Linear response CC2 triplet excitation energies

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Abstract

We report an atomic integral direct implementation of the approximate coupled-cluster singles and doubles method CC2 for the triplet excitation energies of closed shell molecules. Employing an explicitly spin-coupled triplet excitation space we obtain a compact and efficient formulation which needs approximately the same operation count as required for singlet excitation energies. Compared to a spin orbital based approach this gives a reduction by about a factor of 3. A basis set study employing basis sets with up to 432 functions is presented for the lowest triplet excitations in benzene and the results are compared with other theoretical and experimental results. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The evaluation of molecular properties using coupled-cluster (CC) theory has gained increasing popularity over the past 10 years [1,2]. A particularly important strategy has been to use hierarchies of CC models where improved accuracy can be obtained at each level in the hierarchies. A commonly used CC hierarchy for calculating frequency dependent properties consists of CCS(N^4), CC2(N^5), CCSD(N^6), CC3(N^7), CCSDT(N^8) etc. where the number in parentheses denotes the computational cost as a function of the number of orbitals N [3]. CCS, CCSD [4] and CCSDT [5–7] refer to the standard CC models containing all singles, all singles and doubles, and all singles, doubles and triples excitations, respectively. CC2 is an approximation to CCSD where the doubles equation is truncated to lowest (first) order in the fluctuation potential [3] while CC3 is an approximation to CCSDT where the triples equation is truncated to lowest (second) order [8].

Excitation energies are in CC theory obtained as eigenvalues of the CC linear response eigenvalue equation. CC2 determine single replacement dominated excitation energies correct through second-order while they are correct through third-order in CC3. In this Letter we describe the calculation of triplet excitation energies in the CC2 model using an integral direct approach and an explicit spin-coupled triplet excitation space.

Triplet excitation energies have previously been calculated using second-order models. These include the second-order polarization propagator approach (SOPPA) [9] and the complete active space second-order

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perturbation approach (CASPT2) [10]. In SOPPA the excitation energies are determined as the eigenvalues of a generalized random phase (RPA) eigenvalue equation that is correct through second-order in the fluctuation potential. In CASPT2 an excitation energy is obtained by subtracting the total energies of the ground and excited states. A major advantage of CASPT2 compared to the other second-order approaches is that excitation energies may be obtained also for open shell systems. Triplet CCSD excitation energies have also been reported by Stanton and Bartlett [11] using a spin orbital based approach.

In this Letter we report an implementation of the CC2 model for the calculation of triplet excitation energies for molecules with a closed shell single-reference dominated ground state. After a short introduction to CC response theory in Section 2 we derive in Section 3 and Section 4 a convenient parametrization of the triplet double excitation space. In Section 5 this parametrization is employed to obtain an efficient formulation of the linear transformation required for the calculation of triplet excitation energies. In Section 6 we present a CC2 basis set investigation of the triplet excitation energies of benzene and compare the results with the ones obtained in SOPPA, CASPT2 and experimental studies.

2. Theory

Using the single-reference CC ansatz

$$|CC\rangle = \exp(T)|HF\rangle \tag{1}$$

the similarity transformed Schrödinger becomes

$$\exp(-T)H|CC\rangle = E|HF\rangle, \tag{2}$$

where $|HF\rangle$ is the Hartree–Fock reference state, H the Hamiltonian, and T is the cluster operator. For a N electron system the cluster operator becomes

$$T = T_1 + T_2 + \cdots + T_N, \tag{3}$$

$$T_i = \sum_{\mu_i} t_{\mu_i} \tau_{\mu_i}. \tag{4}$$

In the last equation τ_{μ_i} is an i-electron excitation operator and t_{μ_i} the corresponding cluster amplitude. The amplitudes t_{μ_i} are determined by projecting the Schrödinger equation in Eq. (1) onto a manifold of excitations out of the reference state

$$\langle \mu | = \langle HF | \tau_\mu^\dagger, \tag{5}$$

$$\Omega_\mu = \langle \mu | \exp(-T)H|CC\rangle = 0. \tag{6}$$

The projection from the left with the reference state $|HF\rangle$ gives the CC energy,

$$E = \langle HF|H|CC\rangle. \tag{7}$$

In the CCSD model the cluster-operator is truncated after the T_2 term. The CC2 model is an approximation to the CCSD model retaining the CCSD singles equations in their original form whereas the CCSD doubles equations are approximated to first order in the fluctuation potential and with the singles excitation amplitudes treated as zero-order parameters. The CC2 equations become [3]:

$$\langle \mu_1 | \hat{H} + [\hat{H}, T_2]|HF\rangle = 0, \tag{8}$$

$$\langle \mu_2 | \hat{H} + [F, T_2]|HF\rangle = 0, \tag{9}$$

where F is the SCF Fock operator and $\hat{H}$ is the T_1 transformed Hamiltonian

$$\hat{H} = \exp(-T_1)H\exp(T_1). \tag{10}$$

In CC response function theory excitation energies are obtained as the eigenvalues ω of the non-symmetric eigenvalue equation

$$\mathbf{A}\mathbf{R} = \omega\mathbf{R}, \tag{11}$$

where $\mathbf{A}$ is the Jacobian for the vector function Ω_μ

$$A_{\mu v} = \frac{d\Omega_\mu}{dt_v} \tag{12}$$

which in the CC2 model can be written as

$$A_{\mu_i v_j} = \begin{pmatrix} \langle \mu_1|[\hat{H}, \tau_{v_1}] + [[\hat{H}, \tau_{v_1}], T_2]|\mathrm{HF}\rangle & \langle \mu_1|[\hat{H}, \tau_{v_2}]|\mathrm{HF}\rangle \\ \langle \mu_2|[\hat{H}, \tau_{v_1}]|\mathrm{HF}\rangle & \langle \mu_2|[F, \tau_2]|\mathrm{HF}\rangle \end{pmatrix}. \tag{13}$$

To get an efficient solution for triplet excitation energies requires an explicit and efficient parametrization of the triplet excitation space.

3. Triplet excitations

Using the second quantization creation and annihilation operators, $a^\dagger$ and a, an explicitly spin coupled manifold of triplet single excitation operators is conveniently obtained by

$$T_{ai} = a_{a\alpha}^\dagger a_{i\alpha} - a_{a\beta}^\dagger a_{i\beta}. \tag{14}$$

In Eq. (14) and in the following we use the indices $a, b, c, \ldots$, for virtual (unoccupied) orbitals and the indices $i, j, k, \ldots$, for occupied orbitals. The indices α and β indicate spin functions with $m_S = +\frac{1}{2}$ and $m_S = -\frac{1}{2}$, respectively.

To obtain an operator manifold for triplet double excitations the creation and annihilation operators $\{a_{a\alpha}^\dagger, a_{a\beta}^\dagger\}$, $\{a_{b\alpha}^\dagger, a_{b\beta}^\dagger\}$, $\{-a_{i\beta}, a_{i\alpha}\}$ and $\{-a_{j\beta}, a_{j\alpha}\}$ with $a > b$ and $i > j$ must be coupled to spin-adapted two-electron excitations with a total spin of 1. Coupling of spin functions of four independent particles with spin $\frac{1}{2}$ leads to three linear independent triplet spin functions. Using the genealogical coupling scheme the three triplet double excitation operators can be expressed as $O_4^{1,0}(\frac{1}{2}, 1, \frac{3}{2}, 1)$, $O_4^{1,0}(\frac{1}{2}, 1, \frac{1}{2}, 1)$ and $O_4^{1,0}(\frac{1}{2}, 0, \frac{1}{2}, 1)$, where the number in parentheses describes the intermediate spin couplings [12]. The explicit expressions for the three operators are obtained as

$$O_4^{1,0}\left(\frac{1}{2}, 1, \frac{3}{2}, 1\right) = \frac{1}{\sqrt{6}}\left(a_{a\alpha}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\alpha} + a_{a\alpha}^\dagger a_{i\alpha} a_{b\beta}^\dagger a_{j\beta} - a_{a\beta}^\dagger a_{i\beta} a_{b\alpha}^\dagger a_{j\alpha} - a_{a\beta}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\beta} - a_{a\alpha}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\alpha} \right.$$
$$\left. + a_{a\beta}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\beta}\right), \tag{15}$$

$$O_4^{1,0}\left(\frac{1}{2}, 1, \frac{1}{2}, 1\right) = \frac{1}{\sqrt{3}}\left(a_{a\beta}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\beta} - \frac{1}{2} a_{a\alpha}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\alpha} - \frac{1}{2} a_{a\alpha}^\dagger a_{i\alpha} a_{b\beta}^\dagger a_{j\beta} + \frac{1}{2} a_{a\beta}^\dagger a_{i\beta} a_{b\alpha}^\dagger a_{j\alpha} \right.$$
$$\left. + \frac{1}{2} a_{a\beta}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\beta} - a_{a\alpha}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\alpha}\right), \tag{16}$$

$$O_4^{1,0}\left(\frac{1}{2}, 0, \frac{1}{2}, 1\right) = \frac{1}{2}\left(a_{a\alpha}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\alpha} - a_{a\alpha}^\dagger a_{i\alpha} a_{b\beta}^\dagger a_{j\beta} - a_{a\beta}^\dagger a_{i\beta} a_{b\alpha}^\dagger a_{j\alpha} + a_{a\beta}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\beta}\right), \tag{17}$$

where $a > b$ and $i > j$. A more convenient form can be obtained by the following linear combinations:

$$-\sqrt{\frac{2}{3}} O_4^{1,0}\left(\frac{1}{2}, 1, \frac{3}{2}, 1\right) - \frac{2}{\sqrt{3}} O_4^{1,0}\left(\frac{1}{2}, 1, \frac{1}{2}, 1\right) = a_{a\alpha}^\dagger a_{j\alpha} a_{b\beta}^\dagger a_{i\beta} - a_{a\beta}^\dagger a_{j\beta} a_{b\alpha}^\dagger a_{i\alpha} = \frac{1}{2}\left(T_{aj}E_{bi} - T_{bi}E_{aj}\right), \tag{18}$$

$$\sqrt{\frac{2}{3}}O_4^{1,0}\left(\frac{1}{2},1,\frac{3}{2},1\right) - \frac{1}{\sqrt{3}}O_4^{1,0}\left(\frac{1}{2},1,\frac{1}{2},1\right) + O_4^{1,0}\left(\frac{1}{2},0,\frac{1}{2},1\right) = a_{a\alpha}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\alpha} - a_{a\beta}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\beta}$$

$$= \frac{1}{2}\left(T_{ai}E_{bj} + T_{bj}E_{ai}\right), \tag{19}$$

$$\sqrt{\frac{2}{3}}O_4^{1,0}\left(\frac{1}{2},1,\frac{3}{2},1\right) - \frac{1}{\sqrt{3}}O_4^{1,0}\left(\frac{1}{2},1,\frac{1}{2},1\right) - O_4^{1,0}\left(\frac{1}{2},0,\frac{1}{2},1\right) = a_{a\alpha}^\dagger a_{i\alpha} a_{b\beta}^\dagger a_{j\beta} - a_{a\beta}^\dagger a_{i\beta} a_{b\alpha}^\dagger a_{j\alpha}$$

$$= \frac{1}{2}\left(T_{ai}E_{bj} - T_{bj}E_{ai}\right). \tag{20}$$

As our triplet excitation operator manifold we choose

$$^{(+)}T_{aibj} = (T_{ai}E_{bj} + T_{bj}E_{ai}) \quad \text{with } a > b, \ i > j, \tag{21}$$

$$^{(-)}T_{aibj} = \left(T_{ai}E_{bj} - T_{bj}E_{ai}\right) \quad \text{with } (ai) > (bj). \tag{22}$$

The diagonal elements vanish since $T_{ai}E_{ai} = 0$. If $a = b$ and $i \neq j$ or $a \neq b$ and $i = j$ there is only one way to obtain a triplet excitation operator in accordance with Eqs. (21) and (22).

The operator $^{(+)}T_{aibj}$ has the symmetries

$$^{(+)}T_{aibj} = {}^{(+)}T_{bjai} = -^{(+)}T_{ajbi} = -^{(+)}T_{biaj} \tag{23}$$

while the operator $^{(-)}T_{aibj}$ has the symmetries

$$^{(-)}T_{aibj} = -^{(-)}T_{bjai}. \tag{24}$$

In our subsequent derivation it is convenient to have the possibility to write the two electron triplet excitation operators both with and without constraints in the summation indices. Introducing amplitudes $^{(+)}R_{ij}^{ab}$ and $^{(-)}R_{ij}^{ab}$ which satisfy the same symmetries as the operators $^{(+)}T_{aibj}$ and $^{(-)}T_{aibj}$ we obtain

$$^{(+)}R_2 = \sum_{c>d,k>l} {}^{(+)}R_{kl}^{cd}\left(T_{ck}E_{dl} + T_{dl}E_{ck}\right) = \frac{1}{4}\sum_{ckdl} {}^{(+)}R_{kl}^{cd}\left(T_{ck}E_{dl} + T_{dl}E_{ck}\right)$$

$$= \frac{1}{2}\sum_{ckdl} {}^{(+)}R_{kl}^{cd}\,T_{ck}E_{dl}, \tag{25}$$

$$^{(-)}R_2 = \sum_{ck>dl} {}^{(-)}R_{kl}^{cd}\left(T_{ck}E_{dl} - T_{dl}E_{ck}\right)$$

$$= \frac{1}{2}\sum_{ckdl} {}^{(-)}R_{kl}^{cd}\left(T_{ck}E_{dl} - T_{dl}E_{ck}\right)$$

$$= \sum_{ckdl} {}^{(-)}R_{kl}^{cd}\,T_{ck}E_{dl}. \tag{26}$$

The triplet–double excitation operators may therefore be expressed both with and without constraints in the summation indices. Alternative spin-coupling schemes for the triplet two electron excitation operators are given in [14].

4. Triplet basis

The triplet basis is defined by the triplet excitation operators,

$$T_{ai}|\text{HF}\rangle = |(3)_i^a\rangle, \tag{27}$$

$$(T_{ai}E_{bj} + T_{bj}E_{ai})|\text{HF}\rangle = |(+)_{ij}^{ab}\rangle \; {}^{a>b}_{i>j}, \tag{28}$$

$$(T_{ai}E_{bj} - T_{bj}E_{ai})|\text{HF}\rangle = |(-)_{ij}^{ab}\rangle \; (ai) > (bj) \tag{29}$$

which is linear independent and together with

$$\langle {}^a_i(3)| = \frac{1}{2}\langle\text{HF}|\,T_{ia}, \tag{30}$$

$$\langle {}^{ab}_{ij}(+)| = \frac{1}{8}\langle\text{HF}|\,(E_{jb}T_{ia} + E_{ia}T_{jb}), \tag{31}$$

$$\langle {}^{ab}_{ij}(-)| = \frac{1}{8}\langle\text{HF}|\,(E_{jb}T_{ia} - E_{ia}T_{jb}) \tag{32}$$

forms an orthonormal basis. It is furthermore convenient to note that

$$\langle {}^{ab}_{ij}(+)|E_{ck}T_{dl}|\text{HF}\rangle = \frac{1}{2}\tilde{P}_{ij}P_{ij}^{ab}\,\delta_{aibj,ckdl}, \tag{33}$$

$$\langle {}^{ab}_{ij}(-)|E_{ck}T_{dl}|\text{HF}\rangle = \frac{1}{2}\tilde{P}_{ij}^{ab}\,\delta_{aibj,ckdl} \tag{34}$$

with the permutation operators P_{ij}^{ab}, $\tilde{P}_{ij}^{ab}$ and $\tilde{P}_{ij}$ defined as

$$P_{ij}^{ab}A_{ij}^{ab} = A_{ij}^{ab} + A_{ji}^{ba}, \tag{35}$$

$$\tilde{P}_{ij}^{ab}A_{ij}^{ab} = A_{ij}^{ab} - A_{ji}^{ba}, \tag{36}$$

$$\tilde{P}_{ij}A_{ij}^{ab} = A_{ij}^{ab} - A_{ji}^{ab}. \tag{37}$$

5. Linear transformation

The excitation energies for the CC2 model are the eigenvalues of the CC2 Jacobian, which in the three component form of the previous sections may be expressed as

$$A_{\mu_i\nu_j} = \begin{pmatrix} \langle\mu_1|[\hat{H},\tau_{\mu_1}] + [[\hat{H},\tau_{\mu_1}],T_2]|\text{HF}\rangle & \langle\mu_1|[\hat{H},\tau_{\nu_{2+}}]|\text{HF}\rangle & \langle\mu_1|[\hat{H},\tau_{\nu_{2-}}]|\text{HF}\rangle \\ \langle\mu_{2+}|[\hat{H},\tau_{\mu_1}]|\text{HF}\rangle & \delta_{\mu_{2+}\nu_{2+}}\omega_{\mu_{2+}} & 0 \\ \langle\mu_{2-}|[\hat{H},\tau_{\mu_1}]|\text{HF}\rangle & 0 & \delta_{\mu_{2-}\nu_{2-}}\omega_{\mu_{2-}} \end{pmatrix}, \tag{38}$$

where $\omega_{\mu_{2+}}$ and $\omega_{\mu_{2-}}$ equals the orbital energy difference

$$\omega_{aibj+} = \omega_{aibj-} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j. \tag{39}$$

The Jacobian differs from the CCSD Jacobian in the doubles–singles and in the doubles–doubles block.

The CC2 eigenvalue problem must be solved iteratively. This requires the ability to carry out linear transformations with the CC Jacobian. The transformation of the trial vectors may, using a simplified notation, be expressed as

$$\begin{pmatrix} \rho_1 \\ \rho_{2+} \\ \rho_{2-} \end{pmatrix} = \begin{pmatrix} A_{1\,1} & A_{1\,2+} & A_{1\,2-} \\ A_{2+\,1} & A_{2+\,2+} & A_{2+\,2-} \\ A_{2-\,1} & A_{2-\,2+} & A_{2-\,2-} \end{pmatrix} \begin{pmatrix} R_1 \\ R_{2+} \\ R_{2-} \end{pmatrix}. \tag{40}$$

Inserting the expression for the CC2 Jacobian in Eq. (38) into Eq. (40) we obtain

$$^{(3)}\rho_{ai}^1 = \left\langle {}^a_i (3)|[\hat{H}, {}^{(3)}R_1] + [[\hat{H}, {}^{(3)}R_1], T_2]|HF \right\rangle, \tag{41}$$

$$^{(3)}\rho_{aibj+} = \left\langle {}^{ab}_{ij} (+)|[\hat{H}, {}^{(3)}R_1]|HF \right\rangle, \tag{42}$$

$$^{(3)}\rho_{aibj-} = \left\langle {}^{ab}_{ij} (-)|[\hat{H}, {}^{(3)}R_1]|HF \right\rangle, \tag{43}$$

$$^{(+)}\rho_{ai} = \left\langle {}^a_i (3)|[\hat{H}, {}^{(+)}R_2]|HF \right\rangle, \tag{44}$$

$$^{(+)}\rho_{aibj+} = \left\langle {}^{ab}_{ij} (+)|[F, {}^{(+)}R_2]|HF \right\rangle, \tag{45}$$

$$^{(+)}\rho_{aibj-} = 0, \tag{46}$$

$$^{(-)}\rho_{ai} = \left\langle {}^a_i (3)|[\hat{H}, {}^{(-)}R_2]|HF \right\rangle, \tag{47}$$

$$^{(-)}\rho_{aibj+} = 0, \tag{48}$$

$$^{(-)}\rho_{aibj-} = \left\langle {}^{ab}_{ij} (-)|[F, {}^{(-)}R_2]|HF \right\rangle. \tag{49}$$

The explicit forms of the terms are

$$^{(3)}\rho_{ai} = \sum_c {}^{(3)}R_i^c \left(\hat{F}_{ac} - \sum_{dkl} t_{lk}^{da} L_{ldkc} \right) + \sum_{ckl} t_{li}^{ac} \hat{g}_{l\bar{k}kc} - \sum_k {}^{(3)}R_k^a \left(\hat{F}_{ki} + \sum_{cdl} t_{il}^{dc} L_{lckd} \right) - \sum_k \hat{g}_{a\bar{k}ki}, \tag{50}$$

$$^{(3)}\rho_{aibj+} = \frac{1}{2}\tilde{P}_{ij} \left(\hat{g}_{\bar{b}jai} + \hat{g}_{bj\bar{a}i} + \hat{g}_{b\bar{j}ai} + \hat{g}_{bja\bar{i}} \right), \tag{51}$$

$$^{(3)}\rho_{aibj-} = \frac{1}{2} \left(\hat{g}_{\bar{b}jai} - \hat{g}_{bj\bar{a}i} + \hat{g}_{b\bar{j}ai} - \hat{g}_{bja\bar{i}} \right), \tag{52}$$

$$^{+}\rho_{ai} = 2 \left(\sum_{cdk} {}^{(+)}R_{ik}^{dc} \hat{g}_{adkc} - \sum_{ckl} {}^{(+)}R_{lk}^{ac} \hat{g}_{kcli} + \sum_{ck} {}^{(+)}R_{ik}^{ac} \hat{F}_{kc} \right), \tag{53}$$

$$^{(+)}\rho_{aibj+} = \left(\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j \right) {}^{(+)}R_{ij}^{ab}, \tag{54}$$

$$^{(+)}\rho_{aibj-} = 0, \tag{55}$$

$$^{(-)}\rho_{ai} = 2 \left(\sum_{cdk} {}^{(-)}R_{ik}^{dc} \hat{g}_{adkc} - \sum_{ckl} {}^{(-)}R_{lk}^{ac} \hat{g}_{kcli} + \sum_{ck} {}^{(-)}R_{ik}^{ac} \hat{F}_{kc} \right), \tag{56}$$

$$^{(-)}\rho_{aibj+} = 0, \tag{57}$$

$$^{(-)}\rho_{aibj-} = \left(\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j \right) {}^{(-)}R_{ij}^{ab}. \tag{58}$$

The transformations with $^{(3)}R_1$, $^{(3)}R_{2+}$ and $^{(3)}R_{2-}$ are done at the same time which gives computational savings

$$\begin{aligned}
^{(3)}\rho_{ai,\text{Transformed}} = {} & \sum_c {}^{(3)}R_i^c \left(\hat{F}_{ac} - \sum_{dkl} t_{lk}^{da} L_{ldkc} \right) + \sum_{ckl} t_{li}^{ac} \hat{g}_{l\bar{k}kc} - \sum_k {}^{(3)}R_k^a \left(\hat{F}_{ki} + \sum_{cdl} t_{il}^{dc} L_{lckd} \right) \\
& - \sum_k \hat{g}_{a\bar{k}ki} + 2 \sum_{cdk} \left({}^{(+)}R_{ik}^{dc} + {}^{(-)}R_{ik}^{dc} \right) \hat{g}_{adkc} - 2 \sum_{ckl} \left({}^{(+)}R_{lk}^{ac} + {}^{(-)}R_{lk}^{ac} \right) \hat{g}_{kcli} \\
& + 2 \sum_{ck} \left({}^{(+)}R_{ik}^{ac} + {}^{(-)}R_{ik}^{ac} \right) \hat{F}_{kc},
\end{aligned} \tag{59}$$

$$^{(3)}\rho_{aibj+,\text{Transformed}} = \frac{1}{2}\tilde{P}_{ij}\left(\hat{g}_{\bar{b}jai} + \hat{g}_{bj\bar{a}i} + \hat{g}_{b\bar{j}ai} + \hat{g}_{bja\bar{i}}\right) + \left(\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j\right)^{(+)}R_{ij}^{ab}, \tag{60}$$

$$^{(3)}\rho_{aibj-,\text{Transformed}} = \frac{1}{2}\left(\hat{g}_{\bar{b}jai} - \hat{g}_{bj\bar{a}i} + \hat{g}_{b\bar{j}ai} - \hat{g}_{bja\bar{i}}\right) + \left(\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j\right)^{(-)}R_{ij}^{ab}. \tag{61}$$

The terms $^{(3)}\rho_{ai}$, $^{(+)}\rho_{ai}$ and $^{(-)}\rho_{ai}$ are identical to the terms in the CCSD model [15]. The $^{(+)}\rho_{aibj+}$ and the $^{(-)}\rho_{aibj-}$ terms are just doubles amplitudes multiplied with an orbital energy difference. The $^{(3)}\rho_{aibj+}$ and $^{(3)}\rho_{aibj-}$ terms are calculated by a direct transformation of the AO integrals to the MO basis. For CC2, the computationally most demanding steps are the calculations of the transformed integrals $\hat{g}_{bjai}$, $\hat{g}_{b\bar{j}ai}$, and $\hat{g}_{abkc}$. In the spin coupled formulation the dominant contribution to the operation count for these transformations is $\approx 3N^4O$. In a spin orbital approach the integrals $\hat{g}_{bjai}$ and $\hat{g}_{b\bar{j}ai}$ have to be computed for three different spin cases ($\alpha\alpha\alpha\alpha$, $\beta\beta\beta\beta$ and $\alpha\alpha\beta\beta$), while the integrals $\hat{g}_{abkc}$ with three virtual indeces have to be computed for four spin cases ($\alpha\alpha\alpha\alpha$, $\beta\beta\beta\beta$, $\alpha\alpha\beta\beta$ and $\beta\beta\alpha\alpha$), which leads to an operation count of $\approx 17/2N^4O$. Together with the three spin cases for R_{cd}^{ab} and ρ_{aibj}, this results in an overall increase of operation count, memory and disc space requirements by about a factor of 3.

6. Excitation energies for benzene

6.1. Basis sets

The CC2 basis sets investigation of the triplet excitation energies of benzene are given in Table 1. The same basis sets were used as in the previous basis set investigation for the singlet excitation energies [13]. The calculations were carried out at the same geometry as in CASPT2 [16] and SOPPA [17] calculations. The ground state energies are given in Table 1 of Ref. [13] (The MP2-energy for the ANO1-basis set should have been −231.634979 Hartree.). In the basis set study we have focused on a systematic extension of Dunning's aug-cc-pVDZ basis set. Diffuse functions were added at the center of mass (CM) to describe the Rydberg states. As diffuse CM functions we have used both the contracted optimized atomic natural orbital (ANO) center function and systematic sets of s,p,d primitive functions where the CM s,p,d primitive functions had the following exponents: CM1 (0.01); CM2 (0.01;0.0033); and for CM3 (0.01;0.0033;0.0011). The effect of adding tight functions was investigated by the CM2(t)-functions which had exponents of (0.01;0.03) for the primitive s,p,d functions. The largest number of CM functions that we have used were the uncontracted set from the ANO center function corresponding to the primitive functions suggested by Kaufmann et al. [18] which are referred to as CM8. After examining the effect of CM functions we have improved the description of the valence region by replacing the aug-cc-pVDZ basis set with the aug-cc-pVTZ basis set.

Comparing the results in Table 1 it can be seen that the different CM function expansions give quite similar results. Going from CM1 to CM2 changes the excitation energies by less than 0.02 eV while going from CM2 to CM3 has no significant change. Adding more tight CM functions also has very little effect except for the 2^3E_{1g} state where the difference between the CM2(t) and the other basis sets is about 0.05 eV. Comparing all the CM basis set results we see changes of less than 0.01 eV for most states. A few states differ by around 0.03 eV while the 2^3E_{1g} state differs by as much as 0.08 eV. A reasonably accurate description is obtained keeping two primitive functions in the CM basis.

The effect of improving the description of the valence space is seen by comparing the excitation energies calculated with the aug-cc-pVDZ-CM2 and the aug-cc-pVTZ-CM2 basis sets. Going from aug-cc-pVDZ-CM2 to aug-cc-pVTZ-CM2 shifts all the excitation energies less than 0.2 eV. The valence excitation energies are all shifted down except the 1^3E_{2g} state that is shifted up by 0.15 eV. The Rydberg states are

Table 1
C_6H_6 CC2 triplet excitation energies (eV)

One electron basis	pVDZ	aug-pVDZ	aug-pVDZ-CM1	aug-pVDZ-CM1(ANO)	aug-pVDZ-CM2	aug-pVDZ-CM2(t)	aug-pVDZ-CM3	aug-pVDZ-CM8	pVTZ	aug-pVDZ-CM2
Valence $^3\pi\pi^*$										
1 $^3B_{1u}$	4.378	4.350	4.350	4.350	4.350	4.350	4.350	4.349	4.358	4.345
1 $^3E_{1u}$	5.200	5.083	5.083	5.083	5.083	5.082	5.083	5.082	5.105	5.058
1 $^3B_{2u}$	6.133	5.906	5.906	5.906	5.906	5.905	5.906	5.905	5.965	5.873
1 $^3E_{2g}$			7.637	7.623	7.628	7.630	7.628	7.607		7.782
Rydberg $^3\pi\pi^*$										
2 $^3E_{1u}$			7.030	7.020	7.029	7.024	7.029	6.999		7.178
1 $^3A_{1g}$			7.597	7.584	7.591	7.590	7.591	7.567		7.750
2 $^3E_{2g}$			7.997	7.996	7.991	7.996	7.991	7.988		7.965
1 $^3A_{2g}$			7.683	7.669	7.670	7.678	7.670	7.652		7.833
Rydberg $^3\pi\sigma^*$										
1 $^3E_{1g}$		6.308	6.265	6.269	6.265	6.263	6.265	6.259		6.416
1 $^3A_{2u}$		6.824	6.761	6.762	6.761	6.759	6.761	6.755		6.921
1 $^3E_{2u}$		6.933	6.858	6.859	6.857	6.855	6.857	6.851		7.018
1 $^3A_{1u}$		7.043	6.951	6.952	6.950	6.949	6.950	6.944		7.111
2 $^3E_{1g}$			7.394	7.371	7.391	7.341	7.390	7.315		7.508
1 $^3B_{2g}$			7.412	7.411	7.409	7.409	7.409	7.404		7.572
1 $^3B_{1g}$			7.428	7.428	7.426	7.426	7.426	7.419		7.588
3 $^3E_{1g}$					7.456		7.454	7.427		7.599
4 $^3E_{1g}$					7.701		7.701	7.695		7.869

Table 2
C_6H_6 triplet excitation energies in the ANO1 basis set (eV)

Basis method	aug-cc-pVTZ-CM2 CC2	ANO1 CASSCF[a]	CASPT2[a]	CCS	CC2	CCSD[b]	CCSD[b] %T_1	RPA[c]	SOPPA[c]
Valence $^3\pi\pi^*$									
1 $^3B_{1u}$	3.95[d]	4.345	4.05	3.89	3.363	4.328	3.962	98.9	Instability	3.75
1 $^3E_{1u}$	4.75[d]	5.058	5.07	4.49	4.878	5.079	4.920	97.9	4.70	4.48
1 $^3B_{2u}$	5.60[d]	5.873	6.93	5.49	5.490	5.932	5.840	98.5	5.07	5.50
1 $^3E_{2g}$	7.24–7.74[a]	7.782	7.61	7.12	7.596	7.638	7.712	97.9	7.24	7.41
Rydberg $^3\pi\pi^*$									
2 $^3E_{1u}$		7.178	6.92	6.98	7.118	7.044	7.182	98.4	7.11	6.92
1 $^3A_{1g}$		7.750	7.42	7.62	7.652	7.601	7.782	98.5	7.64	7.50
2 $^3E_{2g}$		7.965	7.44	7.55	7.927	7.993	7.875	98.1	7.85	7.57
1 $^3A_{2g}$		7.833	7.50	7.70	7.856	7.685	7.880	98.3	7.85	7.59
Rydberg $^3\pi\sigma^*$									
1 $^3E_{1g}$		6.416	6.22	6.34	6.535	6.370	6.501	98.3	6.44	6.14
1 $^3A_{2u}$		6.921	6.61	6.80	6.847	6.789	6.923	98.5	6.82	6.64
1 $^3E_{2u}$		7.018	6.73	6.90	7.092	6.882	7.041	98.3	7.08	6.74
1 $^3A_{1u}$		7.111	6.83	7.00	7.286	6.969	7.145	98.2	7.28	6.84
2 $^3E_{1g}$		7.508	7.31	7.57	7.534	7.439	7.607	98.4	7.51	7.32
1 $^3B_{2g}$		7.572	7.27	7.53	7.656	7.444	7.632	98.3	7.65	7.33
1 $^3B_{1g}$		7.588	7.27	7.53	7.690	7.461	7.657	98.3	7.69	7.35
3 $^3E_{1g}$		7.599	7.27	7.53	7.708	7.499	7.678	98.4	7.69	7.35

a See [16].
b See [15].
c See [17].
d See [20].

generally shifted up by 0.14 ± 0.03 eV except for the 2^3E_{2g} state which is shifted down by 0.03 eV. The special behavior of the 2^3E_{2g} state is caused by the small energy difference between this state and the valence 1^3E_{2g} state leading to a large coupling between these states. The Rydberg state therefore has a large valence component and vice versa.

6.2. Triplet excitation energies

In Table 2 we compare results obtained using different methods. Experimental results for the three lowest valence states are obtained from [20] and represent the energies at the Frank–Condon maxima. The experimental excitation energy for the fourth valence state has been obtained from Lorentzon et al. [16]. The calculations have all been performed using the ANO1 basis set [16] except for CC2 where also results are given for the aug-cc-pVTZ-CM2 basis set. The ANO1 basis set is of double-zeta quality. The lower ground state energy in the ANO1 basis set than in the aug-cc-pVDZ set is probably due to a better description of the core as described in Ref. [13]. This better description however is unimportant for the excitation energies and the ANO1 and the aug-cc-pVDZ-CM2 excitation energies are thus also quite similar. Comparing the CC2 and the CASPT2 results differences of less than 0.6 eV are found for the valence states. For the Rydberg states there are differences of up to 0.3 eV. The differences between CC2 and SOPPA are up to 0.6 eV for the valence states while differences of up to 0.4 eV are found for the Rydberg states.

The difference between the CCS and CC2 excitation energies are between −0.4 and 1.0 eV. For CC2 and CCSD the differences are between −0.4 and 0.2 eV. Generally the CC2 excitation energies for the valence states are closer to the CCSD excitation energies than the CCS results while for the Rydberg excitation energies the CCS results are the ones closest to the CCSD results. For all but the 1^3E_{2g} excitation energies the correction from CCS to CC2 and from CC2 to CCSD is in opposite directions.

It is difficult to make more definite statements about the relative performance of the various models from a comparison with experiments since the basis set error is still significant and geometry and vibrational effects have not been considered. Consideration of geometry relaxation and zero-point energy will in general lead to smaller excitation energies.

The percent single excitation component $\%T_1$ in the CCSD excitation vector in the ANO1 basis calculation is also given in Table 2. The triplet excitation energies usually have larger $\%T_1$ than the corresponding singlet excitation energies due to the fact that the double excitations that often give large contributions to the singlet states are the double excitations from one orbital to another and these double excitations have no triplet component. From Table 2 it can be seen that the lowest percent single excitation in the CCSD triplet excitation energies is 97.9% which should be compared to 85% for the corresponding singlet excitation energies, see Table 6 of Ref. [19]. The stronger single excitation dominance in the triplet excitation energies means that the triplet excitation energies are expected to be described at least as accurately as the corresponding singlet excitation energies.

7. Conclusion

In this Letter we have presented a direct atomic integral driven implementation of CC2 triplet excitation energies using an explicit triplet spin coupled excitation space. We have carried out a basis set investigation for the triplet excitation energies of benzene with basis sets containing up to 432 basis functions. As expected the Rydberg states requires diffuse basis functions. In accordance with a previous basis set investigation on the singlet excitation energies we found that primitive CM functions were as good as CM functions constructed from elaborate contraction schemes with several primitive basis functions. The basis set saturation for the Rydberg states using CM functions was fast and much more efficient than adding atom centered diffuse functions. In order to estimate basis set saturation of the valence space we have

compared results from the basis sets aug-cc-pVDZ-CM2 and aug-cc-pVTZ-CM2. It was found that the lowest triplet valence excitation energies generally changed by less than 0.1 eV while the excitation energies for the Rydberg states generally increased by approximately 0.14 eV. To make more conclusive statements of the accuracy that can be obtained for triplet excitation energies using the CC2 model more extensive work is required i.e., comparing the results in the CCS, CC2, CCSD, CC3 hierarchy with full configuration interaction (FCI) results. Work in this direction is in progress.

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References

[1] O. Christiansen, P. Jørgensen, C. Hättig, Int. J. Quantum Chem. 68 (1998) 1.
[2] R.J. Bartlett, in: D.R. Yakony (Ed.), Modern Electronic Structure Theory, World Scientific, Singapore, 1995, p. 1047.
[3] O. Christiansen, H. Koch, P. Jørgensen, Chem. Phys. Lett. 243 (1995) 409.
[4] G.P. Purvis, R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910.
[5] J. Noga, R.J. Bartlett, J. Chem. Phys. 86 (1987) 7041.
[6] J. Noga, R.J. Bartlett, J. Chem. Phys. 89 (1988) 3401 erratum.
[7] G.E. Scuseria, H.F. Schaefer III, Chem. Phys. Lett. 152 (1988) 382.
[8] H. Koch, O. Christiansen, P. Jørgensen, A.M. Sánchez de Merás, T. Helgaker, J. Chem. Phys. 106 (1997) 1808.
[9] E.S. Nielsen, P. Jørgensen, J. Oddershede, J. Chem. Phys. 73 (1980) 6238.
[10] K. Anderson, P.-Å. Malmqvist, B.O. Roos, J. Chem. Phys. 96 (1992) 1218.
[11] J. Stanton, R.J. Bartlett, J. Chem. Phys. 98 (1993) 7029.
[12] T. Helgaker, P. Jørgensen, J. Olsen, Molecular Electronic Structure Theory, Wiley, New York, 2000.
[13] O. Christiansen, H. Koch, P. Jørgensen, T. Helgaker, Chem. Phys. Lett. 263 (1996) 530.
[14] J. Paldus, B.G. Adams, J. Cizek, Int. J. Quantum Chem. 11 (1977) 813.
[15] K. Hald, C. Hättig, P. Jørgensen, J. Chem. Phys., accepted.
[16] J. Lorentzon, P.Å. Malmqvist, M. Fulscher, B.O. Roos, Theo. Chim. Acta. 91 (1995) 91.
[17] M.J. Packer, E.K. Dalskov, T. Enevoldsen, H.J.Aa. Jensen, J. Oddershede, J. Chem. Phys. 105 (1996) 5886.
[18] K. Kaufmann, W. Baumeister, M. Jungen, J. Phys. B 22 (1989) 2223.
[19] O. Christiansen, H. Koch, A. Halkier, P. Jørgensen, T. Helgaker, A. Sánchez de Merás, J. Chem. Phys. 105 (1996) 6921.
[20] J.P. Doering, J. Chem. Phys. 51 (1969) 2866.