Triplet excitation energies in the coupled cluster singles and doubles model using an explicit triplet spin coupled excitation space

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Triplet excitation energies are calculated from the response eigenvalue equation for the coupled cluster singles and doubles (CCSD) model using an integral direct approach and an explicit spin coupled triplet excitation space. The cost of one linear transformation for the triplet excitation energy is about two times the cost of one linear transformation for the singlet excitation energy. The triplet excitation spectrum of benzene is calculated using from 147 to 432 basis functions. The calculated triplet excitation energies are compared with experimental and other theoretical values. © *2000 American Institute of Physics.* [S0021-9606(00)30742-5]

I. INTRODUCTION

Excitation energies may be calculated using two different strategies. One approach is to calculate the total energies of each individual state and obtain the excitation energy as the energy difference between two states. Models that use this approach are i.e., multireference configuration interaction (MRCI)[1] and multireference perturbation theory (MRMP), i.e., CASPT2.[2–4] The other approach is to use response-function methods where excitation energies are calculated directly from a response eigenvalue equation. Examples of this approach are the response eigenvalue equation for self-consistent field (SCF),[5] also known as the random phase approximation (RPA), and coupled cluster (CC) wave functions.

CC response theory was originally introduced by Monkhorst and later generalized by many authors.[6–15] In CC response theory the ground state energy is obtained by solving a nonlinear set of equations, while the excitation energies are obtained by solving a linear response eigenvalue problem. In order to obtain accurate excitation energies, a balanced description is required of the ground and excited states. In coupled cluster theory the accuracy of excitation energies therefore depends on how accurate the single-determinant reference function describes the ground state, how well the ground state is described by the truncation in the coupled cluster operator, and how accurate the excitation manifold can describe the excitation process to the state of interest.

Since the coupled cluster approach was introduced in quantum chemistry,[16–18] the method has gained increasing popularity, offering an efficient treatment of the dynamical correlation.[19] The coupled cluster singles and doubles (CCSD) model has been implemented using different formulations.[20–26] This work describes a CCSD implementation of triplet excitation energies using the integral-direct technique of Koch *et al.*[25,26]

Triplet excitation energies at the CCSD level have previously been presented by Stanton and Bartlett[12] using a spin-orbital basis formulation. We explicitly spin couple the operators of the excitation space to triplet spin. The parametrization we use constitutes a generalization of the one used in the singlet case[27,28] and leads to working equations of similar structure.[27] The explicit spin coupling leads to a significantly more efficient formulation than using the spin-orbital basis.

After introducing the coupled cluster response eigenvalue equation in Sec. II we describe the explicit parametrization of the triplet excitation space and its use to obtain an efficient implementation of the linear transformation that is required for the calculation of triplet excitation energies. In Sec. III we outline the implementation and in Sec. IV we report calculations of triplet excitation energies for benzene. The last section contains some concluding remarks.

II. TRIPLET EXCITATION ENERGIES IN THE INTEGRAL-DIRECT CCSD MODEL

A. Coupled cluster theory

The single-reference coupled cluster ansatz for a closed shell system is

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

where the reference state is taken to be the Hartree–Fock $|\mathrm{HF}\rangle$ state. For a N-electron state the cluster operator T truncates at excitation level N,

$$T = T_1 + T_2 + \cdots + T_N, \tag{2}$$

where for example the one- and two-electron cluster operators are

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$$T_1=\sum_{ai} t_i^a E_{ai}, \tag{3}$$

$$T_2=\sum_{(ai)\geqslant(bj)} t_{ij}^{ab} E_{ai}E_{bj}=\frac{1}{2}\sum_{abij} \tilde{t}_{ij}^{ab} E_{ai}E_{bj}, \tag{4}$$

with

$$\tilde{t}_{ij}^{ab}=(1+\delta_{ai,bj})\, t_{ij}^{ab}. \tag{5}$$

Indices *i,j,k,l* and *a,b,c,d* refer, respectively, to the occupied and unoccupied orbitals in the reference state. A shorthand notation for the cluster operators are

$$T=\sum_{\mu} t_\mu \tau_\mu, \tag{6}$$

where t_μ are the cluster amplitude and τ_μ are the corresponding excitation operator. Inserting the CC ansatz into the Schrödinger equation and multiplying from the left with $\exp(-T)$, we obtain the similarity transformed Schrödinger equation

$$\exp(-T)H\exp(T)|\mathrm{HF}\rangle=E|\mathrm{HF}\rangle. \tag{7}$$

In second quantization the electronic Hamiltonian H can be written as

$$H=\sum_{pq} h_{pq}E_{pq}+\frac{1}{2}\sum_{pqrs}(pq|rs)e_{pqrs}, \tag{8}$$

where E_{pq} are the generators of the unitary group and

$$e_{pqrs}=E_{pq}E_{rs}-\delta_{qr}E_{ps}. \tag{9}$$

The cluster amplitudes are determined by projecting the similarity transformed Schrödinger equation onto a manifold of excitations out of the reference state:

$$|\mu\rangle=\tau_\mu|\mathrm{HF}\rangle, \tag{10}$$

$$\Omega_\mu=\langle\mu|\exp(-T)H|\mathrm{CC}\rangle=0. \tag{11}$$

The CC energy is obtained by projection onto the reference state

$$E=\langle\mathrm{HF}|H|\mathrm{CC}\rangle. \tag{12}$$

Coupled cluster response functions have been derived using different strategies.[6,10,15] The excitation energies are poles of the linear response function, and are determined as the eigenvalues of the nonsymmetric coupled cluster Jacobian

$$\mathbf{A}\mathbf{R}_\mathbf{k}=\omega_k\mathbf{R}_\mathbf{k}. \tag{13}$$

We have used that by choice of $\{\mu\}$ the metric of the eigenvalue equation can be made diagonal:

$$S_{\mu\nu}=\langle\mu|\exp(-T)\tau_\nu|\mathrm{CC}\rangle=\delta_{\mu\nu}. \tag{14}$$

The coupled cluster Jacobian is defined as

$$A_{\mu\nu}=\frac{\partial\Omega_\mu}{\partial t_\nu}. \tag{15}$$

In standard CC theory, the Jacobian becomes

$$A_{\mu\nu}=\langle\mu|\exp(-T)[H,\tau_\nu]|\mathrm{CC}\rangle. \tag{16}$$

We describe the calculation of triplet excitation energies where the excitation operator τ_ν (and consequently the projection manifold $\langle\mathrm{HF}|\tau_\nu^\dagger$) are explicit spin coupled to have triplet spin.

B. Triplet excitations

From the annihilation and creation operators of second quantization, $a^\dagger$ and a, one can construct spin coupled single excitation singlet and triplet excitation operators as

$$S_{pq}^{0,0}=\frac{1}{\sqrt{2}}(a_{p\alpha}^\dagger a_{q\alpha}+a_{p\beta}^\dagger a_{q\beta})=\frac{1}{\sqrt{2}}E_{pq}, \tag{17}$$

$$T_{pq}^{1,0}=\frac{1}{\sqrt{2}}(a_{p\alpha}^\dagger a_{q\alpha}-a_{p\beta}^\dagger a_{q\beta})=\frac{1}{\sqrt{2}}T_{pq}. \tag{18}$$

The operator $E_{ai}T_{bj}$ is a triplet tensor operator with zero spin-projection on the *z*-axis, since it satisfies[29]

$$[S_z,S_{ai}^{0,0}T_{bj}^{1,0}]=0 \tag{19}$$

and

$$[S_\pm,S_{ai}^{0,0}T_{bj}^{1,0}]=\sqrt{2}\,(S_{ai}^{0,0}\,T_{bj}^{1,\pm1}). \tag{20}$$

There are three different ways to couple four different particles to triplet spin. Thus the triplet excitation space is spanned by the operators

$$\frac{1}{2}(T_{aj}E_{bi}-T_{bi}E_{aj})=a_{a\alpha}^\dagger a_{j\alpha}a_{b\beta}^\dagger a_{i\beta}-a_{a\beta}^\dagger a_{j\beta}a_{b\alpha}^\dagger a_{i\alpha}, \tag{21}$$

$$\frac{1}{2}(T_{ai}E_{bj}-T_{bj}E_{ai})=a_{a\alpha}^\dagger a_{i\alpha}a_{b\beta}^\dagger a_{j\beta}-a_{a\beta}^\dagger a_{i\beta}a_{b\alpha}^\dagger a_{j\alpha}, \tag{22}$$

$$\frac{1}{2}(T_{ai}E_{bj}+T_{bj}E_{ai})=a_{a\alpha}^\dagger a_{i\alpha}a_{b\alpha}^\dagger a_{j\alpha}-a_{a\beta}^\dagger a_{i\beta}a_{b\beta}^\dagger a_{j\beta}, \tag{23}$$

for $a>b$ and $i>j$. As our triplet excitation operators we choose

$${}^{(+)}T_{aibj}=(T_{ai}E_{bj}+T_{bj}E_{ai})\ a>b,\ i>j, \tag{24}$$

$${}^{(-)}T_{aibj}=(T_{ai}E_{bj}-T_{bj}E_{ai})\ (ai)>(bj). \tag{25}$$

We note that 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. (24) and (25). The diagonal elements vanish since $T_{ai}E_{ai}=0$. The operator ${}^{(+)}T_{aibj}$ has the symmetries

$${}^{(+)}T_{aibj}={}^{(+)}T_{bjai}=-{}^{(+)}T_{ajbi}=-{}^{(+)}T_{biaj}, \tag{26}$$

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

$${}^{(-)}T_{aibj}=-{}^{(-)}T_{bjai}. \tag{27}$$

In our subsequent derivation it is convenient to be able to write the two-electron triplet excitation operators both with and without constraints in the summation indices similar to the singlet operator in Eq. (4). Introducing amplitudes ${}^{(+)}R_{ij}^{ab}$ and ${}^{(-)}R_{ij}^{ab}$ which satisfy the same symmetries as the operators ${}^{(+)}T_{aibj}$ and ${}^{(-)}T_{aibj}$, respectively, we obtain

$$
\begin{aligned}
{}^{(+)}R_2 &= \sum_{c>d,k>l} {}^{(+)}R_{kl}^{cd}(T_{ck}E_{dl}+T_{dl}E_{ck}) \\
&= \frac{1}{4}\sum_{ckdl} {}^{(+)}R_{kl}^{cd}(T_{ck}E_{dl}+T_{dl}E_{ck}) \\
&= \frac{1}{2}\sum_{ckdl} {}^{(+)}R_{kl}^{cd}\,T_{ck}E_{dl}, \qquad (28)
\end{aligned}
$$

$$
\begin{aligned}
{}^{(-)}R_2 &= \sum_{ck>dl} {}^{(-)}R_{kl}^{cd}(T_{ck}E_{dl}-T_{dl}E_{ck}) \\
&= \frac{1}{2}\sum_{ckdl} {}^{(-)}R_{kl}^{cd}(T_{ck}E_{dl}-T_{dl}E_{ck}) \\
&= \sum_{ckdl} {}^{(-)}R_{kl}^{cd}T_{ck}E_{dl}. \qquad (29)
\end{aligned}
$$

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 double excitation operators have been given in Ref. 30.

C. Triplet basis

The triplet excitation manifold is defined by the excitation operators

$$T_{ai}|\mathrm{HF}\rangle = |(3)_i^a\rangle, \qquad (30)$$

$$(T_{ai}E_{bj}+T_{bj}E_{ai})|\mathrm{HF}\rangle = |(+)_{ij}^{ab}\rangle \;\; a>b,\; i>j, \qquad (31)$$

$$(T_{ai}E_{bj}-T_{bj}E_{ai})|\mathrm{HF}\rangle = |(-)_{ij}^{ab}\rangle \;\; (ai)>(bj), \qquad (32)$$

and forms together with the projection manifold,

$$\langle {}_i^a(3)\,| = \frac{1}{2}\langle \mathrm{HF}|\,T_{ia}, \qquad (33)$$

$$\langle {}_{ij}^{ab}(+)| = \frac{1}{8}\langle \mathrm{HF}|\,(E_{jb}T_{ia}+E_{ia}T_{jb}), \qquad (34)$$

$$\langle {}_{ij}^{ab}(-)| = \frac{1}{8}\langle \mathrm{HF}|\,(E_{jb}T_{ia}-E_{ia}T_{jb}), \qquad (35)$$

an orthonormal basis. It is convenient to note that

$$\langle {}_{ij}^{ab}(+)|E_{ck}T_{dl}|\mathrm{HF}\rangle = \frac{1}{2}\tilde{P}_{ij}P_{ij}^{ab}\,\delta_{aibj,ckdl}, \qquad (36)$$

$$\langle {}_{ij}^{ab}(-)|E_{ck}T_{dl}|\mathrm{HF}\rangle = \frac{1}{2}\tilde{P}_{ij}^{ab}\,\delta_{aibj,ckdl}, \qquad (37)$$

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

$$P_{ij}^{ab}(A_{ij}^{ab}) = A_{ij}^{ab}+A_{ji}^{ba}, \qquad (38)$$

$$\tilde{P}_{ij}^{ab}(A_{ij}^{ab}) = A_{ij}^{ab}-A_{ji}^{ba}, \qquad (39)$$

$$\tilde{P}_{ij}(A_{ij}^{ab}) = A_{ij}^{ab}-A_{ji}^{ab}. \qquad (40)$$

D. The CCSD model

Following Ref. 25, the CCSD amplitude equations can be written as

$$
\begin{aligned}
\Omega_\mu &= \langle \mu|\exp(-T_1-T_2)H\exp(T_1+T_2)|\mathrm{HF}\rangle \\
&= \langle \mu|\exp(-T_2)\,\hat{H}\exp(T_2)|\mathrm{HF}\rangle = 0, \qquad (41)
\end{aligned}
$$

where we have introduced the T_1 similarity transformed Hamiltonian

$$\hat{H} = \exp(-T_1)H\exp(T_1). \qquad (42)$$

Since the T_1 operator is a one-particle operator, the transformation of the Hamiltonian conserves the particle rank and can be expressed as

$$\hat{H} = \hat{h}+\hat{g} = \sum_{pq}\;\hat{h}_{pq}E_{pq} + \frac{1}{2}\sum_{pqrs}\;\hat{g}_{pqrs}e_{pqrs}, \qquad (43)$$

where the integrals $\hat{h}_{pq}$ and $\hat{g}_{pqrs}$ are calculated as

$$\hat{h}_{pq} = \sum_{\mu\nu}\;\Lambda_{\mu p}^{p}\Lambda_{\nu q}^{h}h_{\mu\nu}, \qquad (44)$$

$$\hat{g}_{pqrs} = \sum_{\mu\nu\rho\sigma}\;\Lambda_{\mu p}^{p}\Lambda_{\rho r}^{p}\Lambda_{\nu q}^{h}\Lambda_{\sigma s}^{h}(\mu\nu|\rho\sigma). \qquad (45)$$

Λ^p and Λ^h are effective molecular orbital (MO) transformation matrices (particle and hole) defined as

$$\Lambda^p = C[1-t_1^T], \qquad (46)$$

$$\Lambda^h = C[1+t_1]. \qquad (47)$$

In the last equations,

$$t_1 = \begin{bmatrix} 0 & 0 \\ t_{ai} & 0 \end{bmatrix}, \qquad (48)$$

where the orbitals are ordered with the occupied orbitals preceding the unoccupied orbitals.

Using the T_1-transformed Hamiltonian, the CCSD Jacobian can be expressed in the coupled cluster doubles (CCD) form

$$
\begin{aligned}
A_{\mu\nu} &= \langle \mu|\exp(-T_2)[\hat{H},\tau_\nu]\exp(T_2)|\mathrm{HF}\rangle \\
&= \langle \mu|[\hat{H},\tau_\nu]|\mathrm{HF}\rangle + \langle \mu|[[\hat{H},\tau_\nu],T_2]|\mathrm{HF}\rangle. \qquad (49)
\end{aligned}
$$

This enables us to write the CCSD triplet Jacobian in matrix form as

$$A_{\mu\nu}=\begin{pmatrix} \langle {}^{(3)}\mu_1|\hat{H}_1|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_1|\hat{H}^{(1)}_{2+}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_1|\hat{H}^{(1)}_{2-}|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2+}|\hat{H}_1|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2+}|\hat{H}^{(1)}_{2+}+\hat{H}^{(2)}_{2+}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2+}|\hat{H}^{(1)}_{2-}+\hat{H}^{(2)}_{2-}|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2-}|\hat{H}_1|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2-}|\hat{H}^{(1)}_{2+}+\hat{H}^{(2)}_{2+}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2-}|\hat{H}^{(1)}_{2-}+\hat{H}^{(2)}_{2-}|\mathrm{HF}\rangle \end{pmatrix}, \tag{50}$$

where

$$\hat{H}_1=[\hat{H}+[\hat{H},T_2],\tau_{\nu_1}], \tag{51}$$

$$\hat{H}^{(1)}_{2\pm}=[\hat{H},\tau_{\nu_{2\pm}}], \tag{52}$$

$$\hat{H}^{(2)}_{2\pm}=[[\hat{H},T_2],\tau_{\nu_{2\pm}}]. \tag{53}$$

E. Transformation of the trial vectors

When solving large eigenvalue equations, iterative techniques are required. The key computational step is the linear transformation of a trial vector with the Jacobian matrix. We describe how to perform a linear transformation using an atomic orbital (AO) integral driven approach.

The trial vector in the triplet case is

$$R=\begin{pmatrix} {}^{(3)}R_1 \\ {}^{(+)}R_2 \\ {}^{(-)}R_2 \end{pmatrix}. \tag{54}$$

Here the different parts of the vector contain the independent parameters. The transformed vector can be written

$$\rho=\mathbf{AR}, \tag{55}$$

or in terms of the singles and doubles components,

$$\begin{pmatrix} {}^{(3)}\rho_1 \\ {}^{(+)}\rho_2 \\ {}^{(-)}\rho_2 \end{pmatrix}=\begin{pmatrix} A_{11}\,{}^{(3)}R_1+A_{12}\,{}^{(+)}R_2+A_{13}\,{}^{(-)}R_2 \\ A_{21}\,{}^{(3)}R_1+A_{22}\,{}^{(+)}R_2+A_{23}\,{}^{(-)}R_2 \\ A_{31}\,{}^{(3)}R_1+A_{32}\,{}^{(+)}R_2+A_{33}\,{}^{(-)}R_2 \end{pmatrix}. \tag{56}$$

TABLE I. The linear transformed vector components.

$$\begin{aligned}
{}^{(3)}\rho^{(1)}_{ai} =\ & \Sigma_c\,{}^{(3)}R^c_i\,{}^{(1)}E^{(1)}_{ac}-\Sigma_k\,{}^{(3)}R^a_k\,{}^{(1)}E^{(2)}_{ki}-\Sigma_k\hat{g}_{\bar{a}\bar{k}ki}+2\,\Sigma_{ck}({}^{(+)}R^{ac}_{ik}+{}^{(-)}R^{ac}_{ik})\hat{F}_{kc} \\
& +\Sigma_{ckl}t^{\,ac}_{\,li}\hat{g}_{\bar{l}\bar{k}kc}+2\,\Sigma_{cdk}({}^{(+)}R^{cd}_{ik}+{}^{(-)}R^{cd}_{ik})\hat{g}_{ackd}-2\,\Sigma_{ckl}({}^{(+)}R^{ac}_{kl}+{}^{(-)}R^{ac}_{kl})\hat{g}_{kilc} \\
{}^{(3)}\rho^{(+)}_{aibj} =\ & \tfrac{1}{2}\tilde{P}_{ij}[\Sigma_{\alpha\beta}\Lambda^p_{\alpha a}\Lambda^p_{\beta b}\,{}^{(+)}\tilde{\rho}^{BF}_{\alpha i\beta j}+\Sigma_{kl}t^{\,ab}_{\,kl}\,{}^{(+)}\tilde{\Gamma}_{kilj}+\Sigma_{kl}\,{}^{(+)}R^{ab}_{kl}\,\Gamma_{kilj} \\
& +P^{ab}_{ij}(\Sigma_c\,{}^{(+)}R^{ac}_{ij}\,{}^{(1)}E^{(1)}_{bc}-\Sigma_k\,{}^{(+)}R^{ab}_{ik}\,{}^{(1)}E^{(2)}_{kj}-\Sigma_{ck}t^{\,cb}_{\,ik}\,{}^{(1)}\tilde{C}_{ckaj} \\
& -2\Sigma_{ck}\,{}^{(+)}R^{bc}_{jk}\,{}^{(1)}C_{ckai}+{}^{(3)}\rho^{com}_{aibj})] \\
{}^{(3)}\rho^{(-)}_{aibj} =\ & \tfrac{1}{2}[\Sigma_{\alpha\beta}\Lambda^p_{\alpha a}\Lambda^p_{\beta b}\,{}^{(-)}\tilde{\rho}^{BF}_{\alpha i\beta j}+\Sigma_{kl}t^{\,ab}_{\,kl}\,{}^{(-)}\tilde{\Gamma}_{kilj}-2\Sigma_{kl}\,{}^{(-)}R^{ab}_{kl}\,\Gamma_{kilj} \\
& +\tilde{P}^{ab}_{ij}(-2\Sigma_c\,{}^{(-)}R^{ac}_{ij}\,{}^{(1)}E^{(1)}_{bc}+2\Sigma_k\,{}^{(-)}R^{ab}_{ik}\,{}^{(1)}E^{(2)}_{kj}+\Sigma_{ck}t^{\,cb}_{\,ik}\,{}^{(3)}\tilde{C}_{ckaj} \\
& +2\Sigma_{cl}\,{}^{(-)}R^{cb}_{ik}\,{}^{(1)}C_{ckaj}-2\Sigma_{ck}\,{}^{(-)}R^{bc}_{jk}\,{}^{(1)}C_{ckai}+{}^{(3)}\rho^{com}_{aibj})] \\
{}^{(3)}\rho^{com}_{aibj} =\ & \Sigma_{\alpha\beta}\,\Lambda^p_{\alpha a}\overline{\Lambda}^p_{\beta b}\rho^{BF}_{\alpha i\beta j}-\Sigma_{ck}t^{\,ca}_{\,ik}\,{}^{(3)}\tilde{D}_{ckbj}+\Sigma_c t^{\,ac}_{\,ij}\,{}^{(3)}\tilde{E}^{(1)}_{bc}-\Sigma_k t^{\,ab}_{\,ik}\,{}^{(3)}\tilde{E}^{(2)}_{kj} \\
& +\Sigma_{ck}t^{\,ac}_{\,ik}\,{}^{(1)}\tilde{D}_{ckbj}+2\Sigma_{ck}({}^{(+)}R^{bc}_{jk}+{}^{(-)}R^{bc}_{jk})\,{}^{(3)}D_{ckai}
\end{aligned}$$

Explicit expressions for the transformed vectors are given in Tables I and II. For convenience we have introduced some notational simplifications. We use an over-bar to indicate that the index has been transformed with the ${}^{(3)}R_1$ amplitudes, and have introduced two different intermediates,

$$A^{-}_{pqrs}=-\sum_k\,{}^{(3)}R^p_k A_{kqrs}, \tag{57}$$

$$B^{-}_{pqrs}=\sum_a\,{}^{(3)}R^a_q B_{pars}. \tag{58}$$

Likewise we have introduced the ''barred'' particle and hole matrices,

$$\overline{\Lambda}^p_{\mu r}=-\sum_k\,{}^{(3)}R^r_k\Lambda^p_{\mu k}, \tag{59}$$

$$\overline{\Lambda}^h_{\mu q}=\sum_a\,{}^{(3)}R^a_q\Lambda^h_{\mu a}. \tag{60}$$

III. IMPLEMENTATION

The AO integrals are calculated in distributions with three free and one fixed AO index,

$$I^{\delta}_{\alpha\beta,\gamma}=\hat{g}_{\alpha\beta\gamma\delta}\ \text{with}\ \alpha\geqslant\beta. \tag{61}$$

All distributions with δ belonging to the same shell are calculated simultaneously and then written to disk. The distributions are subsequently read back in one at a time in a loop over the δ index belonging to the shell in question. Inside the

TABLE II. Intermediates in CCSD triplet linear transformation from the right.

Global intermediates	Local intermediates
$\rho^{BF}_{\alpha i\beta j}=\hat{g}_{\alpha i\beta j}+\Sigma_{cd}t^{dc}_{ij}\hat{g}_{\alpha d\beta c}$	${}^{(+)}\tilde{\rho}^{BF}_{\alpha i\beta j}=\hat{g}_{\alpha i\bar{\beta}\bar{j}}+\hat{g}_{\alpha\bar{i}\beta\bar{j}}+\Sigma_{cd}\,{}^{(+)}R^{cd}_{ij}\hat{g}_{\alpha c\beta d}$ ${}^{(-)}\tilde{\rho}^{BF}_{\alpha i\beta j}=\hat{g}_{\alpha i\bar{\beta}\bar{j}}-\hat{g}_{\alpha\bar{i}\beta\bar{j}}-2\Sigma_{cd}\,{}^{(-)}R^{cd}_{ij}\hat{g}_{\alpha c\beta d}$
$\Gamma_{kilj}=\hat{g}_{kilj}+\Sigma_{cd}t^{cd}_{ij}\hat{g}_{kcld}$	${}^{(+)}\tilde{\Gamma}_{kilj}=\hat{g}_{l\bar{j}\bar{k}i}+\hat{g}_{lj\bar{k}\bar{i}}+\Sigma_{cd}\,{}^{(+)}R^{cd}_{ij}\hat{g}_{ldkc}$ ${}^{(-)}\tilde{\Gamma}_{kilj}=\hat{g}_{kil\bar{j}}-\hat{g}_{k\bar{i}lj}-2\Sigma_{cd}\,{}^{(-)}R^{cd}_{ij}\hat{g}_{kcld}$
${}^{(1)}C_{ckaj}=\hat{g}_{kiac}-\Sigma_{dl}t^{ad}_{li}\hat{g}_{lckd}$	${}^{(1)}\tilde{C}_{ckaj}=\hat{g}_{\bar{a}ckj}+\hat{g}_{ack\bar{j}}$ ${}^{(3)}\tilde{C}_{ckaj}=\hat{g}_{\bar{a}ckj}-\hat{g}_{ack\bar{j}}$
${}^{(3)}D_{ckai}=\hat{g}_{aikc}+\Sigma_{dl}t^{ad}_{il}\hat{L}_{kcld}-\Sigma_{dl}t^{da}_{il}\hat{g}_{ldkc}$	${}^{(1)}\tilde{D}_{ckai}=\hat{L}_{\bar{a}ikc}+\hat{L}_{a\bar{i}kc}$ ${}^{(3)}\tilde{D}_{ckai}=\hat{g}_{\bar{a}ikc}+\hat{g}_{a\bar{i}kc}$
${}^{(1)}E^{(1)}_{bc}=\hat{F}_{bc}-\Sigma_{dkl}t^{db}_{kl}\hat{L}_{lckd}$	${}^{(3)}\tilde{E}^{(1)}_{bc}=\hat{F}_{b\bar{c}}-\Sigma_k\hat{g}_{\bar{b}k\bar{k}c}+2\Sigma_{dkl}\,{}^{(-)}R^{db}_{kl}\hat{g}_{lckd}+\Sigma_{dkl}\,2\,{}^{(+)}R^{db}_{kl}\hat{g}_{ldkc}$
${}^{(1)}E^{(2)}_{kj}=\hat{F}_{kj}+\Sigma_{cdl}t^{cd}_{lj}\hat{L}_{lckd}$	${}^{(3)}\tilde{E}^{(2)}_{kj}=\hat{F}_{k\bar{j}}-\Sigma_l\hat{g}_{k\bar{l}\bar{l}j}+2\Sigma_{cdl}\,{}^{(-)}R^{cd}_{jl}\hat{g}_{ldkc}+\Sigma_{cdl}\,2\,{}^{(+)}R^{cd}_{jl}\hat{g}_{kcld}$

δ loop, one integral distribution is kept in core together with two packed result vectors and the two R_2 amplitudes in the squared form as well as some small intermediates. The total memory requirement for the triplet excitation energy calculation is thus of the order of $3V^2O^2+\frac{1}{2}N^3$, where V and O are the number of virtual and occupied orbitals, respectively, and N is the total number of orbitals. For comparison the requirement for the ground state calculation is $\frac{3}{2}V^2O^2+\frac{1}{2}N^3$.

To get an effective algorithm for the calculation of the linear transformed vectors, we have considered the operation count, the vectorization of the code, as well as the memory and scratch-space requirements. The use of global and local intermediates gives a significant reduction in the operation count. The global intermediates do not depend on the trial vector, and are therefore only constructed once. The local intermediates on the other hand depend on the trial vector and are recalculated in each linear transformation. The additional scratch-space requirements from the use of intermediates do not exceed a few times V^2O^2.

For most contributions the implementation follows the outlines described in Refs. 26 and 27, with straightforward generalizations accounting for the antisymmetry of ${}^{(-)}R_{ij}^{ab}$ with respect to permutation of (ai) and (bj). An exception is the BF terms,

$$\rho_{aibj}^{BF\pm}=\frac{1}{2}\sum_{\alpha\beta}\Lambda_{\alpha a}^{p}\Lambda_{\beta b}^{p}\,{}^{(\pm)}\tilde{\rho}_{\alpha i\beta j}^{BF}, \tag{62}$$

where we employ the full symmetry of the ${}^{(\pm)}R_2$ to reduce the operation count. Introducing intermediates similar to those defined in Ref. 26,

$${}^{(P/M)}N_{ci,j}^{\delta}=\sum_{d}\,{}^{(+/-)}R_{ji}^{dc}\Lambda_{\delta d}^{h}, \tag{63}$$

$${}^{(P/M)}M_{\gamma,ij}^{\delta}=\Lambda_{\gamma i}^{h}\overline{\Lambda}_{\delta j}^{h}+\sum_{c}\,({}^{P/M}N_{ci,j}^{\delta}\Lambda_{\gamma c}^{h}), \tag{64}$$

$${}^{(P/M)}M_{\gamma,ij}^{\delta\pm}={}^{(P/M)}M_{\gamma,ij}^{\delta}\pm{}^{(P/M)}M_{\gamma,ji}^{\delta}, \tag{65}$$

$$J_{\alpha\beta,\gamma}^{\delta\pm}=((\alpha\gamma|\beta\delta)\pm(\beta\gamma|\alpha\delta))(1+\delta_{\gamma\delta})^{-1}, \tag{66}$$

the BF terms can be computed as

$${}^{(M)}\Omega_{\alpha\beta,ij}^{B\pm}=\frac{1}{2}\sum_{\gamma\geqslant\delta}J_{\alpha\beta,\gamma}^{\delta\pm}\,{}^{(M)}M_{\gamma,ij}^{\delta\mp}, \tag{67}$$

$$\rho_{aibj}^{BF-}=\sum_{\alpha\beta}\,({}^{(M)}\Omega_{\alpha\beta,ij}^{B+}+{}^{(M)}\Omega_{\alpha\beta,ij}^{B-})\Lambda_{\alpha a}^{p}\Lambda_{\beta b}^{p}, \tag{68}$$

and

$${}^{(P)}\Omega_{\alpha\beta,ij}^{B-}=\frac{1}{2}\sum_{\gamma\geqslant\delta}J_{\alpha\beta,\gamma}^{\delta-}\,{}^{(P)}M_{\gamma,ij}^{\delta-}, \tag{69}$$

$$\rho_{aibj}^{BF+}=\tilde{P}_{ij}\sum_{\alpha\beta}\,{}^{(P)}\Omega_{\alpha\beta,ij}^{B-}\Lambda_{\alpha a}^{p}\Lambda_{\beta b}^{p}. \tag{70}$$

For the last equation we have used that the ${}^{(+)}R_2$ coefficients are antisymmetric with respect to interchange of two occupied indices, and thus ${}^{(P)}M_{\gamma,ij}^{\delta+}=0$.

The Γ intermediates can be calculated from the BF intermediates as in Ref. 27, where an outline of the algorithm for calculating the integral-direct triplet excitation energies also can be found. It should be noted that the terms $\Sigma_{\alpha\beta}\Lambda_{\alpha a}^{p}\overline{\Lambda}_{\beta b}^{p}\rho_{\alpha i\beta j}^{BF}$, $\Sigma_{ck}t_{ik}^{ca}\,{}^{(3)}\tilde{D}_{ckbj}$, $\Sigma_{c}t_{ij}^{ac}\,{}^{(3)}\tilde{E}_{bc}^{(1)}$, $\Sigma_{k}t_{ik}^{ab}\,{}^{(3)}\tilde{E}_{kj}^{(2)}$, $\Sigma_{ck}t_{ik}^{ac}\,{}^{(1)}\tilde{D}_{ckbj}$, and $\Sigma_{ck}({}^{(+)}R_{jk}^{bc}+{}^{(-)}R_{jk}^{bc})\,{}^{(3)}D_{ckai}$ occur both in the calculation of ${}^{(+)}\rho_{\mathrm{Trans}}$ and ${}^{(-)}\rho_{\mathrm{Trans}}$. These terms are only calculated once and then added to either ${}^{(+)}\rho_{\mathrm{Trans}}$ or ${}^{(-)}\rho_{\mathrm{Trans}}$. The only difference is due to the different permutation symmetries.

TABLE III. Operation counts of the singlet and triplet excitation energy implementations. The nomenclature refers to Tables II and III in Ref. 27 and the corresponding triplet terms. The intermediates are restricted to have a maximum size of the order N^2O^2.

Term	Singlet	Triplet
Γ intermediate	$NO^3(N+O)$	$2NO^3(N+O)$
A terms	V^2O^4	$2V^2O^4$
BF terms	$1/4N^4O^2+4N^3O^2$	$3/8N^4O^2+6N^3O^2$
C terms	$2V^3O^3$	$5V^3O^3$
D terms	$2V^3O^3$	$3V^3O^3$
E terms	N^2VO^2	$2N^2VO^2$
G terms	$N^3O^2+N^2VO$	$2N^3O^2+N^2VO$
H terms	NVO^3	$2NVO^3$
I terms	V^2O^2	...
J terms	VO	...
Sum	$1/4N^4O^2+4V^3O^3+V^2O^4$	$3/8N^4O^2+8V^3O^3+2V^2O^4$

In Table III the operation count is listed term by term. Furthermore the operation count for the implementation of the singlet excitation energy is given. The scaling of the triplet implementation is between 1.5 and 2 of the corresponding singlet implementation. However the number of singlet and triplet double excitation coefficients are not equal. For four different indices we have 50% more parameters in the triplet case.

IV. BENZENE TRIPLET EXCITED STATES

In this section we report calculations of the lowest triplet excitation energies of benzene using the CC2 (Ref. 31) and the CCSD model. We use the same geometry as in older CASPT2 (Ref. 32) and SOPPA (Ref. 33) calculations. To understand the excitation spectrum recall that a Hückel π electron calculation gives the molecular orbitals $1a_{2u}$, $1e_{1g}$, $1e_{2u}$, and $1b_{2g}$ and the π electron ground state configuration $1a_{2u}^2 1e_{1g}^4$. The excitation spectrum contains valence π electron states originating from the configurations $1a_{2u}^2 1e_{1g}^3 1e_{2u}^1({}^{1,3}E_{1u},{}^{1,3}B_{1u},{}^{1,3}B_{2u})$ and $1a_{2u}^1 1e_{1g}^4 1e_{2u}^1({}^{1,3}E_{2g})$. The excitation spectrum also contains Rydberg excitations. We consider here only the $n=3$ Rydberg series representing excitations out of the $1e_{1g}$ orbital. The excitation $(e_{1g}\rightarrow 3p_0,3d_1)$ are classified as Rydberg $\pi\pi^*$ excitations while excitations of the type $(e_{1g}\rightarrow 3s,3p_1,3d_2,3d_0)$ are classified as Rydberg $\pi\sigma^*$ excitations.

To give a proper description of the Rydberg states the standard aug-cc-pVDZ and aug-cc-pVTZ basis sets have been augmented with two diffuse functions centered at the center-of-mass (CM). The saturation of diffuse CM functions at the aug-cc-pVDZ level has previously been investigated.[34,31] We denote the basis sets used aug-cc-pVDZ-CM2 and aug-cc-pVTZ-CM2, undestanding that two

TABLE IV. C_6H_6 Coupled Cluster triplet excitation energies.

One electron basis:	ANO1			aug-pVDZ-CM2			aug-pVTZ-CM2			
CC Model:	CCS	CC2	CCSD	CCS	CC2	CCSD	CCS	CC2	CCSD	$\%T_1$
Valence $^3\pi\pi^*$										
$1\,^3B_{1u}$	3.363	4.328	3.961	3.394	4.350	3.999	3.385	4.345	3.974	98.9
$1\,^3E_{1u}$	4.878	5.079	4.920	4.893	5.083	4.930	4.881	5.058	4.903	97.9
$1\,^3B_{2u}$	5.490	5.932	5.840	5.470	5.906	5.808	5.449	5.873	5.755	98.5
$1\,^3E_{2g}$	7.596	7.637	7.712	7.605	7.628	7.727	7.595	7.782	7.719	97.9
Rydberg $^3\pi\pi^*$										
$2\,^3E_{1u}$	7.118	7.044	7.182	7.124	7.029	7.171	7.117	7.178	7.287	98.4
$1\,^3A_{1g}$	7.652	7.601	7.782	7.659	7.591	7.775	7.655	7.750	7.897	98.5
$2\,^3E_{2g}$	7.927	7.993	7.875	7.907	7.991	7.872	7.906	7.965	7.979	98.3
$1\,^3A_{2g}$	7.856	7.684	7.880	7.605	7.670	7.879	7.872	7.833	8.009	98.4
Rydberg $^3\pi\sigma^*$										
$1\,^3E_{1g}$	6.535	6.370	6.501	6.430	6.275	6.385	6.437	6.416	6.510	98.4
$1\,^3A_{2u}$	6.847	6.789	6.923	6.837	6.761	6.895	6.849	6.921	7.023	98.5
$1\,^3E_{2u}$	7.092	6.882	7.041	7.089	6.857	7.019	7.101	7.018	7.152	98.3
$1\,^3A_{1u}$	7.286	6.969	7.145	7.295	6.950	7.132	7.308	7.111	7.268	98.2
$2\,^3E_{1g}$	7.534	7.439	7.607	7.480	7.391	7.530	7.444	7.508	7.595	98.4
$1\,^3B_{2g}$	7.656	7.444	7.631	7.649	7.409	7.591	7.662	7.572	7.724	98.3
$1\,^3B_{1g}$	7.691	7.461	7.657	7.681	7.426	7.615	7.692	7.588	7.748	98.3
$3\,^3E_{1g}$	7.708	7.499	7.678	7.700	7.456	7.631	7.707	7.599	7.754	98.3

diffuse center-of-mass functions have been added. Calculations have also been carried out with the ANO basis supplemented with an optimized diffuse Rydberg CM function. This basis is here referred to as the ANO1 basis.[32]

Triplet excitation energies obtained at the CCS [for the triplet excitation energies, this is equivalent to the configuration interaction singles (CIS) also known as the Tamm Dancoff approximation (TDA)], CC2, and CCSD level with the aug-cc-pVDZ-CM2, aug-cc-pVTZ-CM2, and ANO1 basis sets are given in Table IV. Comparing the results in Table IV the change from aug-cc-pVDZ-CM2 to aug-cc-pVTZ-CM2 for the valence states range from -0.05–-0.01 eV excluding the $1\,^3E_{2g}$ state at the CC2 level which increases by 0.15 eV. The Rydberg excitations are increased in CCSD by about 0.12 eV. Comparing the triplet excitation energies for the CCS, CC2, and the CCSD model it is seen that for all three basis sets the CC2 valence excitation energies are in general closer to the CCSD excitation energies than are the corresponding CCS excitation energies. On the contrary for the Rydberg excitations in general the CCS excitation energies are closer to the CCSD excitation energies. The CCS model thus gives a reasonable description for the Rydberg states and here CC2 does not lead to any improvement due to an overestimation of the double contribution. The above findings are in accordance with previous observations for singlet excitation energies.[27,34]

In Table V triplet excitation energies are given for different methods and using the ANO1 basis. The same geometry was used in all the calculations. If we compare the SOPPA (the second-order polarization propagator approach), CC2, and CASPT2 results in Table V with the CCSD results, we observe a different behavior for the valence and the Rydberg excitations and these are therefore discussed separately. For the valence states the difference between the CCSD results and the results obtained using the second-order models are CASPT2: -0.6–-0.1 eV, SOPPA: -0.4–-0.2 eV, and CC2: -0.1–$+0.4$ eV. For the Rydberg states the corresponding differences are CASPT2: -0.2–-0.1 eV, SOPPA: -0.4–-0.2 eV, and -0.2–-0.1 eV for CC2 except for the $2\,^3E_g$ that has a large valence contribution in CC2. The different second-order methods thus give rather different results and all differ significantly from the CCSD results.

For comparison we have in Table VI given the CCSD/aug-cc-pVTZ-CM2 singlet and triplet excitation energies together with the experimental excitation energies. As discussed previously the aug-cc-pVTZ-CM2 basis set may be expected to give results close to the basis set limit. From the percent single excitation contribution $\%T_1$ in the excitation vectors it is seen that the triplet excitations are more dominated by single excitation contributions than the corresponding singlet excitation. For the singlet valence states $\%T_1$ is 85%–95% while it is 98%–99% for the valence triplet state. For the singlet Rydberg states $\%T_1$ is 95%–96% while it is 98%–99% for the triplet Rydberg states. The larger $\%T_1$ in the triplet excitations means that we may expect smaller correlation errors in the CCSD triplet excitation energies than in the corresponding singlet excitation energies.

For the singlet valence states the magnitude of the contribution from triple excitations depends significantly on the considered state. For example in CC3 calculations on the valence singlet excitation energies the triple excitation contribution to the $1\,^1B_{2u}$ state was -0.11 eV while it was -0.765 eV for the valence state $2\,^1E_{2g}$. It is therefore difficult to estimate the correlation error in the CCSD valence triplet excitation energies based on a comparison with trends in the singlet spectrum. However we note that the correlation error for the triplet excitations may be expected to be smaller than for the corresponding singlet excitations.[35]

The Rydberg singlet and triplet states originate from different spin couplings of the molecular cation and the electron in the Rydberg orbital. The singlet and triplet Rydberg exci-

TABLE V. Triplet excitation energies for benzene in the ANO1 basis set.

State	CASSCF Ref. 32	CASPT2 Ref. 32	RPA Ref. 33	SOPPA Ref. 33	CCS	CC2	CCSD	CCSD $\%T_1$	Expt.
					This work				
Valence $^3\pi\pi^*$									
$1\ ^3B_{1u}$	4.05	3.89	Instability	3.75	3.363	4.328	3.962	98.9	3.94[a]
$1\ ^3E_{1u}$	5.07	4.49	4.70	4.48	4.878	5.079	4.920	97.9	4.76[a]
$1\ ^3B_{2u}$	6.93	5.49	5.07	5.50	5.490	5.932	5.840	98.5	5.60[a]
$1\ ^3E_{2g}$	7.61	7.12	7.24	7.41	7.596	7.638	7.712	97.9	7.24–7.74[b]
Rydberg $^3\pi\pi^*$									
$2\ ^3E_{1u}$	6.92	6.98	7.11	6.92	7.118	7.044	7.182	98.4	
$1\ ^3A_{1g}$	7.42	7.62	7.64	7.50	7.652	7.601	7.782	98.5	
$2\ ^3E_{2g}$	7.44	7.55	7.85	7.57	7.927	7.993	7.875	98.1	
$1\ ^3A_{2g}$	7.50	7.70	7.85	7.59	7.856	7.685	7.880	98.3	
Rydberg $^3\pi\sigma^*$									
$1\ ^3E_{1g}$	6.22	6.34	6.44	6.14	6.535	6.370	6.501	98.3	
$1\ ^3A_{2u}$	6.61	6.80	6.82	6.64	6.847	6.789	6.923	98.5	
$1\ ^3E_{2u}$	6.73	6.90	7.08	6.74	7.092	6.882	7.041	98.3	
$1\ ^3A_{1u}$	6.83	7.00	7.28	6.84	7.286	6.969	7.145	98.2	
$2\ ^3E_{1g}$	7.31	7.57	7.51	7.32	7.534	7.439	7.607	98.4	
$1\ ^3B_{2g}$	7.27	7.53	7.65	7.33	7.656	7.444	7.632	98.3	
$1\ ^3B_{1g}$	7.27	7.53	7.69	7.35	7.690	7.461	7.657	98.3	
$3\ ^3E_{1g}$	7.36	7.56	7.71	7.38	7.708	7.499	7.678	98.4	

[a]Reference 36.
[b]Reference 32.

TABLE VI. C_6H_6 CCSD singlet and triplet excitation energies in the aug-pVTZ-CM2 basis set.

Spin	Singlet CCSD	Singlet Exp. (Origin)	Singlet $\%T_1$	Triplet CCSD	Triplet Exp.	Triplet $\%T_1$
Valence $\pi\pi^*$						
$1\ B_{1u}(e_{1g}\rightarrow e_{2u})$	6.481	6.0348[a]	95	3.974	3.95[b]	99
$1\ E_{1u}(e_{1g}\rightarrow e_{2u})$	7.227	6.8656[a]	95	4.903	4.75[b]	98
$1\ B_{2u}(e_{1g}\rightarrow e_{2u})$	5.180	4.7873,[a] 4.790[c]	91	5.755	5.60[b]	99
E_{2g}[d]	9.168	7.805[e]	87	7.719	7.24–7.74[f]	98
Rydberg $\pi\pi^*$						
$2\ E_{1u}(e_{1g}\rightarrow 3p_0)$	7.501	7.413[g]	95	7.287	(7.20)[h]	98
A_{1g}[i]	7.984	7.807,[e] 7.808,[j] 7,819[k]	96	7.897	(7.72)[h]	99
E_{2g}[l]	7.972	⋯	95	7.979	⋯	98
$1\ A_{2g}(e_{1g}\rightarrow 3d_1)$	8.009	⋯	95	8.009	⋯	98
Rydberg $\pi\sigma^*$						
$1\ E_{1g}(e_{1g}\rightarrow 3s)$	6.563	6.334[m]	95	6.510	(6.28)[h]	98
$1\ A_{2u}(e_{1g}\rightarrow 3p_1)$	7.092	6.932,[n] 6.928[a,g]	95	7.023	(6.86)[h]	99
$1\ E_{2u}(e_{1g}\rightarrow 3p_1)$	7.169	6.953[n]	95	7.152	(6.94)[h]	98
$1\ A_{1u}(e_{1g}\rightarrow 3p_1)$	7.262	⋯	96	7.268	⋯	98
$2\ E_{1g}(e_{1g}\rightarrow 3d_0)$	7.671	7.535,[e] 7.540[j]	95	7.595	(7.46)[h]	98
$1\ B_{2g}(e_{1g}\rightarrow 3d_2)$	7.760	⋯	95	7.724	⋯	98
$1\ B_{1g}(e_{1g}\rightarrow 3d_2)$	7.751	⋯	95	7.748	⋯	98
$3\ E_{1g}(e_{1g}\rightarrow 3d_2)$	7.772	⋯	95	7.754	⋯	98

[a]Reference 44.
[b]Reference 36.
[c]Reference 38.
[d]$2\ ^1E_{1g}(a_{2u}\rightarrow e_{2u})$ and $1\ ^3E_{1g}(a_{2u}\rightarrow e_{2u})$.
[e]Reference 41.
[f]Reference 32.
[g]Reference 37.
[h]See text.
[i]$2\ ^1A_{1g}(e_{1g}\rightarrow 3d_1)$ and $1\ ^3A_{1g}(e_{1g}\rightarrow 3d_1)$.
[j]Reference 43.
[k]Reference 42.
[l]$1\ ^1E_{1g}(e_{1g}\rightarrow 3d_1)$ and $2\ ^3E_{1g}(e_{1g}\rightarrow 3d_1)$.
[m]Reference 39.
[n]Reference 40.

tation energies will therefore approach each other for the higher Rydberg states where the interaction with the other states becomes vanishing. This is confirmed by the results in Table VI, where for example the CCSD excitation energies to the $\pi\sigma^*$ singlet and triplet Rydberg state are 6.563 and 6.510 eV, respectively, for the $1\,E_{1g}$ state while it is 7.772 and 7.754 for the $3\,E_{1g}$ state. As expected the triplet Rydberg excitation energies are a little smaller than the corresponding singlet Rydberg excitation energies. For the singlet Rydberg excitations the triples contribution is small. For example in the CC3 calculations on the Rydberg singlet excitation energies for benzene the triples contribution was less than one-hundreth of an eV. The triplet Rydberg excitations may therefore be expected also to have small triple contributions and the vertical CCSD/aug-cc-pVTZ-CM2 may therefore be expected to be rather accurate.

The vertical CCSD/aug-cc-pVTZ-CM2 singlet Rydberg excitation energies were in Ref. 27 between 0.09 and 0.23 eV higher than the experimental Rydberg excitation energies, mainly due to the fact that geometry relaxation and zero-point vibrational effects were neglected. Due to the similarity between singlet and triplet Rydberg states we may estimate experimental triplet Rydberg excitation energies by subtracting from the CCSD/aug-cc-pVTZ-CM2 triplet vertical excitation energies the difference between the vertical singlet CCSD/aug-cc-pVTZ-CM2 excitation energy and the singlet experimental Rydberg excitation energy. For example the estimate for the $\pi\sigma^*$ $1\,^3E_{2u}$ experimental Rydberg excitation energy becomes 7.152 eV–(7.169 eV–6.953 eV) $\approx$6.93 eV. The estimated ''experimental'' Rydberg triplet excitation energies are given in parantheses in Table VI. No experimental triplet Rydberg excitation energies have so far been reported.

V. CONCLUSION

In this work we have presented an implementation of CCSD triplet excitation energies using an explicit spin-coupled triplet space. The implementation is integral-direct and the cost for one linear transformation for the triplet excitation energies is about two times the cost for one linear transformation for the singlet case.

The triplet spectrum has been calculated for benzene using basis sets of both augmented double zeta and triple zeta quality and with different sets of diffuse CM functions. We have found that the triplet excitation energies are more single excitation dominated than the corresponding singlet excitation energies and the CCSD triplet excitation energies may therefore be expected to have smaller correlation errors than the corresponding singlet excitation energies. From a comparison with the singlet spectrum we have estimated the correlation error for the CCSD triplet vertical valence excitation energies still to be considerabe while the CCSD triplet vertical Rydberg excitation energies may be expected to have very small correlation errors. We have also estimated experimental triplet Rydberg excitation energies based on a comparison with the singlet spectrum. In general we have found that the triplet excitation energies are more single excitation dominated than the corresponding singlet excitation energies.

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