



Integral direct calculation of CC2 excitation energies: singlet excited states of benzene

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Abstract

The calculation of excitation energies has been implemented in the CC2 model using an atomic integral direct algorithm where integrals are generated in distributions with one atomic index fixed and three indices free. The calculations are dominated by the recalculation of atomic integrals. Singlet excitation energies have been calculated for benzene and a basis set analysis has been carried out with basis sets containing up to 432 basis functions. The CC2 excitation energies have been compared with other theoretical and experimental results. Basis set effects of the order of 0.2 eV are found in benzene going from augmented double-zeta basis sets to augmented triple-zeta quality. The differences between the CC2 results and results obtained by the CASPT2 method are of the same order of magnitude as the basis set errors except for the 2^1E_{2g} state. For this state, large discrepancies are found between the results obtained by coupled cluster methods and CASPT2.

1. Introduction

In recent years a growing interest has focused on coupled cluster based methods for evaluating molecular properties. A variety of static and frequency dependent molecular properties have been calculated at the coupled cluster singles and doubles (CCSD) level, whereas CCSD with perturbative corrections for triples [1], CCSD(T), has provided highly accurate results for a wide range of frequency independent molecular properties [2]. Excitation energies and transition matrix elements cannot be calculated in CCSD(T) since CCSD(T) is a two step approach and therefore does not have a response function with a pole structure in accordance with exact theory.

In a series of Letters, we have introduced two new coupled cluster models, CC2 [3] and CC3 [4–6]. CC2 is an approximation to CCSD, and CC3 an approximation to coupled cluster singles, doubles and triples (CCSDT). Both approximations are based on a perturbational analysis of the cluster amplitude equations in terms of the fluctuation potential, and on the importance of singles in property calculations. In CC2, the CCSD doubles equation is approximated to the lowest non-vanishing order in perturbation theory, i.e. first order, and in CC3 the CCSDT triples equation is approximated to the lowest non-vanishing order, i.e. second order. For a set of Hartree–Fock (HF) orbitals, the singles enter to second order in perturbation theory only. However, they respond to

external perturbations to zero order in the fluctuation potential and the singles are therefore treated as zero order parameters in both CC2 and CC3. By incorporating CC2 and CC3 in the standard hierarchy of coupled-cluster models CCS, CCSD, CCSDT, ..., we obtain a new hierarchy $CCS(N^4)$, $CC2(N^5)$, $CCSD(N^6)$, $CC3(N^7)$, $CCSDT(N^8)$ etc. where the numbers in parentheses indicate the computational cost in terms of the scaling of the calculations with the number of orbitals N . Total energies, excitation energies, transition matrix elements and frequency dependent molecular properties are obtained with increasing accuracy at higher levels in this hierarchy with a convergence towards the exact result unique to coupled cluster methods. This is clearly seen from the perturbation analysis in Ref.[4], and from the benchmark calculations of total energies and in particular excitation energies of Ref. [5].

An important feature of the new coupled cluster hierarchy is the possibility of deriving at each level a response function with a pole structure that is consistent with exact theory [3,6]. From the response functions we can determine frequency dependent properties, excitation energies and transition moments. For static properties, the new levels CC2 and CC3 fit in with the existing models MP2 and CCSD(T), being of the same accuracy. The CC2 total energy is of similar quality as the MP2 total energy in the sense that it is correct through second order. Hättig and Hess [7] and Aiga et al. [8] have derived frequency dependent polarizabilities in the MP2 approach. The structure of MP2 polarizabilities is not compatible with the true linear response function, thus excitation energies and transition moments cannot be identified. No such problems are encountered in CC2. The same comments apply for higher order perturbation schemes and CCSD(T) relative to higher level iterative coupled cluster models as CC3.

The second-order polarization propagator approximation (SOPPA) [9] is a linear response function approach whose pole structure is compatible with exact theory and where molecular properties, excitation energies and transition moments are correct through second order by definition. SOPPA is a non-variational approach with an N^5 operation count. In contrast to CC2 where the response function is identified from a quasi-energy derivative, SOPPA is obtained assuming the Hellmann–Feynman theorem

is fulfilled. SOPPA therefore does not contain corrections due to the non-fulfilment of the conditions of the Hellmann–Feynman theorem.

Excited states can be classified as being dominated by single, double or higher electron replacements with respect to the ground state. Single replacement dominated excitations are obtained with increasing accuracy in the coupled cluster hierarchy as follows: CCS excitation energies are correct through first order in the fluctuation potential, CC2 through second order, CCSD through second order with the inclusion of all higher order terms from singles and doubles, CC3 through third order, etc. The special treatment of singles in CC2 and CC3 is important, since otherwise triple models would give excitation energies for single replacement excitations that are correct to second order only [6] Examples of methods correct to second order are the CCSDT-1a [10] and CCSDT-1b [11] models. Numerical examples have confirmed the superiority of CC3 over these methods [5,6]. Excitation energy in the CCSDT-1a model was first presented by Watts and Bartlett [12]. Double replacement dominated excitations cannot be properly described in CC2. They are correct through first order in CCSD and through second order in the approximate triples models CCSDT-1a, CCSDT-1b and CC3.

Recently, Head-Gordon et al. presented a doubles correction to the configuration interaction singles (CIS) excitation energies denoted CIS(D) [13]. This model can be described as a type of non-iterative CC2 starting from the CCS solution (CIS and CCS excitation energies are identical). Similar non-iterative versions of the CC3 model can be designed. Recently Stanton et al. [14] presented a detailed comparison of CIS, CIS(D) and CCSD for a number of molecules. The CIS(D) vertical excitation energies calculated close to the equilibrium structure are in reasonable agreement with CCSD, while away from the equilibrium structure CIS(D) may fail to give an improvement of CIS. We present comparisons of iterative and non-iterative second order models in forthcoming publications.

Our approach for determining excitation energies is based on linear response theory, and the excitation energies are thus obtained by solving linear response eigenvalue equations. Alternatively, excitation energies may be obtained from separate calculations on

the ground state and the excited states. This approach has been most extensively employed within the framework of multi-reference configuration interaction (MRCI) [15] and second order perturbation theory with a complete active space reference (CASPT2) [16]. In these approaches, care is needed to ensure a balanced description of the ground state and the excited states, and to ensure that convergence is obtained on the correct states.

Atomic integral direct methods have significantly extended the application range of the Hartree–Fock and MP2 approaches. A similar development has recently taken place for CC wavefunctions, where atomic integral direct CCSD techniques have been presented based on a strategy where integrals are generated in distributions with one fixed and three free atomic indices [17]. Ground state CCSD total energies have been calculated with more than 500 basis functions [18]. The same technique has also been extended to the calculation of CCSD excitation energies [19]. The integral direct techniques for CCSD may easily be applied to CC2 since CC2 is an approximation to CCSD. We present in this Letter CC2 calculations of excitation energies using integral direct techniques. These and the above mentioned CCSD excitation energies represent the first integral direct calculations of excitation energies at a correlated level.

The integral direct CC2 technique is applied to investigations of the basis set dependency on calculations of the singlet excitation energies of benzene. Since CC2 is a reasonably accurate correlation model, the CC2 results may be used to estimate basis set uncertainties in other theoretical calculations. We shall compare the CC2 excitation energies with the excitation energies obtained in CASPT2 and SOPPA calculations as well as in experimental studies.

2. Theory

The CCSD energy is determined from

$$E = \langle HF | H \exp(T_1 + T_2) | HF \rangle. \quad (1)$$

The CCSD cluster amplitudes are obtained from the CCSD amplitude equations

$$\langle \mu_i | \exp(-T_1 - T_2) H \exp(T_1 + T_2) | HF \rangle = 0 \quad (2)$$

$i = 1, 2,$

where $\{\langle \mu_1 |, \langle \mu_2 | \}$ denotes the single and double excitation manifold. Introducing T_1 transformed operators as

$$\hat{O} = \exp(-T_1) O \exp(T_1), \quad (3)$$

we may write the CCSD amplitude equations as

$$\langle \mu_1 | \hat{H} + [\hat{H}, T_2] | HF \rangle = 0, \quad (4)$$

$$\langle \mu_2 | \hat{H} + [\hat{H}, T_2] + \frac{1}{2} [[\hat{H}, T_2], T_2] | HF \rangle = 0. \quad (5)$$

We partition the Hamiltonian H into a Fock operator F and a fluctuation operator U , describing the difference between the true electron–electron repulsion and the Fock potential,

$$H = F + U. \quad (6)$$

The CC2 model is defined from approximations in the CCSD equations as follows: the CCSD singles equations are retained in their original form, but the doubles equations are approximated to be correct to first order only, with the singles treated as zero order parameters. Since T_2 enters in first order, the CC2 equations become

$$\langle \mu_1 | \hat{H} + [\hat{H}, T_2] | HF \rangle = 0, \quad (7)$$

$$\langle \mu_2 | [F, T_2] + \hat{H} | HF \rangle = 0. \quad (8)$$

The CCSD amplitude equations are given in Ref. [17] in terms of t_2 amplitudes and integrals of the T_1 transformed Hamiltonian. In the same Letter an atomic integral direct algorithm for implementing these equations is described. The CC2 equations are a subset of the CCSD equations and a CC2 atomic integral direct implementation of the optimization of the reference function follows immediately from the above. The doubles equations in CC2 give an MP2 like expression, but with T_1 transformed integrals (denoted with hats)

$$(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) \hat{t}_{ij}^{ab} + (\hat{a}i | \hat{b}j) = 0, \quad (9)$$

where we assume an orthonormal basis.

In Ref. [6] we discussed different strategies for the derivation of coupled cluster response functions and described an approach, that is applicable also in the case where approximations are introduced into the cluster equations. In this approach we identify response functions as derivatives of a quasi energy.

The quasi energy approach is described in detail by Sasagane et al. [20] The CC2 response function is given in Ref. [3]. Excitation energies and transition moments may be determined as poles and residues of the linear response function. The poles of the coupled cluster linear response function occurs at plus and minus the eigenvalues of the coupled cluster Jacobian and the CC2 excitation energies are thus determined from

$$AS_k = \omega_k S_k, \quad (10)$$

where the CC2 Jacobian is

$$A_{\mu_i, \nu_j} = \begin{pmatrix} \langle \mu_1 [\hat{H}, \tau_{\nu_1}] + [[\hat{H}, \tau_{\nu_1}], T_2] | HF \rangle & \langle \mu_1 [\hat{H}, \tau_{\nu_2}] | HF \rangle \\ \langle \mu_2 [\hat{H}, \tau_{\nu_1}] | HF \rangle & \delta_{\mu\nu} \omega_{\mu_2} \end{pmatrix}. \quad (11)$$

The doubles–doubles block is diagonal with the diagonal elements ω_{μ_2} as the sum and differences of orbital energies.

The CC2 eigenvalue equations must be solved iteratively. Iterative techniques require the ability to carry out linear transformations with the CC Jacobian, and this is the crucial step in an integral direct calculation of excitation energies. An integral-direct algorithm can be used similar to the one for the optimization of the CC reference state. The essential ideas of this algorithm may be summarised as follows: The integrals are calculated in integral distributions with one fixed atomic orbital (AO) index and three free AO indices. Looping over all distributions, we calculate the contributions to the coupled cluster vector function or linear transformations of the Jacobian. In this loop only storage of the order N^3 integrals are needed in contrast to conventional techniques where the order of N^4 integrals are stored on disk. As in our most recent implementation of the CCSD total energy we only perform a partial transformation of the AO integral distributions. The new integral code for evaluating the AO integrals is described in Ref. [18].

We briefly review here the transformation of trial vectors on the CC2 Jacobian. We refer to Ref. [19] for a more detailed discussion on the implementation of the individual terms. Let C denote a right trial vector with single and double excitation amplitudes

C_1 and C_2 , respectively. The corresponding transformed vector is

$$\rho = AC. \quad (12)$$

The transformations can be written out in single and double excitation components as

$$\begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix} = \begin{pmatrix} \rho_1^1 + \rho_1^2 \\ \rho_2^1 + \rho_2^2 \end{pmatrix} = \begin{pmatrix} A_{11}C_1 + A_{12}C_2 \\ A_{21}C_1 + A_{22}C_2 \end{pmatrix}. \quad (13)$$

Introducing the CCSD Jacobian in the form in Eq. (11) and expanding, we obtain the following expressions

$$\rho_{ai}^1 = \langle a | \tilde{H} | HF \rangle + \langle a | [\tilde{H}, T_2] | HF \rangle, \quad (14)$$

$$\rho_{aij}^1 = \langle a | [\tilde{H}, T_2] | HF \rangle, \quad (15)$$

$$\rho_{ai}^2 = \langle a | [\hat{H}, C_2] | HF \rangle, \quad (16)$$

$$\rho_{aij}^2 = \langle a | [\hat{H}, C_2] | HF \rangle, \quad (17)$$

where C_1 and C_2 are single and double excitation operators with the trial vectors as expansion coefficients and where \tilde{H} is a C_1 transformed operator

$$\tilde{H} = [\hat{H}, C_1]. \quad (18)$$

Comparing with the equations determining the reference (Eqs. (7) and (8)), we find that the same types of terms are included as in the linear transformations in Eqs. (14)–(17). The linear transformations containing a double excitation trial vector (Eqs. (16) and (17)) are similar to the T_2 parts of the equations for energy optimization (Eqs. (7) and (8)), and the implementation of these is a generalization to amplitudes that are not totally symmetric. The singles result vector from the transformation with a singles trial vector (Eq. (14)) is identical to the one of CCSD. The extra C_1 transformation may be absorbed in the transformation from atomic to molecular integrals, as shown explicitly in Ref. [19]. Implementation of Eq. (15) also gives contributions similar to those of energy optimization, where one molecular orbital index is transformed at a time with C_1 ,

$$\begin{aligned} \rho_{aij}^1 &= (ai|\tilde{b}j) = (\bar{a}i|\hat{b}j) + (\hat{a}i|\hat{b}j) + (ai|\hat{b}j) \\ &\quad + (ai|\hat{b}\bar{j}). \end{aligned} \quad (19)$$

The bars denote the additional C_1 transformation, and again we assume an orthonormal basis. The development of an integral direct CC2 code is thus rather straightforward building on the capability to perform CCSD direct excitation energy calculations. We have discussed here the structure of the implementation, to emphasize the relative ease with which CC2 is implemented in an integral direct algorithm. We refer to Ref. [19] for details. We also note that the essential transformations needed to do CIS(D) calculations are obtained as subsets of the CC2 transformations and the algorithm therefore apply for this model as well.

3. Application to benzene

3.1. Basis sets

We report CC2 calculations of the singlet excitation energies of benzene. We first discuss the basis

set and then go on to compare the CC2 results with recent CASPT2 [21] and SOPPA [22] results and experiment.

The results of the CC2 basis set investigation are given in Tables 1 and 2. Table 1 gives information about the basis sets and lists the total energies obtained in HF, MP2 and CC2 calculations. Table 2 gives the singlet excitation energies, classified as valence and Rydberg $\pi\pi^*$ and $\pi\sigma^*$ excitations as in the study of Lorentzon et al. [22]. In addition to the $n = 3$ Rydberg series we give a few results for the $n = 4, 5, 6$ series converging to the first ionization potential, and for the first state of E_{2g} symmetry corresponding to the second ionization potential. All calculations are carried out at the same geometry as in the CASPT2 and SOPPA studies.

The basis set study focuses on a systematic extension of the aug-cc-pVDZ basis of Dunning with diffuse functions placed at the center of mass (CM) to describe the Rydberg states. When saturation is obtained in the CM functions, the aug-cc-pVDZ

Table 1
Basis set description and C_6H_6 total molecular energies in hartree ^a

Basis	Atom fixed basis	CM functions	Cont./prim.	HF	MP2	CC2
pVDZ	C: [941/321] H: [41/21]		114 /198	-230.722061	-231.520625	-231.527855
aug-pVDZ	C: [1052/432] H: [52/32]		192 /276	-230.728102	-231.556186	-231.563272
aug-pVDZ-CM8	C: [1052/432] H: [52/32]	CM: [888/888] see Ref. [23]	264/348	-230.729133	-231.558858	-231.565954
aug-pVDZ-CM1(ANO)	C: [1052/432] H: [52/32]	CM: [888/111] see Ref. [21]	201/348	-230.728156	-231.556390	-231.563476
aug-pVDZ-CM1	C: [1052/432] H: [52/32]	CM: [111/111] 0.01	201/285	-230.728157	-231.556382	-231.563468
aug-pVDZ-CM2	C: [1052/432] H: [52/32]	CM: [222/222] (0.01,0.00333)	210/294	-230.728171	-231.556430	-231.563516
aug-pVDZ-CM3	C: [1052/432] H: [52/32]	CM: [333/333] (0.01,0.00333, 0.00111)	219/303	-230.728175	-231.556442	-231.563528
aug-pVDZ-CM2(t)	C: [1052/432] H: [52/32]	CM: [222/222] (0.01,0.03)	210/294	-230.728401	-231.557151	-231.564236
pVTZ	C:[10521/4321] H: [521/321]	H: [521/321]	264/348	-230.779012	-231.822079	-231.831772
aug-pVTZ-CM2	C:[11632/5432] H: [632/432]	CM: [222/222] (0.01,0.00333)	432/516 (0.01,0.00333)	-230.780888	-231.855173	-231.864721
ANO1:	C:[1494/431] H: [84/21]	CM: [888/111] see Ref. [21]	147/558	-230.771810	-230.634979	-231.666327
ANO2:	C:[1494/432] H: [84/32]		192/486	-230.781011	-230.696847	-231.706550

^a Geometry as in Ref. [21]. $R_{CC} = 1.3950 \text{ \AA}$, $R_{CH} = 1.0850 \text{ \AA}$.

basis is replaced by the aug-cc-pVTZ basis to investigate the effect of an improved description of the valence region. The augmentation with CM functions was done both using the contracted optimized atomic natural orbital (ANO) center function of Lorentzon et al. and by adding systematically sets of s, p, d primitive functions. The latter procedure started with the exponents (0.01) for the CM primitive functions (CM1) and diffuse functions were added in an even-tempered fashion giving the sets (0.01, 0.0033) (CM2) and (0.01, 0.0033, 0.0011) (CM3). The effect of adding more tight functions were examined using the set of exponents (0.01, 0.03) (CM2(t)). Calculations are also reported with the uncontracted set of orbitals from the ANO Rydberg set (CM8), corresponding to the primitive functions suggested by Kaufmann et al. [23].

From Table 2 it is seen that adding the ANO CM function and a single primitive set with exponent (0.01) gives similar results with differences less than 0.01 eV. The addition of one more diffuse set of CM functions with exponent 0.0033 has little or no effect on the excitation energies except that one additional Rydberg state of ${}^1E_{2g}$ symmetry is obtained at 8.173 eV. Adding further diffuse or tight CM functions have no effect on the reported excitation energies. The CM functions (0.01, 0.0033) thus appear sufficient for an accurate description of the Rydberg character of the excitations considered. Similar conclusions can be made comparing with the cc-pVDZ-CM8 basis set results. It is seen that results of similar quality are obtained for the basis set with a few primitive functions as with a contracted set of spd functions.

Table 2
C₆H₆ singlet excitation energies in eV ^a

Basis	cc-pVDZ	aug-cc-pVDZ	aug-cc-pVDZ-CM8	aug-cc-pVDZ-CM1(ANO)	aug-cc-pVDZ-CM1	aug-cc-pVDZ-CM2	aug-cc-pVDZ-CM3	aug-cc-pVDZ-CM2(t)	aug-cc-pVTZ-CM2
1^1B_{2u} (V- $\pi\pi^*$)	5.384	5.392		5.274	5.274	5.274	5.274	5.274	5.232
1^1B_{1u}	6.796	6.502		6.502	6.502	6.502	6.502	6.502	6.463
1^1E_{1u}	7.635	7.173	6.968	6.984	6.992	6.991	6.991	6.987	7.070
2^1E_{2g}	9.174	8.997	8.959	8.948	8.948	8.951	8.951	8.906	8.909
2^1E_{1u} (R- $\pi\pi^*$, $n=3$)		7.981	7.275	7.284	7.284	7.283	7.283	7.282	7.319
2^1A_{1g}		8.888	7.623	7.640	7.656	7.644	7.644	7.642	7.806
1^1E_{2g}		8.739	7.618	7.634	7.648	7.638	7.638	7.649	7.798
1^1A_{2g}		8.850	7.648	7.665	7.680	7.667	7.667		7.829
1^1E_{1g} (R- $\pi\sigma^*$, $n=3$)		6.350	6.297	6.307	6.304	6.304	6.304	6.302	6.452
1^1A_{2u}		6.883	6.805	6.813	6.811	6.811	6.811	6.809	6.970
1^1E_{2u}		6.947	6.862	6.870	6.869	6.868	6.869	6.866	7.028
1^1A_{1u}		7.035	6.937	6.945	6.944	6.943	6.944	6.942	7.120
1^1B_{2g}		7.578	7.431	7.438	7.439	7.436	7.436	7.437	7.600
1^1B_{1g}		7.565	7.420	7.428	7.429	7.425	7.426	7.426	7.587
2^1E_{1g}		7.575	7.367	7.412	7.425	7.422	7.422	7.392	7.557
3^1E_{1g}		8.174	7.439	7.459	7.488	7.482	7.481	7.451	7.613
3^1E_{2g} (R- $e_{2g}\sigma-a_{1g}$, $n=3$)		8.827	8.769	8.783	8.781	8.781	8.780	8.777	8.879
1^1E_{2g} (R- $\pi\pi^*$, $n=4$)			8.150			8.173	8.164		8.339
1^1A_{1g}			8.155			8.179	8.169		8.339??
1^1A_{2g}			8.161			8.185	8.174		8.353
1^1E_{2g} (R- $\pi\pi^*$, $n=5$)			8.394				8.403		
1^1A_{1g}			8.397				8.406		
1^1A_{2g}			8.400				8.408		
1^1E_{2g} (R- $\pi\pi^*$, $n=6$)			8.577						
1^1A_{1g}			8.582						
1^1A_{2g}			8.584						

^a Geometry as in Ref. [21] The geometry is $R_{CC} = 1.3950 \text{ \AA}$ and $R_{CH} = 1.0850 \text{ \AA}$. Excitation energies are converged to an uncertainty of 0.001 eV. The blank entries are due to excitations not obtained due to basis set inadequacy, or from converging only a specified number of roots.

To address the problem of saturating the valence space, we have carried out calculations using an aug-cc-pVTZ basis augmented with the CM2 functions. Going from aug-cc-pVDZ-CM2 to aug-cc-pVTZ-CM2, we improve the description of the valence space and include additional 1f(C) and 1d(H) diffuse functions. Improving the valence space description gives a significant decrease in the total energy of the ground state (compare the cc-pVDZ and cc-pVTZ results in Table 1). The additional diffuse atom centered functions have some effect on the total energy, whereas the CM functions have very little effect. For the excitation energies in Table 2, we observe changes in the valence excitation energies ranging from -0.04 to 0.08 eV. The Rydberg excitations shift by 0.16 ± 0.03 eV going from the double to the triple zeta basis description. The 2^1E_{1u} state is an exception that only shifts by 0.04 eV. For a balanced description of the ground state and the Rydberg states it is essential to have a good description of the valence region. All Rydberg states (except the one denoted 3^1E_{2g}) have the same cation core with an additional electron in a Rydberg orbital. The constant difference between aug-cc-pVDZ-CM2 and aug-cc-pVTZ-CM2 suggests that the added flexibility in the aug-cc-pVTZ-CM2 basis is most important for the ground state, which contains one more valence electron than the Rydberg state. We conclude that a basis set of augmented double zeta polarization quality may give errors of the order 0.1 – 0.2 eV, even when supplemented with diffuse functions.

3.2. Excitation energies

In Table 3, we report the singlet excitation energies of benzene using CCS, CC2 and CCSD in the ANO basis of Lorentzon et al. (ANO1). The CASPT2 result of Ref. [21] and the RPA and SOPPA results of Ref. [22] are also listed in Table 3 and use the ANO1 basis. We note that this ANO basis set is of double zeta quality. From Table 1, we see that the total energies of the ground state are somewhat lower than those obtained with Dunning's valence double zeta basis. The triple zeta results are lower still. The lower energy of the ANO basis compared to Dunning's valence double zeta basis is probably due to a better description of the core, since the

ANO basis contains considerably more tight primitive functions. The improved description of the core is unimportant for describing the excitation energies, and the CC2 excitation energies in the ANO basis and in the aug-cc-pVDZ-CM2 basis are quite similar.

Comparing CASPT2 and CC2 in the ANO1 basis, we find differences less than 0.2 eV for all the Rydberg excitations. For the valence excited states the differences are larger, but still less than 0.4 eV for the 1^1B_{2u} , 1^1B_{1u} and 1^1E_{1u} states. The 2^1E_{2g} state will be discussed later. The differences between CC2 and SOPPA are larger, up to 0.6 eV, with the SOPPA excitation energies usually being smaller than the CC2 excitation energies. Comparing excitation energies in the CCS-CC2-CCSD sequence, almost all excitations, shift between -0.1 and 0.2 eV going from CC2 to CCSD. The shifts are in opposite direction of the shifts from CCS to CC2, which are between -0.7 and 0.7 eV. CC2 clearly represents a major improvement on CCS and is relatively close to CCSD.

CASPT2 calculations have also been reported using another ANO basis [23] (ANO2). It is noteworthy that differences of up to 0.2 eV are obtained in these different CASPT2 calculations. Similar differences are also found in CC2 calculations using the two different ANO basis sets. However, there is little correspondence between the differences obtained in the CASPT2 and in CC2 calculations for the individual excitations. This may be a consequence of the use of different active spaces in the CASPT2 calculations.

Since the basis set error is at least a few tenths of an eV and no investigations of geometry and vibrational effects have been performed in this study, it is not possible to make definite statements concerning the relative performance of the various models from a comparison with experiment. However, the neglect of zero-point vibration and geometry relaxation in the excited states will typically lead to a too high excitation energy. Assuming additivity of the basis set errors, we find that the CASPT2 results will probably not be improved in a triple zeta basis. The CC2 error relative to the experimental results as listed in Table 3 is of the order 0.2 to 0.3 eV for the valence excitations (again excluding the 2^1E_{2g} excitation). We find that the shifts in excitation energies when going from double-zeta to triple-zeta quality

Table 3
 C_6H_6 singlet excitation energies in eV^a , weight of singles excitation vector in CCSD

Basis	Method	Exp. ^b	aug-cc-pVTZ-CM2		ANO1		ANO2						
			CC2	CASSCF Ref. [21]	CASPT2 Ref. [21]	CCS	CC2	CCSD	%T ₁ (CCSD)	RPA Ref. [22]	SOPPA Ref. [22]	CASPT2 Ref. [24]	CC2
1^1B_{2u} (V- $\pi\pi^*$)		4.90	5.232	4.80	4.84	6.028	5.265	5.189	91	5.82	4.69	4.70	5.245
1^1B_{1u}		6.20	6.463	7.32	6.30	6.193	6.556	6.590	95	5.88	6.01	6.10	6.517
1^1E_{1u}		6.94	7.070	8.53	7.03	7.176	7.018	7.171	95	7.16	6.75	7.06	7.213
2^1E_{2g}		7.8 / 9.4	8.909	7.96	7.90	10.583	8.967	9.177	88			7.77	8.914
3^1E_{2g} (R- $\sigma\sigma^*$)			8.879			10.835	8.918	9.413	95				
2^1E_{1u} (R- $\pi\pi^*$)		7.41	7.319	6.46	7.16	8.056	7.371	7.579	94	7.50	7.03		7.03
2^1A_{1g}		7.81	7.806	7.14	7.74	7.778	7.656	7.855	96	7.77	7.56		7.56
1^1E_{2g}		7.81	7.798	7.09	7.77	7.801	7.651	7.847	95	7.80	7.55		7.55
1^1A_{2g}		7.81	7.829	7.08	7.81	7.856	7.681	7.880	95	7.85	7.59		7.59
1^1E_{1g} (R- $\pi\sigma^*$)		6.334	6.452	6.26	6.38	6.620	6.403	6.547	95	6.54	6.18		6.18
1^1A_{2u}		6.932	6.970	6.66	6.86	6.950	6.838	6.988	96	6.94	6.70		6.70
1^1E_{2u}		6.953	7.028	6.74	6.91	7.119	6.892	7.056	95	7.11	6.76		6.76
1^1A_{1u}		–	7.120	6.82	6.99	7.287	6.962	7.139	95	7.28	6.83		6.83
1^1B_{2g}		7.460	7.600	7.33	7.58	7.685	7.466	7.659	95	7.68	7.35		7.35
1^1B_{1g}		7.460	7.587	7.29	7.58	7.699	7.461	7.660	95	7.70	7.35		7.35
2^1E_{1g}		7.535	7.557	7.33	7.57	7.596	7.457	7.639	95	7.59	7.34		7.34
3^1E_{1g}		–	7.613	7.37	7.57	7.729	7.519	7.698	95	7.73	7.40		7.40

^a Geometry as in Ref. [21]: $R_{CC} = 1.3950 \text{ \AA}$ and $R_{CH} = 1.0850 \text{ \AA}$.

^b Experimental data from the compilation in Ref. [21]. There is some uncertainty about the 2^1E_{2g} state, see text.

for the Rydberg states do not improve the agreement with the experimental excitation energies as compiled by Lorentzon et al. This suggests that the calculation of the Rydberg excitation energies in benzene is not as easy as may appear on the basis of the CASPT2 calculations. These findings thus call for more complete studies of the benzene spectrum.

The 2^1E_{2g} excitation is special due to a large fraction of double replacement character relative to the ground state. The double replacement character is not described at all in CCS and RPA, which is the reason why the CCS result is completely erroneous. In CC2, the double excitation part is only described to zero order, and the accuracy is therefore rather limited. In CCSD, however, the description of the double replacement character is improved to first order. The t_1 weight is 88% in CCSD for the 2^1E_{2g} excitation and it is therefore a borderline case in CCSD. It could be well described in CCSD, however, it may also be the case that the double excitation contribution is underestimated. For the 2^1E_{2g} we may summarise that using ANO1 CASPT2 gives 7.90 eV which is substantially different from the CC2 value of 8.967 and the CCSD value of 9.177. The experimental excitation energy used to identify this excitation is from a laser flash experiment of Nakashima et al. [25]. Three excited states, 7.0, 7.8 and 9.4 eV above the ground state were identified. The first state has been assigned $^1E_{1u}$. Lorentzon et al. chose to assign the second state as 2^1E_{2g} . More elaborate studies, including large basis set CCSD calculations and investigation of the effect of triple excitations are warranted and already in progress [19].

4. Concluding remarks

We have presented a direct atomic integral driven implementation of the CC2 model. CCSD scales as N^6 whereas CC2 scales as N^5 , and in conventional calculations where the integrals are stored on disk, CC2 calculations are therefore approximately a factor N faster than CCSD. However, in integral direct CC2, calculation of the integrals represents the major computational effort. The performance of the integral code thus determines the overall performance. Consider one iteration for obtaining an improved vector

function or a linear transformation of the Jacobian and denote the time used in the integral code T_{int} , (assumed to be the same in CCSD and CC2), the time used in CCSD T_{CCSD} , and the time used in CC2 T_{CC2} . The overall factor between the time used in CCSD and in CC2 is thus

Overall time in CCSD

Overall time in CC2

$$= \frac{T_{\text{int}} + T_{\text{CCSD}}}{T_{\text{int}} + T_{\text{CC2}}} \cong \frac{k_3 N^4 + k_1 O^2 N^4}{K_3 N^4 + k_2 O N^4} = \frac{k_3 + k_1 O^2}{k_3 + k_2 O},$$

where k_1 , k_2 and k_3 are different characteristic constants and O is the number of occupied orbitals. Only the leading terms in CC2 and CCSD are included. For fixed N , the relative cost of CC2 compared to CCSD is thus crucially dependent on the number of electrons and the performance of the integral code.

Diffuse basis functions are required in the calculation of excitation energies for Rydberg states. Our investigations indicate that simple primitive center of mass (CM) functions are as good as CM functions constructed from elaborate contraction schemes containing several primitive functions. No attempt was made to optimize the exponents of the primitive functions, but saturation towards diffuseness appears to be reached rather easily for the considered Rydberg states. The strategy of using CM functions appears to be much more efficient than adding diffuse atom centered functions. The description of the valence space requires a basis set beyond double zeta quality to obtain an accuracy better than 0.2 eV for both valence and Rydberg states.

Based on the present study a detailed comparison with experiment is not possible. The unexpectedly large basis set effects in the calculation of excitation energies for the Rydberg states as well as the discrepancies between CASPT2 and CC2 and CCSD for both valence and Rydberg states suggest that more elaborate investigations are required. These have already been undertaken using large-scale CCSD and CC3 calculations [19].

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