First-order properties for triplet excited states in the approximated coupled cluster model CC2 using an explicitly spin coupled basis

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An implementation is reported for first-order properties of excited triplet states within the approximate coupled cluster model CC2 using an explicitly spin coupled basis for the triplet excitation manifold and the resolution of the identity (RI) approximation for the electron repulsion integrals. Results are presented for the change of the second moment of charge upon excitation in the $\pi\pi^*$ valence and $n=3$ Rydberg states of benzene. Employing large basis sets with up to 828 functions, we obtain results close to the CC2 basis set limit and are able to resolve an uncertainty in the assignment of the lowest $^1E_{1u}$ states. It is found that the often used $\%T_1$ measure for the single excitation contribution to excited states is not reliable for a comparison across different excitation operator manifolds. An alternative diagnostic is proposed which provides a unique measure for the single excitation contribution that is independent of the chosen representation of the excitation operator manifold. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1457434]

I. INTRODUCTION

Coupled cluster response theory has during the last decade developed to the most efficient black box approach for the calculation of accurate excitation energies. It has been implemented for a wide variety of models ranging from CCS, which is equivalent to CIS, to CCSD (Refs. 1, 2) and several models that include also the effect of connected triples either iteratively[3] or by perturbation theory.[4] Recently Hald *et al.* have implemented the models CC2,[5] CCSD,[6] and CC3 (Ref. 7) for triplet excitation energies using an explicitly spin coupled basis for the excitation operators and the corresponding projection manifold. This has lead to a reduction of the computational requirements of about an order of magnitude compared to a spin orbital based formulation. While the use of an explicitly spin coupled basis has been standard for the singlet excitation manifold for many years and is employed in several program packages[8–10] not only for the calculation of excitation energies and transition moments, but also for numerous kinds of derivatives and linear and nonlinear response properties, there have been only few implementations[5–7,11] of electron correlated *ab initio* methods, where an explicitly spin coupled basis has been used for the triplet excitation manifold.

In the present communication we extend the work of Ref. 5 to first-order properties of excited triplet states at the approximate coupled cluster singles and doubles (CC2) level.[12] First-order properties—or expectation values—are an important tool for the characterization and the assignment of excited states. For example, the change of the second moment of charge upon excitation allows to distinguish between valence states and Rydberg states with different main quantum numbers n. Similar, the change of the dipole moment can be used to identify charge transfer excitations in polar molecules. We also note that in coupled cluster response theory the expressions for excited states first-order properties—i.e., for the one-electron density matrices of excited states—are closely related to the expressions for transition moments between two excited states, which require instead the transition density matrices. Thus, the present developments can with minor effort be extended to the calculation of transition moments between two excited triplet states.

The theory derived in Sec. II has been implemented in the RICC2 module[13] of the TURBOMOLE program package,[14] which employs the resolution of the identity (RI) approximation for the electron repulsion integrals.[15] The latter approximation leads again to a dramatic reduction in the computational requirements, and allows us to perform CC2 calculations on much larger molecules or with much larger basis sets than can be done with conventional (integral-direct) implementations. In Sec. III we present for the excited $\pi\pi^*$ valence and $n=3$ Rydberg states of benzene results for the changes of the second moment of charge close to the CC2 basis set limit, employing basis sets with up to 828 functions. For the triplet states these are the first calculations of this property at a level that accounts for dynamic electron correlation. The results allow us to clarify some doubts that have been put forward recently[16] about the assignments of the lowest states with $^1E_{1u}$ symmetry and to correct the assignment of the lowest $^3E_{2g}$ states in recent CC2 calculations.[5,6]

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II. EXCITED TRIPLET STATES IN THE CC2 MODEL

The calculation of triplet excitation energies within the CC2, CCSD, and CC3 models has been described in detail in a series of previous papers by Hald *et al.*[5–7] Therefore, we will here only give a short review of the basic equations.

A convenient basis for the triplet single and double excitation manifold is obtained by the excitation operators,

$$^{(3)}\tau_{ai} = T_{ai}, \tag{1}$$

$$^{(+)}\tau_{aibj} = T_{ai}E_{bj} + T_{bj}E_{ai}, \quad \forall a>b, \ i>j, \tag{2}$$

$$^{(-)}\tau_{aibj} = T_{ai}E_{bj} - T_{bj}E_{ai}, \quad \forall (ai)>(bj), \tag{3}$$

with the second-quantization operators,

$$E_{pq} = a^{\dagger}_{p\alpha}a_{q\alpha} + a^{\dagger}_{p\beta}a_{q\beta}, \tag{4}$$

$$T_{pq} = a^{\dagger}_{p\alpha}a_{q\alpha} - a^{\dagger}_{p\beta}a_{q\beta}. \tag{5}$$

Here and in the following *i, j, k, l* and *a, b, c, d* label, respectively, occupied and unoccupied spatial molecular orbitals. The indices *p, q, r, s* are used for general orbitals and α and β for the spin functions with $m_s = +1/2$ and $-1/2$. The triplet configuration state functions $|\mu\rangle = \tau_\mu|\mathrm{HF}\rangle$ form together with the projection manifold

$$\langle {}^{a}_{i}(3)| = \tfrac{1}{2}\langle \mathrm{HF}|^{(3)}\tau^{\dagger}_{ai}, \tag{6}$$

$$\langle {}^{ab}_{ij}(+)| = \tfrac{1}{8}\langle \mathrm{HF}|^{(+)}\tau^{\dagger}_{aibj}, \tag{7}$$

$$\langle {}^{ab}_{ij}(-)| = \tfrac{1}{8}\langle \mathrm{HF}|^{(-)}\tau^{\dagger}_{aibj}, \tag{8}$$

an orthonormal basis. Within the CC2 model the doubles–doubles block of the Jacobian matrix is diagonal. Thus the CC2 eigenvalue problem,

$$\begin{pmatrix} \mathbf{A}_{\mu_1\nu_1} & \mathbf{A}_{\mu_1\nu_2} \\ \mathbf{A}_{\mu_2\nu_1} & \delta_{\mu_2\nu_2}\epsilon_{\mu_2} \end{pmatrix} \begin{pmatrix} E_{\nu_1}(\omega) \\ E_{\nu_2}(\omega) \end{pmatrix} = \omega \begin{pmatrix} E_{\mu_1}(\omega) \\ E_{\mu_2}(\omega) \end{pmatrix}, \tag{9}$$

with $\epsilon_{aibj} = \epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j$, can be partitioned into a nonlinear eigenvalue problem for only the single excitation part of the eigenvector,

$$\left[\mathbf{A}_{\mu_1\nu_1} - \sum_{\gamma_2} \frac{\mathbf{A}_{\mu_1\gamma_2}\mathbf{A}_{\gamma_2\nu_1}}{\epsilon_{\gamma_2} - \omega}\right] E_{\nu_1}(\omega)$$
$$= \mathbf{A}^{\mathrm{eff}}_{\mu_1\nu_1}(\omega)E_{\nu_1}(\omega)$$
$$= \omega E_{\mu_1}(\omega), \tag{10}$$

and a linear equation which gives the double excitation part of the eigenvectors in terms of the single excitation part,

$$E_{\mu_2}(\omega) = -\frac{\Sigma_{\nu_1}\mathbf{A}_{\mu_2\nu_1}E_{\nu_1}(\omega)}{\epsilon_{\mu_2} - \omega}. \tag{11}$$

The advantage of solving the nonlinear eigenvalue problem in Eq. (10) instead of the linear eigenvalue problem in Eq. (9) is that it does not require storage of double excitation trial or eigenvectors on file. This reduces the disk space required for the vectors from $\mathcal{O}(n^2N^2)$ to $\mathcal{O}(nN)$, where *n* and *N* is the number of electrons and basis functions, respectively.

Solution of the CC2 eigenvalue problem with iterative techniques requires the linear transformation of trial vectors with the Jacobian. In coupled cluster theory the Jacobian is not symmetric and right and left eigenvectors are in general different. Thus, if one wants to compute not only excitation energies but also excited state properties, both the multiplication of the Jacobian matrix with a trial vector from the right as well as the multiplication with a trial vector from the left must be implemented. The left eigenvectors $\overline{E}_\mu$ fulfill the equations,

$$\overline{E}_{\mu_1}(-\omega)\left[\mathbf{A}_{\mu_1\nu_1} - \sum_{\gamma_2} \frac{\mathbf{A}_{\mu_1\gamma_2}\mathbf{A}_{\gamma_2\nu_1}}{\epsilon_{\gamma_2} - \omega}\right]$$
$$= \overline{E}_{\mu_1}(-\omega)\mathbf{A}^{\mathrm{eff}}_{\mu_1\nu_1}(\omega)$$
$$= \omega\overline{E}_{\nu_1}(-\omega), \tag{12}$$

$$\overline{E}_{\nu_2}(-\omega) = -\frac{\Sigma_{\mu_1}\overline{E}_{\mu_1}(-\omega)\mathbf{A}_{\mu_1\nu_2}}{\epsilon_{\nu_2} - \omega}. \tag{13}$$

Note, that right eigenvectors E_μ are associated with plus the eigenvalue as frequency, while left eigenvectors $\overline{E}_\mu$ are associated with minus the eigenvalue as frequency.[17] Explicit expressions for a vector obtained by multiplying the Jacobian with a triplet trial vector from the right have been derived in Refs. 5 and 6. To obtain concise expressions we define the modified AO to MO transformation matrices,

$$\Lambda^p = \mathbf{C}[\mathbf{1} - \mathbf{t}^T_{\mu_1}], \tag{14}$$

$$\Lambda^h = \mathbf{C}[\mathbf{1} + \mathbf{t}_{\mu_1}], \tag{15}$$

the integrals in the Λ^p, Λ^h-basis,

$$(pq\hat{|}rs) = \sum_{\mu\nu\kappa\lambda} \Lambda^p_{\mu p}\Lambda^h_{\nu q}\Lambda^p_{\kappa r}\Lambda^h_{\lambda s}(\mu\nu|\kappa\lambda) \tag{16}$$

and the inactive Fock matrix

$$\hat{F}_{pq} = \sum_{pq} \Lambda^p_{\mu p}\Lambda^h_{\nu q}F_{\mu\nu} + \sum_{ck} [2(pq\hat{|}ck) - (pk\hat{|}cq)]t_{ck}, \tag{17}$$

where t_{μ_1} are the ground-state single excitation cluster amplitudes. The transformed vector obtained by multiplying a trial vector $R_{\nu_1}(\omega)$ onto the Jacobian from the right,

$$\rho^R_{\mu_1}(\omega) = \mathbf{A}^{\mathrm{eff}}_{\mu_1\nu_1}(\omega)R_{\nu_1}(\omega), \tag{18}$$

can then be expressed in the compact form given in Table I. The doubles excitation part of the trial vectors is thereby generated on the fly from one-index transformed MO integrals as

$$^{(+)}R^{ab}_{ij} = \frac{1}{2}\frac{(\overline{ai}|bj) + (\overline{bj}|ai) - (\overline{aj}|bi) - (\overline{bi}|aj)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b + \omega}, \tag{19}$$

$$^{(-)}R^{ab}_{ij} = \frac{1}{2}\frac{(\overline{bj}|ai) - (\overline{ai}|bj)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b + \omega}, \tag{20}$$

$$R^{ab}_{ij} = 2(^{(+)}R^{ab}_{ij} + {}^{(-)}R^{ab}_{ij}), \tag{21}$$

with

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TABLE I. Explicit expressions for vectors transformed with the effective Jacobian either from the left or from the right and for effective right hand side vectors derived from $L\mathbf{B}R$ like contractions. All three types of vectors can be split into six contributions, $\rho_S=\rho_S^1+\rho_S^2+\rho_S^3+\rho_S^4+\rho_S^5+\rho_S^6$, which involve the same contractions for all vectors.

$\rho_S(\omega)$	$\mathbf{A}_{SS}^{(\mathrm{eff})}(\omega)R_S(\omega)$	$L_S(\omega)\mathbf{A}_{SS}^{(\mathrm{eff})}(-\omega)$	$(L\mathbf{B}R)_S-\Sigma_D\frac{(L\mathbf{B}R)_D\mathbf{A}_{DS}}{\epsilon_D+\omega_L-\omega_R}$
ρ_{ai}^1	$+\Sigma_d E_{ad}R_{di}$	$+\Sigma_d E_{da}L_{di}$	$+\Sigma_d \overline{E}_{da}L_{di}$
ρ_{ai}^2	$-\Sigma_l R_{al}E_{li}$	$-\Sigma_l L_{al}E_{il}$	$-\Sigma_l L_{al}\overline{E}_{il}$
ρ_{ai}^3	$-\Sigma_{ck}(ki\hat{\vert}ac)R_{ck}$	$-\Sigma_{ck}L_{ck}(ik\hat{\vert}ca)$	$+\Sigma_{ck}L_{ck}[2(\overline{ck}\vert ia)-(\overline{ik}\vert ca)-(ik\vert\overline{ca})]$
ρ_{ai}^4	$+\Sigma_{dlc}R_{il}^{cd}(ld\hat{\vert}ac)$	$+\Sigma_{dlc}L_{il}^{cd}(dl\hat{\vert}ca)$	$+\Sigma_{dlc}F_{il}^{cd}(l\overline{d}\hat{\vert}ca)$ $+\Sigma_{dlc}L_{il}^{cd}[(\overline{dl}\vert ca)+(dl\vert\overline{ca})]$
ρ_{ai}^5	$-\Sigma_{dlk}R_{kl}^{ad}(ld\hat{\vert}ki)$	$-\Sigma_{dlk}L_{kl}^{ad}(dl\hat{\vert}ik)$	$-\Sigma_{dlk}F_{kl}^{ad}(l\overline{d}\hat{\vert}ik)$ $-\Sigma_{dlk}L_{kl}^{ad}[(\overline{dl}\vert ik)+(dl\vert\overline{ik})]$
ρ_{ai}^6	$\Sigma_{ck}(R_{ik}^{ac}\hat{F}_{kc}-t_{ki}^{ac}\overline{F}_{kc})$	$-\Sigma_{ck}(ic\vert ka)C_{ck}$	$\Sigma_{ck}[2(kc\vert ia)-(ic\vert ka)]\overline{C}_{ck}$
	$\overline{F}_{kc}=-\Sigma_{dl}(kd\vert lc)R_{dl}$ $E_{ab}=\hat{F}_{ab}-\Sigma_{dkl}(2t_{kl}^{ad}-t_{lk}^{ad})(ld\vert kb)$ $E_{ji}=\hat{F}_{ji}+\Sigma_{cdk}(2t_{ik}^{cd}-t_{ki}^{cd})(kd\vert jc)$	$C_{ck}=-\Sigma_{dl}t_{kl}^{dc}L_{dfl}$	$\overline{C}_{ck}=+\Sigma_{dl}R_{lk}^{dc}L_{dl}$ $\overline{E}_{ab}=\overline{F}_{ab}-\Sigma_{dkl}R_{kl}^{ad}(ld\vert kb)$ $\overline{E}_{ji}=\overline{F}_{ji}+\Sigma_{cdk}R_{ik}^{cd}(kd\vert jc)$

$$(\overline{pq}|rs)=\sum_{\mu\nu\kappa\lambda}[\overline{\Lambda}_{\mu p}^{p}\Lambda_{\nu q}^{h}+\Lambda_{\mu p}^{p}\overline{\Lambda}_{\nu q}^{h}]\Lambda_{\kappa r}^{p}\Lambda_{\lambda s}^{h}(\mu\nu|\kappa\lambda), \tag{22}$$

$$\overline{\Lambda}^{p}=-\mathbf{C}\mathbf{R}_{\mu_1}^{T}, \tag{23}$$

$$\overline{\Lambda}^{h}=\mathbf{C}\mathbf{R}_{\mu_1}. \tag{24}$$

The multiplication of the effective Jacobian with a trial vector $L_{\nu_1}(\omega)$ from the left

$$\rho_{\mu_1}^{L}(\omega)=L_{\nu_1}(\omega)\mathbf{A}_{\mu_1\nu_1}^{(\mathrm{eff})}(-\omega) \tag{25}$$

can be cast into a similar form, which involves the same types of one-, two-, and three-index contractions. Note the different sign of the frequency argument for trial vector and effective Jacobian. The explicit expressions are given in Table I. Again, the double excitation part of the trial vectors—or, after solution of the eigenvalue problem, the double excitation part of the eigenvectors—can be generated on the fly from one-index transformed MO integrals,

$${}^{(+)}L_{ij}^{ab}=\frac{1}{2}\frac{(\widetilde{ai}|bj)+(\widetilde{bj}|ai)-(\widetilde{aj}|bi)-(\widetilde{bi}|aj)}{\epsilon_i-\epsilon_a+\epsilon_j-\epsilon_b-\omega}, \tag{26}$$

$${}^{(-)}L_{ij}^{ab}=\frac{1}{2}\frac{(\widetilde{bj}|ai)-(\widetilde{ai}|bj)}{\epsilon_i-\epsilon_a+\epsilon_j-\epsilon_b-\omega}, \tag{27}$$

$$L_{ij}^{ab}=2({}^{(+)}L_{ij}^{ab}+{}^{(-)}L_{ij}^{ab}), \tag{28}$$

with

$$(\widetilde{ai}|bj)=L_{ai}\hat{F}_{jb}+\sum_{\mu\nu\kappa\lambda}[\tilde{\Lambda}_{\mu a}^{p}\Lambda_{\nu i}^{h}+\Lambda_{\mu a}^{p}\tilde{\Lambda}_{\nu i}^{h}]\Lambda_{\kappa b}^{p}\Lambda_{\lambda j}^{h}(\mu\nu|\kappa\lambda), \tag{29}$$

$$\tilde{\Lambda}^{p}=\Lambda^{p}\mathbf{L}_{\mu_1}, \tag{30}$$

$$\tilde{\Lambda}^{h}=-\Lambda^{h}\mathbf{L}_{\mu_1}^{T}. \tag{31}$$

For excited state properties in addition to the eigenproblem for the left and right eigenvectors a set of linear equations must be solved for the excited state Lagrangian multipliers,[17–19]

$$\overline{N}\mathbf{A}=-\overline{E}(-\omega)\mathbf{B}E(\omega)=-\overline{n}, \tag{32}$$

where $\mathbf{B}$ is defined as derivative of the Jacobian with respect to the ground-state cluster amplitudes,

$$\mathbf{B}_{\mu\nu\gamma}=\frac{\partial\mathbf{A}_{\mu\nu}}{\partial t_\gamma}. \tag{33}$$

For CC2 the linear equations for the vector $\overline{N}$ can be partitioned into a set of coupled linear equations for only the single excitation part and a set of uncoupled linear equations for the double excitation part,

$$\overline{N}_{\nu_1}\mathbf{A}_{\nu_1\mu_1}^{(\mathrm{eff})}(0)=-\overline{n}_{\mu_1}^{(\mathrm{eff})}, \tag{34}$$

$$\overline{N}_{\nu_2}=-\frac{\overline{n}_{\nu_2}+\overline{N}_{\mu_1}\mathbf{A}_{\mu_1\nu_2}}{\epsilon_{\nu_2}}, \tag{35}$$

with the *effective* right-hand side vector $\overline{n}_{\mu_1}^{(\mathrm{eff})}$ for the single excitation part of $\overline{N}$ in Eq. (34) given by

$$\overline{n}_{\mu_1}^{(\mathrm{eff})}=\overline{E}_{\nu_1}\mathbf{B}_{\nu_1\gamma_1\mu_1}E_{\gamma_1}+\overline{E}_{\nu_2}\mathbf{B}_{\nu_2\gamma_1\mu_1}E_{\gamma_1}+\overline{E}_{\nu_1}\mathbf{B}_{\nu_1\gamma_2\mu_1}E_{\gamma_2}-\sum_{\nu_2}\frac{\overline{n}_{\nu_2}\mathbf{A}_{\nu_2\mu_1}}{\epsilon_{\nu_2}}. \tag{36}$$

The double excitation part of the right hand side vectors $\overline{n}_{\mu_2}$ is for CC2 obtained as

$$\overline{n}_{\mu_2}=\sum_{\nu_1\gamma_1}\overline{E}_{\nu_1}\mathbf{B}_{\nu_1\gamma_1\mu_2}E_{\gamma_1}. \tag{37}$$

The expression for $\overline{n}_{\mu_1}^{(\mathrm{eff})}$ can be cast into a form which resembles those for the vectors transformed with the Jacobian matrix. We give these expressions in the last column of Table

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TABLE II. Expressions for the one-particle density matrices D^{Λ}, $D^{\xi}(L)$, and $D^{A}(L,R)$. The formulas for $D^{\xi}(L)$ are given for L having singlet spin symmetry, while the expressions for $D^{A}(L,R)$ are for L, R having triplet symmetry. The ground-state Lagrangian multiplier entering D^{Λ} are denoted by $\bar{t}_{\mu}$.

Block	D^{Λ}	$D_{\xi}(L)$	$D^{A}(L,R)$
occ/occ: $D_{ij}=$	$2\delta_{ij}-\Sigma_{abk}\bar{t}^{ab}_{jk}t^{ab}_{ik}$	$-\Sigma_{abk}L^{ab}_{jk}t^{ab}_{ik}$	$-\Sigma_{a}L_{aj}R_{ai}-\Sigma_{abk}L^{ab}_{jk}R^{ab}_{ik}$
occ/vir: $D_{ia}=$	$\Sigma_{ck}\bar{t}_{ck}[2t^{ac}_{ik}-t^{ac}_{ki}]$	$\Sigma_{ck}L_{ck}[2t^{ac}_{ik}-t^{ac}_{ki}]$	$\Sigma_{ck}L_{ck}R^{ac}_{ik}$ $-\Sigma_{b}(\Sigma_{kjc}L^{bc}_{kj}t^{ac}_{kj})R_{bi}$ $-\Sigma_{j}(\Sigma_{cbk}L^{cb}_{jk}t^{cb}_{ik})R_{aj}$
vir/occ: $D_{ai}=$	$\bar{t}_{ai}$	L_{ai}	0
vir/vir: $D_{ab}=$	$\Sigma_{ijc}\bar{t}^{ac}_{ij}t^{bc}_{ij}$	$\Sigma_{ijc}L^{ac}_{ij}t^{bc}_{ij}$	$\Sigma_{i}L_{ai}R_{bi}+\Sigma_{ijc}{}^{(-)}L^{ac\,(-)}_{ij}R^{bc}_{ij}$ $+\frac{1}{2}\Sigma_{ijc}{}^{(+)}L^{ac\,(+)}_{ij}R^{bc}_{ij}$

I. The matrix $\bar{F}_{pq}$ appearing in Table I is a triplet response version of the inactive Fock matrix, Eq. (17), which was first introduced in Ref. 5,

$$\bar{F}_{pq}=\sum_{\mu\nu}\,[\bar{\Lambda}^{p}_{\mu p}\Lambda^{h}_{\nu q}+\Lambda^{p}_{\mu p}\bar{\Lambda}^{h}_{\nu q}]F_{\mu\nu}-\sum_{ck}\,(pc|kq)R_{ck}. \quad (38)$$

Because of the structure of $\bar{\Lambda}^{p}$ and $\bar{\Lambda}^{h}$, the contribution from the SCF AO Fock matrix $F_{\mu\nu}$ vanishes for the occupied/virtual block $\bar{F}_{kc}$. As for the transformation of trial vectors with the effective Jacobian matrix, the double excitation vectors R^{ab}_{ij}, L^{ab}_{ij}, and F^{ab}_{ij} are generated on the fly from one-index transformed integrals. While R^{ab}_{ij} and L^{ab}_{ij} are calculated, respectively, according to Eqs. (21)–(24) and Eqs. (28)–(31), the vector $F^{ab}_{ij}=(L\mathbf{B}R)_{aibj}$, is obtained as

$$F^{ab}_{ij}=\frac{2(\breve{a}i|bj)+2(\breve{b}j|ai)-(\breve{a}j|bi)-(\breve{b}i|aj)-L_{aj}\bar{F}_{bi}-L_{bi}\bar{F}_{aj}}{\epsilon_i-\epsilon_a+\epsilon_j-\epsilon_b}, \quad (39)$$

with the one-index transformed integrals $(\breve{a}i|bj)$ defined as

$$(\breve{a}i|bj)=-\sum_{k}\left[\sum_{c}\,L_{ci}R_{ck}\right](ka\hat{|}bj)-\sum_{c}\left[\sum_{k}\,L_{ak}R_{ck}\right](ic\hat{|}bj). \quad (40)$$

Once the equations for the excited state left and right eigenvectors $\bar{E}$ and E and the Lagrangian multipliers $\bar{N}$ have been solved, the unrelaxed one-particle density matrix for an excited state can be calculated in the Λ^{p}, Λ^{h}-basis as

$$D^{\mathrm{ex}}_{pq}=D^{\Lambda}_{pq}+D^{A}_{pq}(\bar{E},E)+D^{\xi}_{pq}(\bar{N}), \quad (41)$$

where D^{Λ}_{pq} is the ground-state one-particle density matrix in the Λ^{p}, Λ^{h}-basis and $D^{A}(\bar{E},E)$ and $D^{\xi}(\bar{N})$ are the contributions of, respectively, the excited state eigenvectors and the Lagrangian multiplier vector. The explicit expressions for D^{Λ}, D^{ξ}, and D^{A} are given in Table II. The contractions needed for the three different density matrices are very similar and are evaluated using the same algorithms. The key step is the calculation of the double excitation amplitudes t^{ab}_{ij}, $\bar{t}^{ab}_{ij}$, etc. which are generated on-the-fly from integral intermediates and are immediately contracted to contributions to the density matrices or small intermediates with only two indices. From D^{ex}_{pq} the one-particle density in the AO basis and unrelaxed one-electron first-order properties can be obtained by,

$$D^{\mathrm{ex,AO}}_{\alpha\beta}=\frac{1}{2}\sum_{pq}\,(\Lambda^{p}_{\alpha p}\Lambda^{h}_{\beta q}+\Lambda^{p}_{\alpha q}\Lambda^{h}_{\beta p})D^{\mathrm{ex}}_{pq}, \quad (42)$$

$$\langle A\rangle=\frac{1}{2}\sum_{pq}\,A^{\Lambda}_{pq}(D^{\mathrm{ex}}_{pq}+D^{\mathrm{ex}}_{qp})=\sum_{\alpha\beta}\,A^{\mathrm{ao}}_{\alpha\beta}D^{\mathrm{ex,AO}}_{\alpha\beta}. \quad (43)$$

The symmetrization with respect to the indices p and q in Eqs. (42)–(43) accounts for the non-Hermitian similarity transformed structure of coupled cluster methods. A^{Λ}_{pq} and $A^{ao}_{\alpha\beta}$ denote the matrix elements of the one-particle operator $\hat{A}$ in, respectively, the Λ^{p}, Λ^{h}- and in the atomic orbital basis.

The approach outlined in Eqs. (9)–(43) has been implemented in the RICC2 module[13] of the TURBOMOLE program package[14] which employs the resolution of the identity approximation[15,20] for electron repulsion integrals. This approximation leads to a reduction of the operation count for the construction of the double excitation amplitudes between one and two orders of magnitude, and thus allows us to perform CC2 calculations on much larger systems than has been possible with previous implementations.

III. THE $\pi\pi^{*}$ VALENCE AND $N=3$ RYDBERG STATES OF BENZENE

The $\pi\pi^{*}$ excited valence and $n=3$ Rydberg states of benzene have been subject of numerous theoretical investigations[5,6,11,16,21–28] using a variety of *ab initio* meth-

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TABLE III. Basis set convergence of CC2 vertical energies of the $\pi\pi^*$ valence and $(n=3)$ Rydberg singlet states of benzene. Energies are given in eV. In parentheses the biorthogonal norm $\langle \overline{E_1}|E_1\rangle$ is displayed, serving as a measure for the single excitation character of the transition.

State	aug-cc-pVDZ+CM2		aug-cc-pVTZ+CM2		aug-cc-pVQZ+CM2		aug-cc-pVQZ+CM8	
Valence $\pi\pi^*$								
$1\,^1B_{2u}$	5.276	(90.5)	5.237	(90.2)	5.230	(90.2)	5.230	(90.2)
$1\,^1B_{1u}$	6.501	(93.4)	6.462	(93.2)	6.457	(93.2)	6.457	(93.2)
$1\,^1E_{1u}$	6.989	(92.5)	7.065	(92.2)	7.085	(92.1)	7.083	(92.1)
$2\,^1E_{2g}$	8.952	(85.2)	8.880	(87.0)	8.878	(85.1)	8.882	(85.3)
Rydberg $\pi\pi^*(n=3)$								
$2\,^1E_{1u}$	7.282	(92.2)	7.313	(92.3)	7.340	(92.3)	7.337	(92.3)
$1\,^1E_{2g}$	7.636	(92.4)	7.785	(92.3)	7.838	(92.3)	7.832	(92.3)
$2\,^1A_{1g}$	7.642	(92.5)	7.792	(92.4)	7.844	(92.4)	7.838	(92.4)
$1\,^1A_{2g}$	7.664	(92.3)	7.816	(92.2)	7.869	(92.2)	7.864	(92.2)

ods ranging from RPA and CIS to highly correlated methods as CCSDR(3) and CC3. In most of the calculations small ANO (Ref. 21) or double-ζ type basis sets augmented with a small set of diffuse Rydberg functions were employed. Only few studies used basis sets of triple-ζ quality[5,6,26–28] or investigated convergence with respect to augmentation with diffuse Rydberg functions. Christiansen *et al.*,[26,27] showed that for benzene when going from double-ζ to triple-ζ quality basis sets the lowest excitation energies change by about ± 0.01–0.2 eV, but no estimate exits for basis set effects beyond a triple-ζ description. A balanced treatment of valence space and diffuse Rydberg functions is necessary for a correct description of the character of the different states, which is crucial for the assignment and when calculating transition strengths or properties of the excited states. To obtain CC2 excitation energies and excited state first-order properties close to the complete basis set limit we employed the series of correlation consistent basis sets[29] aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ augmented with a primitive $(2s2p2d)$ set of diffuse center-of-mass functions (exponents 0.01 and 0.0033), as proposed in Ref. 26. To check convergence with respect to augmentation with Rydberg functions we performed in addition a calculation with a larger $(8s8p8d)$ set of center-of-mass functions (aug-cc-pVQZ-CM8), employing the primitive functions of Kaufmann *et al.*[30] The same primitive functions have been used in Ref. 21 for the construction of a $(1s1p1d)$ ANO Rydberg basis. The recently proposed optimized auxiliary basis sets[31] for the Dunning basis sets were used for the resolution of the identity (RI). The RI-errors introduced thereby have been shown to be more than one order of magnitude smaller than the corresponding deviations from the basis set limit for both total MP2 energies and MP2 first-order properties.[31] For CC2 energies and properties the RI-errors are of similar magnitude.[32] No additional auxiliary basis functions were found to be necessary to account for the Rydberg functions. This can be understood from the Gaussian product theorem: Since mainly two-external integrals of the type $(ai|jb)$ contribute, basically a proper representation of the electrostatic potential of a density formed by virtual-occupied products is needed. The diffuse mass-centered functions of CM2 and CM8 largely only contribute to the virtual space. Since their exponents are small, however, they do not significantly enlarge the spectrum of exponents contributing to the product space, which is well fitted by atom-centered auxiliary basis functions.

All calculations employed the geometry of Ref. 21 and the $1s^2$ shells of the carbon atoms were kept frozen in the CC2 calculations.

The results obtained for the CC2 excitation energies for the $\pi\pi^*$ valence and $(n=3)$ Rydberg states are listed in Tables III and IV. For excitation energies the present results for the aug-cc-pVDZ-CM2 and aug-cc-pVTZ-CM2 basis sets are almost equivalent to the numbers reported in Refs. 6 and 27, apart for the rather small effect of the frozen core approximation. We also find for the singlet as well as for the triplet valence $\pi\pi^*$ states shifts between -0.06 and 0.08 eV going from aug-cc-pVDZ-CM2 to aug-cc-pVTZ-CM2, while

TABLE IV. Basis set convergence of CC2 vertical energies of the $\pi\pi^*$ valence and $(n=3)$ Rydberg triplet states of benzene. Energies are given in eV. In parentheses the biorthogonal norm $\langle \overline{E_1}|E_1\rangle$ is displayed, serving as a measure for the single excitation character of the transition.

State	aug-cc-pVDZ+CM2		aug-cc-pVTZ+CM2		aug-cc-pVQZ+CM2		aug-cc-pVQZ+CM8	
Valence $\pi\pi^*$								
$1\,^3B_{1u}$	4.350	(96.1)	4.349	(96.0)	4.360	(95.9)	4.360	(95.9)
$1\,^3E_{1u}$	5.083	(93.1)	5.061	(92.9)	5.065	(92.8)	5.065	(92.8)
$1\,^3B_{2u}$	5.905	(93.1)	5.873	(94.3)	5.875	(94.2)	5.875	(94.2)
$1\,^3E_{2g}$	7.991	(93.9)	7.970	(93.7)	7.979	(93.5)	7.978	(93.5)
Rydberg $\pi\pi^*(n=3)$								
$2\,^3E_{1u}$	7.027	(92.8)	7.165	(92.8)	7.215	(92.8)	7.210	(92.8)
$1\,^3A_{1g}$	7.589	(92.8)	7.737	(92.7)	7.789	(92.7)	7.782	(92.7)
$2\,^3E_{2g}$	7.625	(92.6)	7.770	(92.6)	7.820	(92.7)	7.814	(92.7)
$1\,^3A_{2g}$	7.668	(92.3)	7.820	(92.2)	7.873	(92.2)	7.868	(92.2)

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TABLE V. Basis set convergence of CC2 isotropic second moment of the difference density, calculated for the $\pi\pi^*$ valence and ($n=3$) Rydberg singlet states of benzene. The values are given in atomic units (a_0^2).

State	aug-cc-pVDZ+CM2	aug-cc-pVTZ+CM2	aug-cc-pVQZ+CM2	aug-cc-pVQZ+CM8
Valence $\pi\pi^*$				
$1\,^1B_{2u}$	0.72	0.65	0.64	0.64
$1\,^1B_{1u}$	1.50	1.35	1.33	1.33
$1\,^1E_{1u}$	21.53	12.49	9.76	9.84
$2\,^1E_{2g}$	2.14	8.31	2.83	27.92
Rydberg $\pi\pi^*(n=3)$				
$2\,^1E_{1u}$	11.63	18.54	20.53	20.07
$1\,^1E_{2g}$	54.08	51.78	50.75	50.15
$2\,^1A_{1g}$	56.18	53.95	52.91	52.18
$1\,^1A_{2g}$	56.73	54.63	53.74	53.09

the Rydberg excitations are shifted by 0.14–0.15 eV, with the exception of $2\,^1E_{1u}$, which changes only by 0.03 eV. A similar difference in the behavior of valence and Rydberg states is found when going from aug-cc-pVTZ-CM2 to aug-cc-pVQZ-CM2: For the valence $1\,^1B_{2u}$, $1\,^1B_{1u}$, and $2\,^1E_{2g}$ states the excitation energies decrease by negligible 0.005 eV, while for the triplet valence states the excitation energies increase slightly by 0.002–0.01 eV; only for the $1\,^1E_{1u}$ state, which due to a coupling with the close-by lying $2\,^1E_{1u}$ state has partial Rydberg character (see below), the excitation energy increases by 0.02 eV. For the Rydberg states the shifts are with 0.05 eV significantly larger. Going from the small CM2 Rydberg basis to the larger CM8 set no significant changes are found in the excitation energies for states of pure valence character and also for the $n=3$ Rydberg states the shifts are with ≈ -0.006 eV rather small. An exception is the $2\,^1E_{2g}$ state which adopts partial Rydberg character when going from aug-cc-pVQZ-CM2 to aug-cc-pVQZ-CM8. The latter state has, however, a large contribution from doubly and higher excited determinants and cannot be described accurately at the CC2 level. The aug-cc-pVQZ-CM8 results for the excitation energies are expected to be for $\pi\pi^*$ valence states within 0.01 eV and for the $n=3$ Rydberg states within 0.03 eV of the CC2 complete basis set limit.

In coupled cluster response theory beyond CCS, the accuracy obtained for excitation energies correlates with the weight of the single excitation contribution to the excited state. Usually the single excitation contribution to the norm of the right eigenvector, denoted as $\%T_1$,

$$\%T_1 = \frac{\Sigma_{\nu_1} E_{\nu_1}^2}{\Sigma_{\nu_1} E_{\nu_1}^2 + \Sigma_{\nu_2} E_{\nu_2}^2} \times 100\%$$

is used as a measure for the single excitation contribution. In Ref. 6 it was observed that the $\%T_1$ measure is often significantly higher for triplet excitations than for corresponding singlet excitations of similar character. For example, for the singlet valence states of benzene $\%T_1$ is 85–95% while it is 98–99% for the valence triplet states. For the singlet Rydberg states $\%T_1$ is 95–96% while it is 98–99% for triplet Rydberg states.[6] It was therefore suspected that the CCSD results for the triplet excitation energies might have somewhat smaller errors than the CCSD results for the corresponding singlet excitation energies. However, a problem of the $\%T_1$ measure is, that the values depend on the chosen representation of the excitation operator manifold, i.e., with a different combination of, e.g., ${}^{(+)}\tau_{aibj}$ and ${}^{(-)}\tau_{aibj}$ different results would be obtained for $\%T_1$. This problem is not special for triplet excitations; also for singlet excitations different results for $\%T_1$ are obtained in a spin coupled basis and in a spin–orbital basis. Also, often significant differences are found between $\%T_1$ for left and for right eigenvectors. A unique measure for the weight of the single excitation contributions to an excited state is obtained by the biorthogonal norm,

$$\langle \bar{E}_1 | E_1 \rangle = \sum_{\nu_1} \bar{E}_{\nu_1} E_{\nu_1} \langle \nu_1 | \tau_{\nu_1} | HF \rangle, \tag{44}$$

TABLE VI. Basis set convergence of the CC2 isotropic second moment of the difference density, calculated for the $\pi\pi^*$ valence and ($n=3$) Rydberg triplet states of benzene. The values are given in atomic units (a_0^2).

State	aug-cc-pVDZ+CM2	aug-cc-pVTZ+CM2	aug-cc-pVQZ+CM2	aug-cc-pVQZ+CM8
Valence $\pi\pi^*$				
$1\,^3B_{1u}$	0.42	0.39	0.39	0.39
$1\,^3E_{1u}$	0.65	0.60	0.59	0.59
$1\,^3B_{2u}$	1.00	0.90	0.89	0.89
$1\,^3E_{2g}$	9.40	6.88	8.44	7.90
Rydberg $\pi\pi^*(n=3)$				
$2\,^3E_{1u}$	28.46	26.99	26.34	25.94
$1\,^3A_{1g}$	49.45	47.22	46.19	45.61
$2\,^3E_{2g}$	51.82	47.08	44.16	44.01
$1\,^3A_{2g}$	57.33	55.26	54.39	53.72

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TABLE VII. Comparison of recent and selected preceding results for vertical excitation energies and second moments of charge for the lowest states of E_{1u} symmetry. Energies are given in eV, the expectation value $\langle z^2 \rangle$ is given in atomic units (a_0^2).

Method	Basis	$1\,^1E_{1u}$ ΔE_{vert}	$\langle z^2 \rangle$	$2\,^1E_{1u}$ ΔE_{vert}	$\langle z^2 \rangle$	$1\,^3E_{1u}$ ΔE_{vert}	$\langle z^2 \rangle$	$2\,^3E_{1u}$ ΔE_{vert}	$\langle z^2 \rangle$
CASSCF[a]	ANO1	6.46	79.1	8.53	35.1	5.07	30.3	6.92	74.8
CASPT2[a,b]	ANO1	7.16		7.03		4.49		6.98	
CCS[c]	ANO1	7.18	89.4	8.06	34.3	4.88		7.12	
CC2[c]	ANO1	7.01	79.7	7.37	42.6	5.08		7.04	
CCSD[c]	ANO1	7.17	79.2	7.58	41.4	4.92		7.18	
CC3[c]	ANO1	7.13		7.42					
CCS[d]	Sadlej+CM6	7.18	84.6	7.93	54.6				
CC2[d]	Sadlej+CM6	6.97	73.4	7.29	48.3				
CCSD[d]	Sadlej+CM6	7.12	70.9	7.48	45.6				
CC2[e]	aug-cc-pVQZ+CM8	7.08	48.7	7.34	68.5	5.07	30.1	7.21	81.5
Experiment[f]		6.96		7.41		4.75			

[a]Reference 21. The geometry is identical to the one used in the present work ($R_{CC}=1.395$ Å, $R_{CH}=1.085$ Å).
[b]The energies are ordered as to match their zeroth order CASSCF states.
[c]Singlet excitation energies from Ref. 27, second moments from Ref. 16, triplet excitation energies from Ref. 6. The geometry is identical to the one used in the present work.
[d]Reference 16. A CCSD/TZ2P geometry was used ($R_{CC}=1.392\,369$ Å, $R_{CH}=1.079\,368$ Å).
[e]Present work. For the ground state the expectation value is $\langle z^2 \rangle = 29.8$.
[f]$\Delta E_{\max}$ is given which may differ from ΔE_{vert}. 1 and $2\,^1E_{1u}$: Ref. 40, $1\,^3E_{1u}$: Ref. 36.

with the complete excitation vectors, i.e., for CC2 and CCSD the single excitation and the double excitation contribution, normalized to

$$\langle \overline{E}|E\rangle = \sum_i \sum_{\nu_i} \overline{E}_{\nu_i} E_{\nu_i} \langle \nu_i|\tau_{\nu_i}|HF\rangle = 1. \tag{45}$$

This norm is independent of the chosen operator basis, in particular identical results are obtained in spin orbital (UHF) and explicitly spin coupled (RHF) calculations. It requires however that both left and right eigenvectors are calculated. The results obtained for the $\pi\pi^*$ valence and Rydberg excited states of benzene are given in parentheses in Tables III and IV. The biorthogonal norm $\langle \overline{E}_1|E_1\rangle$ follows the same trends as the $\%T_1$ in Refs. 6, 27, if we only compare within either singlet or triplet states. Typically $\langle \overline{E}_1|E_1\rangle$ is slightly smaller than the $\%T_1$ for the right eigenvectors, in particular for triplet states. Apart from the $2\,^1E_{2g}$ and $2\,^3E_{2g}$ states, which differ very much in character, the $\langle \overline{E}_1|E_1\rangle$ values obtained for corresponding singlet and triplet state are very similar. For the $n=3$ Rydberg states the differences are only about 0.5%. Thus, we have to conclude that the systematic difference obtained between the $\%T_1$ values for singlet and triplet states is an artifact of the different operator basis, and that the $\%T_1$ measure only provides a reliable comparison if used within the same operator basis. The present results suggest that CC2 and also CCSD will give results of similar accuracy for singlet and for triplet excited states, if the states are of similar character.

The second moments of charge are often used as a basis for a subdivision of excited states into valence and Rydberg states of different quantum numbers. We have calculated the change of the isotropic second moments upon excitation

$$\Delta\alpha = \tfrac{1}{3}(\langle r^2\rangle_f - \langle r^2\rangle_0). \tag{46}$$

Tables V and VI list the CC2 results for $\Delta\alpha$ for the singlet and triplet $\pi\pi^*$ valence and $n=3$ Rydberg states. Earlier studies used the expectation value $\langle z^2\rangle$, which does not change the conclusions since for $n=3$ Rydberg states mainly the z component changes. A comparison of preceding and present results for the states of E_{1u} and E_{2g} symmetry is given in Tables VII and VIII, since for these states some differences to earlier studies occur as discussed below.

For the excited singlet states of benzene transition strengths and second moments of charge have been reported at the CASSCF level using an ANO1 basis[21] and for the hierarchy CCS, CC2, and CCSD using a Sadlej POI1 basis[16] augmented with different diffuse Rydberg basis sets. For the triplet states only CASSCF/ANO1 results for the second moment of charge have been reported.[21] In particular the CASSCF results from Ref. 21 for the second moments of charge have been used as basis for assigning the excited states as valence or Rydberg states. Even though the correlation corrections to the excitation energies going from CASSCF to CASPT2 were rather large and the lowest valence and the lowest Rydberg states of E_{1u} symmetry in the singlet space and of E_{2g} symmetry in the triplet space change thereby their order, the same assignment has been used for the coupled cluster calculations in Refs. 5, 6, 26–28. Christiansen *et al.*[16] showed that in correlated calculations (CC2 and CCSD) using both the ANO1 basis and the Sadlej POL1 basis,[33] augmented with diffuse Rydberg functions, the first $^1E_{1u}$ state is more diffuse than the second, as it is the case in CCS and CASSCF calculations which do not or only partially include dynamical correlation (cf. Table VII). Thus it was suspected that the assignment of these states might be wrong. Although, this study investigated only the convergence with respect to diffuse Rydberg functions without testing convergence with respect to the valence basis set (the POL1 basis is still only of double zeta quality for the valence region), it made apparent that the results obtained in Ref. 21 with the ANO1 basis for the second moments of charge of the excited states are not converged and for some of the states (those where perturbation theory changes the ordering) are unreliable.

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TABLE VIII. Comparison of recent and selected preceding results for vertical excitation energies and second moments of charge for the lowest states of E_{2g} symmetry. Energies are given in eV, the expectation value $\langle z^2 \rangle$ is given in atomic units (a_0^2).

Method	Basis	$1\,^1E_{2g}$ ΔE_{vert}	$\langle z^2 \rangle$	$2\,^1E_{2g}$ ΔE_{vert}	$\langle z^2 \rangle$	$1\,^3E_{2g}$ ΔE_{vert}	$\langle z^2 \rangle$	$2\,^3E_{2g}$ ΔE_{vert}	$\langle z^2 \rangle$
CASSCF[a]	ANO1	7.09	88.3	7.96	29.8	7.61	39.3	7.44	77.6
CASPT2[a,b]	ANO1	7.77		7.90		7.12		7.55	
CCS[c]	ANO1	7.80		10.58		7.93		7.60	
CC2[c]	ANO1	7.64		8.97		7.99		7.64	
CCSD[c]	ANO1	7.84		9.17		7.71		7.88	
CC3[c]	ANO1	7.85		8.41		7.51[f]		7.85[f]	
CC2[d]	aug-cc-pVQZ+CM8	7.84	100.1	8.88	64.8	7.98	39.4	7.81	89.3
Experiment[e]		7.81		7.8		6.9, 7.7±0.3			

[a]Reference 21. The geometry is identical to the one used in the present work.
[b]The energies are ordered as to match their zeroth order CASSCF states.
[c]Singlet excitation energies from Ref. 27, triplet excitation energies from Ref. 6. The geometry is identical to the one used in the present work.
[d]Present work. For the ground state the expectation value is $\langle z^2 \rangle = 29.8$.
[e]$\Delta E_{\max}$ is given which may differ from ΔE_{vert}. $1\,^1E_{2g}$: Ref. 39; $2\,^1E_{2g}$: Ref. 41; $^3E_{2g}$: estimates based on data from Refs. 36, 34, and 38 (see text).
[f]Reference 42, the values for the $\%T_1$ measure for the contribution of singly excited determinants are 95.2 ($1\,^3E_{2g}$) and 97.6 ($2\,^3E_{2g}$).

As for the excitation energies we investigated the convergence with respect to the valence basis set using the series aug-cc-pVDZ-CM2, aug-cc-pVTZ-CM2, and aug-cc-pVQZ-CM2, while convergence with respect to diffuse functions was tested by an additional calculation with the large CM8 Rydberg (aug-cc-pVQZ-CM8).

For the triplet states $1\,^3B_{2u}$, $1\,^3B_{1u}$, $1\,^3E_{1u}$ and the singlet states $1\,^1B_{2u}$, $1\,^1B_{1u}$ our results agree with the finding of the previous studies, that these states are of pure valence character. For the triplet states $1\,^3A_{1g}$, and $1\,^3A_{2g}$ and their singlet counterparts $2\,^1A_{1g}$ and $1\,^1A_{2g}$ the values for $\Delta\alpha$ show that these states are of pure Rydberg $n=3$ character; the same applies to the $1\,^1E_{2g}$ state. The results for the triplet state $2\,^3E_{1u}$ indicate some valence/Rydberg mixing, with the state having mostly Rydberg character. So far, the present results support the original assignment for these states.

A rather unsystematic behavior is found for the second moment of charge of the $2\,^1E_{2g}$ state with a sudden change in character going from aug-cc-pVQZ-CM2 to aug-cc-pVQZ-CM8, which indicates a mixing with Rydberg states for $n \geqslant 3$. However, as pointed out above, this state is not accurately described at the CC2 level and therefore no conclusions about its character can be drawn from the present calculations.

For the two lowest singlet states of E_{1u} symmetry we find similar as in Ref. 16, that these states are of mixed valence/Rydberg character, where the degree of the valence/Rydberg mixing and the order of the states is strongly basis set dependent. The present results show that—as noticed in Ref. 16—the Rydberg state is preferred, i.e., lower in energy, in double-ζ type valence basis sets, if these are augmented by a sufficient number of diffuse functions. However, if the quality of the valence basis set is systematically increased going from aug-cc-pVDZ-CM2 to aug-cc-pVTZ-CM2 and aug-cc-pVQZ-CM2 the $1\,^1E_{1u}$ state adopts predominantly valence character. This result does not change if the diffuse Rydberg basis is again improved going from aug-cc-pVQZ-CM2 to aug-cc-pVQZ-CM8. A comparison of the CC2 and CCSD results of Ref. 16 indicates that the valence/Rydberg mixing in these two $^1E_{1u}$ states is not sensitive to correlation effects beyond the CC2 level. Therefore, we conclude that the original assignment of the $1\,^1E_{1u}$ state as the valence state and the $2\,^1E_{1u}$ state as Rydberg state is correct. A misassignment as suspected in Ref. 16 seems to be excluded by the present results.

Another difficult case is the assignment of the lowest two $^3E_{2g}$ states as valence or Rydberg states. At the CASSCF level, the lower state is predicted to possess Rydberg character, whereas the second state is of valence type (cf. Table VIII). The energy ordering changes after applying the second-order CASPT2 correction. In the present study, we find that at the CC2 level the Rydberg $\pi\pi^\star(n=3)\,^3E_{2g}$ state is lower in energy than the valence $\pi\pi^\star\,^3E_{2g}$ state. The results obtained for the change of the second moment of charge $\Delta\alpha$ is not sensitive to the one-electron basis set, although they indicate some valence/Rydberg mixing. In Refs. 5 and 6 no properties of the excited states were available and therefore the excitation energies were assigned based only on their ordering. From the results for $\Delta\alpha$ we must conclude that this lead to a misassignment of the CC2 excitation energies for $1\,^3E_{2g}$ and $2\,^3E_{2g}$ in these studies. The basis set investigation shows, that with increasing quality of the valence basis the Rydberg $^3E_{2g}$ state gets less diffuse and its excitation energy increases such that with aug-cc-pVQZ-CM8 the separation between the CC2 excitation energies between the Rydberg and the valence $^3E_{2g}$ states amounts only to 0.16 eV. This is clearly below the accuracy of CC2 and no conclusions concerning the true ordering of the two states can be drawn from the CC2 excitation energies. By reinspecting the eigenvectors obtained in the ANO1 basis at the CC2 and CCSD levels in Ref. 6 we became aware, that the lowest Rydberg and valence $^3E_{2g}$ states change their ordering between CC2 and CCSD. Thus the CCSD excitation energies for the $^3E_{2g}$ states have been correctly assigned in Ref. 6: $1\,^3E_{2g}$ as valence $\pi\pi^\star$ state and $2\,^3E_{2g}$ as Rydberg $\pi\pi^\star(n=3)$ state. This is in line with the previous CASPT2 results, though a discrepancy for the excitation energies remains.

Experimentally, not much is known about this state. Astier and Meyer[34] reported a transient absorption at 2.9 eV

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after flash excitation in solution, which they attribute it to an $^3E_{2g} \leftarrow 1\,^3B_{1u}$ excitation. This absorption was not found in the gas phase.[35] Nakashima *et al.* did not observe such a band for technical reasons, but instead assigned a broad shoulder at 3.5–4.0 eV to an $^3E_{2g} \leftarrow 1\,^3B_{1u}$ transition. However, they do not exclude the possibility of photoproducts being involved in this band. In gas phase a band in the same region (3.7 eV) was observed but for convincing reasons attributed to the formation of a secondary species (biphenyl).[35] Based on a combination of either of these data with the well established value of 3.95 eV for the $1\,^3B_{1u} \leftarrow \tilde{X}$ transition,[36] excitation energies like 6.83 eV (Ref. 37) or 7.24–7.74 (Ref. 21) are cited in theoretical articles, where the latter value was shifted by -0.2 eV due to solvent effects. Judging from Refs. 38 and 39, rather the opposite sign is expected, i.e., all the reported (singlet) gas phase excitation energies are higher than those obtained in solution. Therefore we expect the $^3E_{2g}$ state either around 6.9 eV or 7.7 ± 0.3 eV above the ground state. For a doubtless assignment of these states further theoretical—transition moments and higher correlated, e.g., CC3, calculations—and experimental efforts are needed.

IV. SUMMARY AND CONCLUSIONS

Expressions have been derived for first-order properties of excited triplet states at the approximate coupled cluster singles and doubles (CC2) level using an explicitly spin coupled basis for the triplet excitation manifold. With this formulation it is now possible to perform calculations for triplet states with essentially the same costs as for excited singlet states. The expressions have been implemented in the RICC2 module of the TURBOMOLE program package, which employs the resolution of the identity approximation for the electron repulsion integrals.

This implementation allowed us to perform calculations for the change of the second moment of charge for the excited $\pi\pi^*$ valence and $n=3$ Rydberg states of benzene using basis sets with up to 828 functions. Using the series of correlation consistent basis sets aug-cc-pVDZ, aug-cc-VTZ, and aug-cc-pVQZ and two different diffuse Rydberg basis sets, we investigated the basis set convergence of the excitation energies and the second moment of charge with respect to both the valence and the Rydberg basis, and obtained results close to the CC2 basis set limit. The results allowed us to clarify the doubts about the assignment of the lowest E_{1u} states. It is found that the singlet states $1\,^1E_{1u}$ and $2\,^1E_{1u}$ have a mixed valence/Rydberg character. The degree of the valence/Rydberg mixing depends strongly on the basis sets, but in the CC2 basis set limit the $1\,^1E_{1u}$ state adopts predominantly valence character. In the triplet case no such strong basis set dependence is found. The lowest valence and Rydberg states of $^3E_{2g}$ symmetry are obtained at the CC2 level in the wrong order. Taking into account the reordering of these states between CC2 and CCSD, the coupled cluster results for these states are in qualitative, but not in quantitative agreement with the CASPT2 results. A rather large discrepancy remains for the excitation energy of the valence $\pi\pi^\star$ $1\,^3E_{2g}$ state. Since both states are clearly dominated by single excitations it is expected that the coupled cluster results are more accurate, in particular because they were obtained with basis sets of higher quality. But further experimental and theoretical efforts are required before definite conclusions can be drawn for these states.

The $\%T_1$ measure for the single excitation contribution to excited states is found to be unreliable for comparison across different excitation operator manifolds. Therefore, we propose the biorthogonal norm $\langle \bar{E}_1 | E_1 \rangle$, based on the overlap between the bra and the ket representations of the excited states, as an alternative measure for the single excitation contribution since it provides a unique result independent of the chosen representation for the excitation operator manifold and independent of the choice of the eigenvectors (left or right). While the $\%T_1$ measure suggests that triplet excited states have a systematically higher single excitation contribution within the coupled cluster response ansatz than corresponding singlet states of the same character, the results for the $\langle \bar{E}_1 | E_1 \rangle$ norm clearly demonstrates that this is an artifact of the difference in the operator manifolds for singlet and triplet excitations.

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