \tau_{\nu}. \quad (5)$$

In these equations,  $\tau_{\nu}$ ,  $\nu = 1, 2, \dots$ , denote the single, double, and higher electron replacement excitation operators and  $t_{\nu}$  the cluster amplitudes.  $\langle \mu |$  is the projection manifold

$$\langle \mu | = \langle HF | \tau_{\mu}^{\dagger}. \quad (6)$$

In CCLR theory, excitation energies  $\omega_j$  correspond to transitions between states, which are orthogonal with respect to the metric (3) and noninteracting with respect to the Jacobian (2).

## B. Size intensity of the excitation energies

We use size extensive and size intensive in analogy with thermodynamics where an extensive property scales with the size of the system and an intensive property is independent of the size of the system. [See, e.g., P. W. Atkins, *Physical Chemistry*, 2nd ed. (Oxford U.P., Oxford, 1982), p. 76.]

We shall now show that the excitation energies in the CCLR model are size intensive. To do so, we need to prove that in a CCLR calculation on a system consisting of systems  $A$  and  $B$  at infinite separation, we obtain the excitation energies of the individual subsystems. Since the subsystems are at infinite separation, the Hamiltonian for the combined system reduces to the sum of the Hamiltonians for the subsystems,

$$H = H_A + H_B. \quad (7)$$

The coupled cluster reference wave function is size extensive, that is, the cluster operator can be written as the sum of the cluster operators of the two subsystems,

$$T = T_A + T_B. \quad (8)$$

The excitation operators  $\{\tau_{\nu}\}$  can be divided into a set referencing subsystem  $A$  only  $\{\tau_A\}$ , a set referencing subsystem  $B$  only  $\{\tau_B\}$ , and a set referencing both  $A$  and  $B$   $\{\tau'_A, \tau'_B\}$ . In a CC model containing excitations through a certain level,  $\tau'_A$  and  $\tau'_B$  contain at most excitations that are one level lower than the highest level. For example, in the CCSD model  $\{\tau'_A, \tau'_B\}$  contains only single excitations in each subsystem.

The projection manifold may analogously be expressed in terms of excitations for subsystem  $A$  ( $\langle HF_B | \tau_A |$ ), for subsystem  $B$  ( $\langle \tau_B | HF_A |$ ), and excitations that couple the two subsystems ( $\langle \tau'_B \tau'_A |$ ). We may thus write the Jacobian in a three component form with the projection manifold  $\{\langle HF_B | \tau_A |, \langle \tau_B | HF_A |, \langle \tau'_B \tau'_A | \}$  constituting the row labels

and the excitation operators  $\{\tau_A, \tau_B, \tau'_A, \tau'_B\}$  constituting the column labels

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{A,A} & \mathbf{A}^{A,B} & \mathbf{A}^{A,A'B'} \\ \mathbf{A}^{B,A} & \mathbf{A}^{B,B} & \mathbf{A}^{B,A'B'} \\ \mathbf{A}^{A'B',A} & \mathbf{A}^{A'B',B} & \mathbf{A}^{A'B',A'B'} \end{pmatrix} \\ = \begin{pmatrix} \mathbf{A}^{A,A} & \mathbf{O} & \mathbf{A}^{A,A'B'} \\ \mathbf{O} & \mathbf{A}^{B,B} & \mathbf{A}^{B,A'B'} \\ \mathbf{O} & \mathbf{O} & \mathbf{A}^{A'B',A'B'} \end{pmatrix}. \quad (9)$$

Here  $\mathbf{A}^{A,A}$  and  $\mathbf{A}^{B,B}$  are the Jacobians for subsystems  $A$  and  $B$ . The zero blocks of the Jacobian in Eq. (9) follow from the identity

$$[\exp(T_B), H_A] = 0, \quad (10)$$

which allows us to integrate the dependence of one of the subsystems. Since the metric in Eq. (3) is the unit matrix, the eigenvalues of the CCLR Jacobian occur when the

$$\begin{vmatrix} \mathbf{A}^{A,A} - \omega \mathbf{I}^{A,A} & \mathbf{O} & \mathbf{A}^{A,A'B'} \\ \mathbf{O} & \mathbf{A}^{B,B} - \omega \mathbf{I}^{B,B} & \mathbf{A}^{B,A'B'} \\ \mathbf{O} & \mathbf{O} & \mathbf{A}^{A'B',A'B'} - \omega \mathbf{I}^{A'B',A'B'} \end{vmatrix} = 0. \quad (11)$$

This equation is satisfied when

$$|\mathbf{A}^{A,A} - \omega \mathbf{I}^{A,A}| |\mathbf{A}^{B,B} - \omega \mathbf{I}^{B,B}| |\mathbf{A}^{A'B',A'B'} - \omega \mathbf{I}^{A'B',A'B'}| = 0, \quad (12)$$

and it follows immediately that the eigenvalues of the two subsystems are also eigenvalues of the combined system. We have thus proven that the CCLR eigenvalue energies are size intensive.

## C. The coupled cluster singles and doubles model

We consider a CCSD reference wave function for a closed shell molecule and write the cluster operator as

$$T = T_1 + T_2 = t_1 \tau_1 + t_2 \tau_2. \quad (13)$$

The single electron replacement manifold is

$$\tau_1 = \left\{ \frac{1}{\sqrt{2}} E_{ai} \right\}, \quad (14)$$

where  $\{E_{ai}\}$  are generators of the unitary group. Letters  $i, j, k, l, \dots$  and  $a, b, c, d, \dots$  refer to occupied and unoccupied orbitals, respectively, in the Hartree-Fock reference state, and  $p, q, r, s, \dots$  are used as general indices. We use the singlet-singlet and triplet-triplet coupling schemes for the double electron replacement manifold; specifically we use

$$\tau_{2s} = \left\{ \frac{1}{2\sqrt{(1+\delta_{ij})(1+\delta_{ab})}} (E_{ai}E_{bj} + E_{aj}E_{bi}) | a \gg b, i \gg j \right\} \quad (15)$$

for the singlet-singlet spin coupled manifold, and

$$\tau_{2t} = \left\{ \frac{\sqrt{3}}{6} (E_{ai}E_{bj} - E_{aj}E_{bi}) | a > b, i > j \right\} \quad (16)$$

for the triplet-triplet spin coupled manifold.<sup>16</sup> This scheme leads to a unit metric and diagonal dominance in the Jacobian. The last point is discussed in Ref. 17, where an order analysis is given of the terms which are included in the CCSDLR approach. The diagonal dominance is important,

as iterative techniques are used to solve Eq. (1). In iterative algorithms, linear transformations are carried out on trial vectors  $\{\mathbf{b}\}$  with the Jacobian as the transformation matrix

$$\sigma = \mathbf{A}\mathbf{b}. \quad (17)$$

In our implementation, we split the trial vectors into three types  $\{\mathbf{b}_1, \mathbf{b}_{2s}, \mathbf{b}_{2t}\}$ , where  $\mathbf{b}_1$  contains the single electron replacement amplitudes,  $\mathbf{b}_{2s}$  the singlet–singlet coupled double replacement amplitudes, and  $\mathbf{b}_{2t}$  the triplet–triplet coupled double replacement amplitudes. This gives significant computational savings, since the linear transformation in Eq. (1),  $\mathbf{A}(\mathbf{b}_1 + \mathbf{b}_{2s} + \mathbf{b}_{2t})$  can be carried out as three separate transformations  $\mathbf{A}\mathbf{b}_1$ ,  $\mathbf{A}\mathbf{b}_{2s}$ , and  $\mathbf{A}\mathbf{b}_{2t}$  with little extra cost. We have described in Ref. 16 how the transformations can be carried out efficiently for trial vectors containing either exclusively single or double replacement amplitudes. The triplet–triplet coefficients in the solution vectors of Eq. (1) are usually an order of magnitude smaller than the singlet–singlet coefficients. This makes it advantageous to split the double replacement trial vectors into components containing either exclusively singlet–singlet amplitudes or exclusively triplet–triplet amplitudes. In Ref. 17, we describe in more detail how a linear transformation of a double replacement vector may be implemented for the singlet–singlet and triplet–triplet components separately with little loss of efficiency.

The iterative algorithm we use is a modification of the Davidson algorithm,<sup>18</sup> where the type of trial vector added depends on the size of the residual. Since a linear transformation of a  $\mathbf{b}_1$  vector scales as  $N^5$  ( $N$  is the number of orbitals), whereas a transformation of a  $\mathbf{b}_2$  vector scales as  $N^6$ , we keep the  $\mathbf{b}_1$  component of the solution vectors better converged than the  $\mathbf{b}_2$  component in the iterative process. In practice, we add a  $\mathbf{b}_1$  trial vector to the reduced space whenever  $R_1 > 0.2 \text{ Max}(R_{2s}, R_{2t})$ . ( $R_j$  denotes the norm of the  $j$ th component of the residual.) Otherwise we add a  $\mathbf{b}_{2s}$  vector if  $R_{2s} > R_{2t}$ , and a  $\mathbf{b}_{2t}$  vector if  $R_{2s} < R_{2t}$ .

Table I shows the convergence characteristics of a calculation on the lowest excitation energy of  $^1A_1$  symmetry for  $\text{H}_2\text{O}$ , using a basis set and geometry of Ref. 19. Convergence is fast, yielding a residual norm less than  $10^{-3}$  in a space of nine  $\mathbf{b}_1$  trial vectors, seven  $\mathbf{b}_{2s}$  vectors, and four  $\mathbf{b}_{2t}$  vectors. The different convergence characteristics of the three subspaces reflect the fact that the diagonal dominance is different for the various parts of the Jacobian matrix. From Table I, it is seen that the residual in one subspace is hardly affected by adding trial vectors to another subspace, indicating small coupling between the various blocks in the Jacobian.

#### D. The numerical accuracy of the excitation energies

The error of the excitation energies appears to be quadratic in the norm of the residual vector. This error is, however, not strictly quadratic as we will now discuss. The Jacobian in Eq. (1) is nonsymmetric and the solutions from the right,

$$(\mathbf{A} - \omega_j \mathbf{S})|X_j^R\rangle = 0, \quad (18)$$

and from the left,

$$\langle X_j^L | (\mathbf{A} - \omega_j \mathbf{S}) = 0, \quad (19)$$

TABLE I. Convergence characteristics for a calculation of the lowest  $^1A_1$  excitation energy for  $\text{H}_2\text{O}$  using the basis set of Ref. 19.

Iteration number	Excitation energy (a.u.)	Total	$t_1$	Residual $t_{2s}$	$t_{2t}$
1	0.441413	5.15E-1	7.25E-2 <sup>a</sup>	3.94E-1	3.25E-1
2	0.358093	2.78E-1	7.28E-2	8.31E-2 <sup>a</sup>	2.55E-1
3	0.332140	3.32E-1	2.96E-2 <sup>a</sup>	1.83E-1	2.74E-1
4	0.293451	1.81E-1	2.93E-2	1.76E-1	3.44E-2 <sup>a</sup>
5	0.280416	7.76E-2	4.01E-2	5.74E-2 <sup>a</sup>	3.33E-2
6	0.278745	7.86E-2	2.00E-2 <sup>a</sup>	6.40E-2	4.10E-2
7	0.278577	7.98E-2	4.88E-3 <sup>a</sup>	6.65E-2	4.40E-2
8	0.276955	5.44E-2	8.55E-3	2.24E-2 <sup>a</sup>	4.88E-2
9	0.275809	2.76E-2	1.18E-2	2.39E-3	7.18E-3 <sup>a</sup>
10	0.275736	2.62E-2	2.97E-3 <sup>a</sup>	2.45E-2	8.87E-3
11	0.275475	1.30E-2	4.03E-3	7.80E-3 <sup>a</sup>	9.59E-3
12	0.275475	1.28E-2	6.73E-4 <sup>a</sup>	7.96E-3	1.00E-2
13	0.275432	8.75E-3	1.34E-3	8.46E-3	1.77E-3 <sup>a</sup>
14	0.275407	3.77E-3	1.87E-3	2.63E-3 <sup>a</sup>	1.96E-3
15	0.275406	3.44E-3	3.83E-4 <sup>a</sup>	2.73E-3	2.05E-3
16	0.275403	2.39E-3	5.90E-4	9.37E-4 <sup>a</sup>	2.12E-3
17	0.275402	2.36E-3	1.43E-4 <sup>a</sup>	9.79E-4	2.14E-3
18	0.275398	1.14E-3	2.35E-4	1.05E-3	3.79E-4 <sup>a</sup>
19	0.275398	1.12E-3	4.63E-5 <sup>a</sup>	1.06E-3	3.85E-4
20	0.275398	4.96E-4	4.70E-5	2.79E-4 <sup>a</sup>	4.07E-4

<sup>a</sup> Trial vector of this type added in this iteration.

are therefore different. Let us assume that we have solved Eq. (1) both from the right to the left in an incomplete (reduced) basis  $\{|b_i\rangle\}$  giving

$$(\mathbf{PAP} - \omega_j^{(0)} \mathbf{PSP})|\zeta_j^R\rangle = 0 \quad (20)$$

and

$$\langle \zeta_j^L | (\mathbf{PAP} - \omega_j^{(0)} \mathbf{PSP}) = 0, \quad (21)$$

where  $\mathbf{P}$  projects onto the reduced space. Both approximate solutions may be written in terms of the exact solution vector and an error vector,

$$|\zeta_j^R\rangle = |X_j^R\rangle + |e_j^R\rangle, \quad (22)$$

$$\langle \zeta_j^L | = \langle X_j^L | + \langle e_j^L |. \quad (23)$$

The error in the excitation energy may now be written as

$$\omega_j^{(0)} - \omega_j = \frac{\langle \zeta_j^L | \mathbf{A} - \omega_j \mathbf{S} | \zeta_j^R \rangle}{\langle \zeta_j^L | \zeta_j^R \rangle} = \frac{\langle e_j^L | \mathbf{A} - \omega_j \mathbf{S} | e_j^R \rangle}{\langle \zeta_j^L | \zeta_j^R \rangle}, \quad (24)$$

where we have used Eqs. (18), (19), (22), and (23). Equation (24) shows that the error in the excitation energy is proportional to the product of the errors in the left and right solution vectors. From the relations

$$\begin{aligned} |R_j^R\rangle &= (\mathbf{A} - \omega_j^{(0)} \mathbf{S})|\zeta_j^R\rangle \\ &= (\mathbf{A} - \omega_j \mathbf{S})|e_j^R\rangle + (\omega_j - \omega_j^{(0)})|\zeta_j^R\rangle \\ &= (\mathbf{A} - \omega_j \mathbf{S})|e_j^R\rangle - \frac{\langle e_j^L | \mathbf{A} - \omega_j \mathbf{S} | e_j^R \rangle}{\langle \zeta_j^L | \zeta_j^R \rangle} |\zeta_j^R\rangle, \end{aligned} \quad (25)$$

it follows that the norm of the residual for the right solution vector is proportional to the norm of the right error vector. Similarly, the norm of the left residual is proportional to the norm of the error of the left solution vector. The error in the excitation energy therefore is related to the product of the

TABLE II. CCLR, CISD, and FCI excitation energies for Be in eV. CCSD ground state total energy — 14.65705331 a.u.

Excitation	Experiment <sup>a</sup>	CISD <sup>b</sup> 1s frozen	CISD	FCI <sup>c</sup>	CCSDLR	% <i>t</i> <sub>1</sub>	% <i>t</i> <sub>2s</sub>	% <i>t</i> <sub>2i</sub>
$X^1S \rightarrow 2s2p^1P$	5.277	5.362	6.239	5.318	5.319	93.80	6.19	0.010
$2s3p^1P$	7.462	7.482	8.389	7.462	7.465	94.89	5.10	0.004
$2s3s^1S$	6.779	6.773	7.693	6.765	6.772	94.58	5.42	0.001
$2s4s^1S$	8.089	8.084	8.973	8.076	8.078	96.74	3.26	0.000
$2p^2^1D$	7.05	7.120	8.034	7.089	7.156	41.06	58.94	0.003
$2s3d^1D$	7.988	8.053	8.974	8.034	8.059	79.15	20.85	0.002

<sup>a</sup> From Ref. 23 unless otherwise indicated.<sup>b</sup> Reference 24.<sup>c</sup> Reference 22.

magnitudes of the left and right residual vectors. For a symmetric matrix, the right and left residual vectors are identical, and quadratic error is obtained in the residual. For a nonsymmetric matrix, the antisymmetric component of the matrix gives independent components to the left and right solution vector, and we may therefore observe linear error in the right residual. As the nonsymmetric part of the Jacobian is of at least third order in the Hartree–Fock fluctuation potential, we observe approximate quadratic errors in Table I.

### III. CALCULATIONS

CCSDLR excitation energies have been calculated for Be, CH<sup>+</sup>, CO, and H<sub>2</sub>O. For Be and CH<sup>+</sup>, the results are compared with full CI (FCI) and experiment. The CO and H<sub>2</sub>O results are compared with experiment only. All calculations have been converged to a right residual norm 10<sup>−3</sup>. The CCSD wave functions were calculated using the energy code of Scuseria *et al.*,<sup>20</sup> together with the SIRIUS MCSCF program.<sup>21</sup>

#### A. Be

For Be, we used the basis of Ref. 22, except that the *s* component of the Cartesian *d* functions was included. The CCSDLR, FCI,<sup>22</sup> CI singles and doubles (CISD), and experimental<sup>23,24</sup> excitation energies are given in Table II, where we also report the percentage of the *t*<sub>1</sub>, *t*<sub>2s</sub>, and *t*<sub>2i</sub> amplitudes in the CCSDLR eigenvectors. The FCI calculations<sup>22</sup> do not include the *s* component of the *d* functions. As the *s* basis is large, the excitation energies are not expected to be affected by this component. The average deviation between the FCI and experiment is 0.026 eV. The FCI results differ from CCSDLR by less than 0.008 eV for all excitations of single replacement character. The excitation  $2p^2^1D$  of double replacement character is less accurately described, the CCSDLR value being 0.065 eV higher than the FCI value. The CISD model contains the same number of parameters as the CCSDLR model, but gives excitation energies that are all about 0.9 eV higher. The reason for this is that in the CISD model, the core 1s electrons are correlated in the  $X^1S$  ground state only, not in the excited state. The 1s core

correlation energy is approximately 0.9 eV. Indeed, the CISD calculation where the 1s orbital is frozen<sup>22</sup> gives excitation energies much closer to CCSDLR. In the CCSDLR model, all single and double excitations from the correlated CCSD reference state are considered. The CCSDLR excitation energies thus incorporate the change in the correlation energy for the 1s core electrons.

#### B. CH<sup>+</sup>

The CH<sup>+</sup> calculations were carried out at the internuclear distance 2.13713 a.u., using the 14σ5π1δ basis of Ref. 25. This basis is large enough to reproduce the main features of the excitation spectrum and still small enough for FCI calculations to be carried out. It therefore gives an excellent opportunity to test the CCSDLR model.

CH<sup>+</sup> has a ground state electronic configuration 1σ<sup>2</sup>2σ<sup>2</sup>3σ<sup>2</sup> with a large nondynamical correlation contribution from 1σ<sup>2</sup>2σ<sup>2</sup>1π<sup>2</sup>. Note that CH<sup>+</sup> has a <sup>1</sup>Π valence state dominated by 1σ<sup>2</sup>2σ<sup>2</sup>3σ<sup>1</sup>1π<sup>1</sup>, a single replacement relative to the ground state. CH<sup>+</sup> further has one valence excited state of <sup>1</sup>Σ<sup>+</sup> symmetry and one of <sup>1</sup>Δ symmetry. Both these states originate from the 1σ<sup>2</sup>2σ<sup>2</sup>1π<sup>2</sup> electronic configuration and are predominantly double replacements relative to the ground state. In Table III, we report CISD, FCI,<sup>25</sup> and CCSDLR excitation energies from the  $X^1\Sigma^+$  ground state to the valence excited states and to some higher states.

TABLE III. CCSDLR, CISD, and FCI excitation energies for CH<sup>+</sup> in eV.

Excitation	CISD <sup>a</sup>	FCI <sup>b</sup>	CCSDLR <sup>c</sup>	% <i>t</i> <sub>1</sub>	% <i>t</i> <sub>2s</sub>	% <i>t</i> <sub>2i</sub>
$X^1\Sigma^+ \rightarrow ^1\Sigma^+$	9.9174	8.5492	9.1089	0.35	99.45	0.17
	14.9409	13.5246	13.5805	92.85	6.42	1.00
	18.6505	17.217	17.3157	86.12	13.27	0.61
<sup>1</sup> Π	4.4573	3.2296	3.2607	96.96	2.67	0.36
	15.5717	14.1271	14.4544	77.39	21.02	1.59
<sup>1</sup> Δ	8.4379	6.9642	7.8876	0.26	99.59	0.15
	18.4884	16.8331	17.3414	35.20	62.69	2.10

<sup>a</sup> CISD ground state total energy: — 38.01420102 a.u.<sup>b</sup> Reference 25. FCI ground state total energy: — 38.019638 a.u.<sup>c</sup> CCSD ground state total energy: — 38.01767017 a.u.

The CCSDLR results are close to FCI<sup>25</sup> for the excitations of single replacement character. For example, the CCSDLR excitation energy to the  ${}^1\Pi$  valence state is 3.2607 eV and the FCI value is 3.2296 eV. The corresponding experimental value<sup>26</sup> is 3.07 eV. The difference between the CCSDLR and FCI results increases with increasing  $t_2$  amplitudes, and the excitations dominated by  $t_2$  are about 1 eV higher than FCI. The  $t_{2i}$  contributions to the CCSDLR solution vectors are very small for all excitations. The CISD excitation energies are substantially higher than the CCSDLR results for the reasons discussed for the Be case.

### C. CO

The CO calculations were carried out at the internuclear distance 2.132242 a.u. The basis set was derived from the Dunning (9s5p)/[4s3p] contractions.<sup>27</sup> Leaving the most diffuse primitive  $s$  and  $p$  orbitals uncontracted, we obtained [5s4p]. To this we added on both centers three diffuse  $s$  functions ( $\alpha_c = 0.05, 0.017, 0.003$ ;  $\alpha_0 = 0.093, 0.031, 0.0093$ ), three diffuse  $p$  functions ( $\alpha_c = 0.036, 0.0115, 0.0036$ ;  $\alpha_0 = 0.07, 0.023, 0.007$ ), and three  $d$  functions ( $\alpha_c = 0.64, 0.16, 0.05333$ ;  $\alpha_0 = 1.23, 0.3, 0.1$ ) in order to describe the excited states and the polarization of the ground state. The final basis is of the form (12s 8 3d)/[8s 6p 3d]. The diffuse  $s$  and  $p$  functions were chosen to continue the approximate geometric progression in the Huzinaga (9s 5p) basis<sup>28</sup> and the  $d$  functions were chosen according to the prescription by Werner and Meyer.<sup>29</sup> The CCSDLR and experimental excitation energies<sup>30</sup> are given in Table IV. All excitations are dominated by single excitations. We therefore expect all excitations to be close to FCI, and that large deviations from experimental results are caused by basis set deficiencies or experimental errors. Most of the excitation energies are within 0.1 eV from experiment. However, for  $X^1\Sigma^+ \rightarrow A^1\Pi$ , the deviation is 0.18 eV and for  $X^1\Sigma^+ \rightarrow I^1\Sigma^-$  0.27 eV. We ascribe these errors to basis set deficiencies in the description of the excited states.

### D. H<sub>2</sub>O

The H<sub>2</sub>O calculations were carried out at the experimental geometry using the coordinates given in Ref. 19. We used the same oxygen basis as for CO, and for hydrogen we used a (6s4p)[4s3p] basis obtained by leaving the most dif-

TABLE V. CCSDLR excitation energies for H<sub>2</sub>O in eV.

Excitation	Experiment <sup>a</sup>	CCSDLR	% $t_1$	% $t_{2s}$	% $t_{2i}$
$X^1A_1 \rightarrow \tilde{B}^1A_1$	9.7	9.747	94.1	4.1	1.8
$\tilde{D}^1A_1$	10.17	10.068	93.9	4.1	2.0
${}^1A_2$	9.1 <sup>b</sup>	9.205	94.2	3.9	1.9
$\tilde{A}^1B_1$	7.4	7.459	94.1	4.2	1.7
$\tilde{C}^1B_1$	10.0	9.833	94.1	3.9	2.0
${}^1B_2$	—	11.169	93.9	3.9	2.2

<sup>a</sup> Reference 32.

<sup>b</sup> Reference 33.

fuse  $s$  and  $p$  orbitals of Sadlej's pol 1 (6s4p)/[3s2p] basis<sup>31</sup> uncontracted. In Table V, we report the experimental<sup>32</sup> and CCSDLR excitation energies together with an amplitude analysis of the CCSDLR eigenvectors. All excitations have about the same  $t_1$  amplitude contribution (94%) and are therefore expected to be of same accuracy. The differences between the CCSDLR and experimental excitation energies about 0.1 eV as in the previous examples. This is to be expected, since the basis sets are of the same quality.

## IV. DISCUSSION AND CONCLUSIONS

The coupled cluster singles and doubles linear response (CCSDLR) model is a black box in the sense that the calculation is completely specified by the orbital basis and the Hartree-Fock occupations. We have used the CCSDLR function to calculate the lowest singlet excitation energies for Be, CH<sup>+</sup>, CO, and H<sub>2</sub>O. The calculations show that excitations corresponding to single electron replacements are accurately described in the CCSDLR model, whereas excitations corresponding to double replacements require cluster operators higher than doubles. The accuracy of the single replacement excitations is unprecedented for a black box model, and the CCSDLR model therefore holds great promise for predictions of the lowest electronic excitations (visible or ultraviolet) of closed-shell molecules dominated by the Hartree-Fock configuration. Furthermore, the quality of the CCSDLR results may be judged from a simple analysis of the amplitudes. Quantitative results (within about 0.1 eV of experiment) can be expected whenever the excitations are dominated by single excitation amplitudes. For double excitations, the true excitation energy can be expected to be lower than the CCSDLR predictions. A prerequisite for quantitative results is that the basis set contains polarization and, more importantly, diffuse functions. All basis sets used in this work are adequate; further improvements are expected to give corrections smaller than the errors in the CCSDLR model. A study of how small the basis set can be and still give reasonable results remains to be done.

An efficient iterative algorithm has been developed for solving the CCSDLR eigenvalue equation. The singlet-singlet and triplet-triplet coupling scheme has been used to parametrize the doubly excited manifold. Trial vectors are split into components containing either single excitation amplitudes, singlet-singlet amplitudes, or triplet-triplet ampli-

TABLE IV. CCSDLR excitation energies for CO in eV.

Excitation	Experiment <sup>a</sup>	CCSDLR	% $t_1$	% $t_{2s}$	% $t_{2i}$
$X^1\Sigma^+ \rightarrow B^1\Sigma^+$	10.78	10.846	92.3	6.1	1.6
$C^1\Sigma^+$	11.40	11.444	92.8	5.6	1.6
$F^1\Sigma^+$	12.4	12.456	92.7	5.6	1.7
$I^1\Sigma^-$	9.88	10.152	94.0	4.9	1.1
$A^1\Pi$	8.51	8.686	93.8	5.3	0.9
$E^1\Pi$	11.53	11.582	92.9	5.4	1.7
$D^1\Delta$	10.23	10.266	91.7	7.4	1.0

<sup>a</sup> Reference 30.

tudes. The triplet–triplet amplitudes are small for all excitations considered.

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