CC3 triplet excitation energies using an explicit spin coupled excitation space

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Triplet excitation energies are derived in the approximate triples model CC3 using an explicit spin coupled triplet excitation space. The explicit spin coupled excitation space gives considerable computational savings compared to the spin–orbital approach. Sample calculations are performed on the Be_2 and CH_2 systems and the performance of the CC3 results are evaluated from a comparison with full configuration interaction (FCI) results. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1388042]

I. INTRODUCTION

The accurate calculation of excitation energies is a difficult task in quantum chemistry since it requires a balanced description of the ground and the excited states. In the framework of linear response methodology coupled cluster (CC) theory may be used to obtain a balanced describtion and hierarchies of CC models have been established where improved accuracy is obtained at each level in the hierarchy. In previous publications the accuracy of singlet excitation energies has been considered using the hierarchy CCS, CC2, CCSD, CC3, CCSDT, …[1–3] where CCS, CCSD and CCSDT are the standard coupled cluster models that include all singles, all singles and doubles, and all singles, doubles and triples excitations, respectively. The CC2 model[4] is an approximation to the CCSD model, where the doubles amplitudes are treated approximately, and CC3[5,6] is an approximation to CCSDT where the triples amplitudes are treated approximately. In this paper we consider the calculation of triplet excitation energies. Earlier CCS, CC2[7] and CCSD[8] triplet excitation energies have been derived using an explicit spin coupled excitation space. Here we describe a CC3 implementation that also use an explicit spin coupled excitation space. We initially discuss how to span the triple triplet excitation space, and then derive the explicit formulas to calculate CC3 triplet excitation energies.

Stanton and Bartlett have previously presented triplet excitation energies at the CCSD level using a spin–orbital basis formulation.[9] The use of an explicit spin coupled basis gives considerable savings in the operation count compared to the above approach. Triples were first introduced into the calculation of excitation energies by Watts and Bartlett.[10,11] In this paper we examine the performance of the triples as introduced in the CC3 model for the calculation of triplet excitation energies. Sample calculations are presented for Be_2 and CH_2. The Be_2 system was chosen since an accurate calculation of the ground and excited state energies for the beryllium dimer is sensitive to electron-correlation effects. Due to the presence of a large static correlation in this molecule the precision of the CC3 model will probably be somewhat lower than for most other molecules.[12] Theoretical studies of the ground state of Be_2 have been numerous,[13–18] whereas studies of the excited states are more sparse.[18–22] The CH_2 system was chosen since it is a commonly studied system which has a small energy difference between the triplet ground state and the lowest singlet state.[23–30]

II. THEORY

A. Coupled cluster theory

Starting from the single-reference coupled cluster ansatz,

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

the similarity transformed Schrödinger equation can be written as

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

where $|\mathrm{HF}\rangle$ is the Hartree Fock reference state, H is the Hamiltonian and T the cluster operator. For an M electron system the cluster operator becomes

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

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

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

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

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giving the amplitude equations

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

The projection with the reference state $|\mathrm{HF}\rangle$ gives the coupled cluster energy,

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

By truncating the cluster operator T after the single, double or triple excitation level one obtains the coupled cluster models CCS, CCSD, and CCSDT, respectively. The CC3 model is an approximation to the CCSDT model where the singles excitation amplitudes are treated as zeroth-order parameters due to their role as orbital relaxation parameters and where the CCSDT triples amplitudes equation is truncated after the lowest nonvanishing order in perturbation theory. The ground state equations for the CC3 model are[6]

$$\langle \mu_1 | \exp(-T_2) \hat{H} \exp(T_2) | HF \rangle + \langle \mu_1 | [H, T_3] | HF \rangle = 0, \tag{8}$$

$$\langle \mu_2 | \exp(-T_2) \hat{H} \exp(T_2) | HF \rangle + \langle \mu_2 | [\hat{H}, T_3] | HF \rangle = 0, \tag{9}$$

$$\langle \mu_3 | [F, T_3] | HF \rangle + \langle \mu_3 | [\hat{H}, T_2] | HF \rangle = 0, \tag{10}$$

where F is the Fock operator and $\hat{H} = \exp(-T_1) H \exp(T_1)$ the T_1 transformed Hamiltonian.

In coupled cluster response theory excitation energies are obtained as the eigenvalues ω of the nonsymmetric eigenvalue equation,

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

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

$$A_{\mu\nu} = \frac{d\Omega_\mu}{dt_\nu}, \tag{12}$$

and $\mathbf{S}$ is the overlap matrix,

$$S_{\mu_i \nu_j} = \langle \mu_i | \tau_{\nu_j} | \mathrm{HF} \rangle. \tag{13}$$

It should be noted that the overlap matrix is the unit matrix in the spin orbital basis. In the CC3 model the Jacobian becomes

$$\mathbf{A}^{\mathrm{CC3}} = \begin{pmatrix} \langle \mu_1 | [\hat{H} + [\hat{H}, T_2], \tau_{\nu_1}] | \mathrm{HF} \rangle & \langle \mu_1 | [\hat{H}, \tau_{\nu_2}] | \mathrm{HF} \rangle & \langle \mu_1 | [H, \tau_{\nu_3}] | \mathrm{HF} \rangle \\ \langle \mu_2 | [\hat{H} + [\hat{H}, T_2 + T_3], \tau_{\nu_1}] | \mathrm{HF} \rangle & \langle \mu_2 | [\hat{H} + [\hat{H}, T_2], \tau_{\nu_2}] | \mathrm{HF} \rangle & \langle \mu_2 | [\hat{H}, \tau_{\nu_3}] | \mathrm{HF} \rangle \\ \langle \mu_3 | [[\hat{H}, T_2], \tau_{\nu_1}] | \mathrm{HF} \rangle & \langle \mu_3 | [\hat{H}, \tau_{\nu_2}] | \mathrm{HF} \rangle & \langle \mu_3 | [F, \tau_{\nu_3}] | \mathrm{HF} \rangle \end{pmatrix}. \tag{14}$$

For the calculation of triplet excitation energies it is convenient to use excitation operators that are explicit spin coupled to triplet spin symmetry. We have recently discussed the explicit spin coupling of the singles and doubles excitation spaces and have determined a nonredundant orthonormal triplet basis leading to a unit overlap matrix. In this paper we discuss the explicit triplet spin coupling of the triples excitation space and determine a nonredundant triples triplet excitation space. However, this triples triplet excitation space does not lead to an orthonormal basis and we introduce a biorthonormal basis to ensure that the overlap matrix is unity.

B. Parametrization of the triplet excitation space

The strategy for spanning the triplet excitation space is to build the excitation operators from single replacement excitation operators that have singlet or triplet symmetry,

$$S^{0,0}_{pq} = \frac{1}{\sqrt{2}} (a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta}) = \frac{1}{\sqrt{2}} E_{pq}, \tag{15}$$

$$T^{1,0}_{pq} = \frac{1}{\sqrt{2}} (a^\dagger_{p\alpha} a_{q\alpha} - a^\dagger_{p\beta} a_{q\beta}) = \frac{1}{\sqrt{2}} T_{pq}. \tag{16}$$

$T^{1,0}$ and $S^{0,0}$, and therefore also T and E, are components of triplet and singlet tensor operators with zero spin projection.[31] Products containing one T and any number of E operators will therefore also be components of triplet tensor operators with zero spin projection. An explicit triplet spin coupled excitation space can therefore be expressed in terms of the products containing one T and any number of E operators. The problem is, however, for a given excitation level to find a nonredundant set. In a recent publication we have parametrized the doubles excitation space as

$$T_{ai} = a^\dagger_{a\alpha} a_{i\alpha} - a^\dagger_{a\beta} a_{i\beta}, \tag{17}$$

$${}^{(+)}T_{aibj} = (T_{ai} E_{bj} + T_{bj} E_{ai}) \begin{matrix} a>b \\ i>j \end{matrix}, \tag{18}$$

$${}^{(-)}T_{aibj} = (T_{ai} E_{bj} - T_{bj} E_{ai}) (ai) > (bj), \tag{19}$$

and used it in the implementation of the CC2 and CCSD model described in Ref. 7 and Ref. 8, respectively. The operator ${}^{(+)}T_{aibj}$ has the symmetries

$${}^{(+)}T_{aibj} = {}^{(+)}T_{bjai} = -{}^{(+)}T_{ajbi} = -{}^{(+)}T_{biaj}, \tag{20}$$

while for ${}^{(-)}T_{aibj}$ we have

$${}^{(-)}T_{aibj} = -{}^{(-)}T_{bjai}. \tag{21}$$

In order to parametrize the triples excitation space we recognize that $T_{ai} E_{bj} E_{ck}$ has 36 components if all indices are different, but that only nine are linear independent. If either two occupied or two virtual indices are equal then there are only 3 linear independent components, whereas if there are two times two indices that are equal then there is

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TABLE I. Triple specific terms to the CC3 transformed vectors for triplet excitation energies.

$\langle_i^a(3)\|[H,{}^{(3)}R_3]\|\mathrm{HF}\rangle$	$=2\Sigma_{delm}({}^{(3)}R_{lim}^{dae}L_{meld}+({}^{(3)}R_{lmi}^{ade}+{}^{(3)}R_{lmi}^{eda})g_{meld})$	(I)
$\langle_{ij}^{ab}(+)\|[[\hat{H},T_3],{}^{(3)}R_1]\|\mathrm{HF}\rangle$	$=\frac{1}{2}P_{ij}^{ab}\tilde{P}_{ij}(\Sigma_{dl}t_{ijl}^{adb}\Sigma_m\hat{g}_{lmmd}-\Sigma_{dlm}(2t_{iml}^{adb}-t_{mil}^{adb}-t_{ilm}^{adb})\hat{g}_{lJmd}$	(II)
	$+\Sigma_{edl}(2t_{ilj}^{ade}-t_{lij}^{ade}-t_{ijl}^{ade})\hat{g}_{beld})=\frac{1}{2}P_{ij}^{ab}\tilde{P}_{ij}Q_{ij}^{ab}$	
$\langle_{ij}^{ab}(-)\|[[\hat{H},T_3],{}^{(3)}R_1]\|\mathrm{HF}\rangle$	$=\frac{1}{2}\tilde{P}_{ij}^{ab}Q_{ij}^{ab}$	(III)
$\langle_{ij}^{ab}(+)\|[\hat{H},{}^{(3)}R_3]\|\mathrm{HF}\rangle$	$=\frac{1}{2}P_{ij}^{ab}\tilde{P}_{ij}(\Sigma_{ld}({}^{(3)}R_{lji}^{dba}+2\,{}^{(3)}R_{ijl}^{abd}+{}^{(3)}R_{ilj}^{dba}+{}^{(3)}R_{lij}^{bda})\hat{F}_{ld}$	(IV)
	$+\Sigma_{del}(2{}^{(3)}R_{lij}^{deb}-{}^{(3)}R_{lij}^{edb}+2{}^{(3)}R_{jil}^{bed}+2{}^{(3)}R_{ijl}^{ebd}+2{}^{(3)}R_{jil}^{dbe}-{}^{(3)}R_{lji}^{bde})\hat{g}_{aeld}$	
	$+\Sigma_{dlm}(2{}^{(3)}R_{lmi}^{dab}-{}^{(3)}R_{mli}^{dab}+2{}^{(3)}R_{iml}^{bad}+2{}^{(3)}R_{mil}^{abd}+2{}^{(3)}R_{lim}^{adb}-{}^{(3)}R_{ilm}^{dba})\hat{g}_{ldmj})$	
$\langle_{ij}^{ab}(-)\|[\hat{H},{}^{(3)}R_3]\|\mathrm{HF}\rangle$	$=\tilde{P}_{ij}^{ab}(\Sigma_{ld}{}^{(3)}R_{ijl}^{abd}\hat{F}_{ld}+\Sigma_{del}({}^{(3)}R_{jil}^{bde}+{}^{(3)}R_{ijl}^{ebd})\hat{g}_{aeld}$	(V)
	$+\Sigma_{dlm}({}^{(3)}R_{iml}^{adb}+{}^{(3)}R_{mil}^{bad})\hat{g}_{ldmj})$	
$\langle_{ijk}^{abc}(3)\|[[H,T_2],{}^{(3)}R_1]\|\mathrm{HF}\rangle$	$=\frac{1}{2}P_{jk}^{bc}\tilde{P}_{jk}(\Sigma_d t_{ik}^{ad}(\hat{g}_{\bar{c}\bar{d}bj}-\hat{g}_{\bar{c}\bar{j}bd}-\hat{g}_{\bar{c}\bar{j}\bar{b}d})+\Sigma_d t_{jk}^{bd}(\hat{g}_{\bar{c}\bar{d}ai}-\hat{g}_{\bar{a}\bar{i}cd}-\hat{g}_{\bar{a}\bar{i}\bar{c}d})$	(VI)
	$+\Sigma_d t_{ki}^{bd}(\hat{g}_{\bar{a}\bar{d}cj}-\hat{g}_{\bar{c}\bar{j}ad}-\hat{g}_{\bar{c}\bar{j}\bar{a}d})-\Sigma_l t_{il}^{ac}(\hat{g}_{\bar{l}\bar{k}bj}-\hat{g}_{b\bar{k}\bar{l}j}-\hat{g}_{\bar{b}\bar{k}lj})$	
	$-\Sigma_l t_{jl}^{bc}(\hat{g}_{\bar{l}\bar{k}ai}-\hat{g}_{\bar{a}\bar{i}\bar{l}k}-\hat{g}_{\bar{a}\bar{i}\bar{l}e})-\Sigma_l t_{kl}^{ba}(\hat{g}_{\bar{l}\bar{i}cj}-\hat{g}_{\bar{c}\bar{j}\bar{l}i}-\hat{g}_{\bar{c}\bar{j}\bar{l}i}))$	
$\langle_{ijk}^{abc}(3)\|[\hat{H},{}^{(3)}R_{2+}]\|\mathrm{HF}\rangle$	$=\frac{1}{2}P_{jk}^{bc}\tilde{P}_{jk}(\Sigma_d{}^{(+)}R_{kj}^{db}\hat{g}_{cdai}-\Sigma_l{}^{(+)}R_{lj}^{cb}\hat{g}_{ailk})$	(VII)
$\langle_{ijk}^{abc}(3)\|[\hat{H},{}^{(3)}R_{2-}]\|\mathrm{HF}\rangle$	$=P_{jk}^{bc}\tilde{P}_{jk}(\Sigma_d({}^{(-)}R_{ki}^{cd}\hat{g}_{bjad}+{}^{(-)}R_{ik}^{ad}\hat{g}_{cjbd})$	(VIII)
	$+\Sigma_l({}^{(-)}R_{lk}^{ac}\hat{g}_{bjli}+{}^{(-)}R_{li}^{ba}\hat{g}_{cjlk}))$	
$\langle_{ijk}^{abc}(3)\|[F,\tau_{\nu_3}]\|\mathrm{HF}\rangle$	$={}^{(3)}R_{ijk}^{abc}(\epsilon_a-\epsilon_i+\epsilon_b-\epsilon_j+\epsilon_c-\epsilon_k)$	(IX)

only one linear independent component. The triples linear excitation space may for all cases be spanned by the linear independent excitation operators:

$$ {}^{(3)}T_{(ai)bjck}=E_{ai}(T_{bj}E_{ck}+T_{ck}E_{bj}), \quad \text{with} \begin{pmatrix} b>c \\ j>k \end{pmatrix}, \tag{22} $$

which satisfies the symmetry relation,

$$ {}^{(3)}T_{(ai)bjck}={}^{(3)}T_{(ai)ckbj}=-{}^{(3)}T_{(ai)bkcj}={}^{(3)}T_{(ai)cjbk}. \tag{23} $$

Introducing the triples triplet amplitudes ${}^{(3)}R_{ijk}^{abc}$ corresponding to the linear independent set of excitation operators we may write the triples triplet tensor operator as

$$ {}^{(3)}R_3=\sum_{ai}\sum_{\substack{b>c\\ j>k}}{}^{(3)}R_{ijk}^{abc}E_{ai}(T_{bj}E_{ck}+T_{ck}E_{bj}), \tag{24} $$

TABLE II. The total energy of the reference states.

Model	Total energy of the reference state
$Be_2\ 1^1\Sigma^+$ state with aug-cc-pVDZ	
SCF	−29.131 662 386 7
CC2	−29.195 659 217 5
CCSD	−29.229 995 625 2
CC3	−29.233 138 295 1
FCI	−29.234 701 529 3
$Be_2\ 1^1\Sigma^+$ state with aug-cc-pVTZ	
SCF	−29.132 782 581 1
CC2	−29.203 921 580 1
CCSD	−29.234 633 005 3
CC3	−29.238 509 785 9
FCI	−29.240 039 087 9
$CH_2\ 1^1A_1$ state with aug-cc-pVDZ	
SCF	−38.884 253 669 8
CC2	−39.000 531 953 4
CCSD	−39.027 888 727 5
CC3	−39.031 483 828 6
FCI	−39.032 446 148 9

straining that the indices $\{a,i\}$ are special. Extending the definition of the excitation amplitudes to arbitrary indices with the excitation amplitudes satisfying the same symmetry relations as the excitation operators in Eq. (23), one finds for ${}^{(3)}R_3$ the alternative formulations:

$$ \begin{aligned} {}^{(3)}R_3&=\frac{1}{4}\sum_{abcijk}{}^{(3)}R_{ijk}^{abc}E_{ai}(T_{bj}E_{ck}+T_{ck}E_{bj}) \\ &=\frac{1}{2}\sum_{abcijk}{}^{(3)}R_{ijk}^{abc}E_{ai}T_{bj}E_{ck}, \end{aligned} \tag{25} $$

which constitute a convenient representation for the triples triplet cluster operator.

C. Triplet basis

The triplet basis is defined by the operation of the triplet excitation operators on the reference state. Thus the triplet kets are

$$ T_{ai}|\mathrm{HF}\rangle=\left|({}^{(3)}{}_i^a)\right\rangle, \tag{26} $$

TABLE III. Triplet excitation energies in mE_h for Be_2 in the aug-cc-pVDZ basis set. The coupled cluster results are the error compared to FCI.

	CCS	CC2	CCSD	CC3	FCI
$1\,^3\Sigma_g^+$	30.8	7.31	−5.12	−3.09	155.38
$2\,^3\Sigma_g^+$	29.6	14.3	0.49	0.26	196.27
$1\,^3\Pi_u$	38.6	13.9	1.55	0.50	110.372
$2\,^3\Pi_u$	−62.2	−55.5	−12.4	−5.17	117.909
$1\,^3\Sigma_g^-$	—	—	−26.9	−13.9	134.351
$1\,^3\Sigma_u^+$	37.0	16.4	4.32	1.79	42.207
$2\,^3\Sigma_u^+$	26.3	11.9	0.10	0.17	183.983
$1\,^3\Pi_g$	32.2	12.7	0.77	0.19	52.3497

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$$(T_{ai}E_{bj}+T_{bj}E_{ai})|\mathrm{HF}\rangle=\left|(+)\begin{matrix}ab\\ij\end{matrix}\right\rangle \quad \left(\begin{matrix}a>b\\i>j\end{matrix}\right), \tag{27}$$

$$(T_{ai}E_{bj}-T_{bj}E_{ai})|\mathrm{HF}\rangle=\left|(-)\begin{matrix}ab\\ij\end{matrix}\right\rangle \quad (ai)>(bj), \tag{28}$$

$$E_{ai}(T_{bj}E_{ck}+T_{ck}E_{bj})|\mathrm{HF}\rangle=\left|(3)\begin{matrix}cba\\kji\end{matrix}\right\rangle \quad \left(\begin{matrix}b>c\\j>k\end{matrix}\right). \tag{29}$$

The single and double excited kets as well as the adjoint of the single and double excited kets,

$$\left\langle\begin{matrix}a\\i\end{matrix}(3)\right|=\frac{1}{2}\langle\mathrm{HF}|\,T_{ia}, \tag{30}$$

$$\left\langle\begin{matrix}ab\\ij\end{matrix}(+)\right|=\frac{1}{8}\langle\mathrm{HF}|\,(E_{jb}T_{ia}+E_{ia}T_{jb}) \quad \left(\begin{matrix}a>b\\i>j\end{matrix}\right), \tag{31}$$

$$\left\langle\begin{matrix}ab\\ij\end{matrix}(-)\right|=\frac{1}{8}\langle\mathrm{HF}|\,(E_{jb}T_{ia}-E_{ia}T_{jb}) \quad (ai)>(bj), \tag{32}$$

form an orthogonal basis. The adjoint of the triples ket

$$\left\langle\overline{\begin{matrix}abc\\ijk\end{matrix}(3)}\right|=\frac{1}{8}\langle\mathrm{HF}|(T_{kc}E_{jb}+T_{jb}E_{kc})E_{ia} \quad \left(\begin{matrix}b>c\\j>k\end{matrix}\right), \tag{33}$$

is not orthogonal to the triples bra states,

$$\begin{aligned}&\left\langle\overline{\begin{matrix}fed\\nml\end{matrix}(3)}\right|E_{ck}(T_{ai}E_{bj}+T_{bj}E_{ai})|\mathrm{HF}\rangle\\&\quad=8P^{de}_{lm}\tilde{P}_{lm}P^{ab}_{ij}(\delta_{ad}\delta_{bf}\delta_{ce}\delta_{mi}\delta_{nk}\delta_{lj}\\&\qquad+\delta_{ad}\delta_{be}\delta_{cf}\delta_{mi}\delta_{nj}\delta_{lk}+\delta_{af}\delta_{be}\delta_{cd}\delta_{mk}\delta_{nj}\delta_{li}\\&\qquad+\delta_{ad}\delta_{bf}\delta_{ce}\delta_{mk}\delta_{nj}\delta_{li}+\delta_{ad}\delta_{be}\delta_{cf}\delta_{mj}\delta_{nk}\delta_{li}).\end{aligned} \tag{34}$$

The permutation operators are given by

$$P^{ab}_{ij}(A^{ab}_{ij})=A^{ab}_{ij}+A^{ba}_{ji}, \tag{35}$$

$$\tilde{P}_{ij}(A^{ab}_{ij})=A^{ab}_{ij}-A^{ab}_{ji}. \tag{36}$$

As we want the overlap matrix to be unity we use a biorthogonal basis satisfying

$$\left\langle\begin{matrix}efg\\nml\end{matrix}(3)\right|(3)\begin{matrix}ijk\\abc\end{matrix}\rangle=P^{ab}_{ij}\tilde{P}_{ij}(\delta_{ec}\delta_{nk}\delta_{bf}\delta_{mj}\delta_{ag}\delta_{li}), \tag{37}$$

where the explicit form of the bra states is given by

$$\begin{aligned}\left\langle\begin{matrix}abc\\ijk\end{matrix}(3)\right|=\frac{1}{80}\Bigg\{&9\left\langle\overline{\begin{matrix}abc\\ijk\end{matrix}(3)}\right|+\left\langle\overline{\begin{matrix}abc\\kji\end{matrix}(3)}\right|+\left\langle\overline{\begin{matrix}abc\\jik\end{matrix}(3)}\right|\\&+\left\langle\overline{\begin{matrix}bac\\ijk\end{matrix}(3)}\right|-\left\langle\overline{\begin{matrix}bac\\kji\end{matrix}(3)}\right|-\left\langle\overline{\begin{matrix}bac\\jik\end{matrix}(3)}\right|\\&+\left\langle\overline{\begin{matrix}cba\\ijk\end{matrix}(3)}\right|-\left\langle\overline{\begin{matrix}cba\\kji\end{matrix}(3)}\right|-\left\langle\overline{\begin{matrix}cba\\jik\end{matrix}(3)}\right|\Bigg\}.\end{aligned} \tag{38}$$

In the development of the linear transformation of the Jacobian on a trial vector it is useful to note that

$$\left\langle\begin{matrix}ab\\ij\end{matrix}(+)\right|E_{ck}T_{dl}|\mathrm{HF}\rangle=\frac{1}{2}\tilde{P}_{ij}P^{ab}_{ij}\,\delta_{aibj,ckdl}, \tag{39}$$

$$\left\langle\begin{matrix}ab\\ij\end{matrix}(-)\right|E_{ck}T_{dl}|\mathrm{HF}\rangle=\frac{1}{2}\tilde{P}^{ab}_{ij}\,\delta_{aibj,ckdl}, \tag{40}$$

$$\begin{aligned}&\left\langle\begin{matrix}abc\\ijk\end{matrix}(3)\right|T_{dl}E_{em}E_{fn}|\mathrm{HF}\rangle\\&\quad=\tfrac{1}{2}P^{bc}_{jk}\tilde{P}_{jk}(\delta_{af}\delta_{be}\delta_{cd}\delta_{in}\delta_{jm}\delta_{kl}+\delta_{ae}\delta_{bf}\delta_{cd}\delta_{im}\delta_{jn}\delta_{kl}\\&\qquad-\delta_{ad}\delta_{be}\delta_{cf}\delta_{il}\delta_{jm}\delta_{kn}).\end{aligned} \tag{41}$$

Here the permutation operators are defined as in Eqs. (35) and (36) and as

$$\tilde{P}^{ab}_{ij}(A^{ab}_{ij})=A^{ab}_{ij}-A^{ba}_{ji}. \tag{42}$$

Equation (41) is obtained from Eq. (37) using

$$\begin{aligned}T_{dl}E_{em}E_{fn}=\tfrac{1}{2}(&E_{em}(T_{dl}E_{fn}+T_{fn}E_{dl})\\&+E_{fn}(T_{dl}E_{em}+T_{em}E_{dl})\\&-E_{dl}(T_{em}E_{fn}+T_{fn}E_{em})).\end{aligned} \tag{43}$$

D. Transformation of the trial vector

Solving a large eigenvalue problem requires iterative methods. The computational most demanding step is the linear transformation of a trial vector with the Jacobian matrix

$$\rho=\mathbf{AR}, \tag{44}$$

where ρ is the transformed vector, **A** is the coupled cluster Jacobian and **R** is a trial vector which in component form may be expressed as

$$\mathbf{R}=\begin{pmatrix}{}^{(3)}R_1\\{}^{(+)}R_2\\{}^{(-)}R_2\\{}^{(3)}R_3\end{pmatrix}. \tag{45}$$

Using the triplet parametrization and the triplet basis functions introduced in Secs. II B and II C, respectively, the CC3 Jacobian from Eq. (14) can be written as

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TABLE IV. Weight of various excitation levels in the FCI wavefunction for excited states in Be_2, and the weight ($\%T_1$) of the single excitations in the coupled cluster calculations.

	$1\,^3\Sigma_g^+$	$2\,^3\Sigma_g^+$	$1\,^3\Pi_u$	$2\,^3\Pi_u$	$1\,^3\Sigma_g^-$	$1\,^3\Sigma_u^+$	$2\,^3\Sigma_u^+$	$1\,^3\Pi_g$
1	82.1	83.1	83.7	29.6	0.00	88.7	74.8	86.4
2	7.46	10.7	6.20	65.1	92.9	5.78	18.8	7.40
3	10.2	5.87	9.90	4.25	5.39	5.40	5.82	5.98
4	0.21	0.31	0.20	1.04	1.70	0.14	0.57	0.21
$\%t_1$(CC2)	99.5	99.2	99.8	98.2	—	99.6	99.2	99.5
$\%t_1$(CCSD)	98.0	98.0	99.2	71.7	0.00	99.0	97.8	98.3
$\%t_1$(CC3)	97.8	97.6	98.9	68.7	0.00	98.9	97.1	98.1

$$\mathbf{A}^{\mathrm{CC3}}=\begin{pmatrix} \langle {}^{(3)}\mu_1|\hat{H}_1^{(1)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_1|\hat{H}_{2+}^{(1)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_1|\hat{H}_{2-}^{(1)}|\mathrm{HF}\rangle & \langle\mu_1|[H,\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2+}|\hat{H}_1^{(1)}+\hat{H}_1^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2+}|\hat{H}_{2+}^{(1)}+\hat{H}_{2+}^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2+}|\hat{H}_{2-}^{(1)}+\hat{H}_{2-}^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2+}|[\hat{H},\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2-}|\hat{H}_1^{(1)}+\hat{H}_1^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2-}|\hat{H}_{2+}^{(1)}+\hat{H}_{2+}^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2-}|\hat{H}_{2-}^{(1)}+\hat{H}_{2-}^{(2)}|\mathrm{HF}\rangle & \langle {}^{(3)}\mu_{2-}|[\hat{H},\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle\mu_3|\hat{H}_3^{(2)}|\mathrm{HF}\rangle & \langle\mu_3|[\hat{H},\tau_{\nu_{2+}}]|\mathrm{HF}\rangle & \langle\mu_3|[\hat{H},\tau_{\nu_{2-}}]|\mathrm{HF}\rangle & \langle\mu_3|[F,\tau_{\nu_3}]|\mathrm{HF}\rangle \end{pmatrix}, \tag{46}$$

with the following definitions of the operators:

$$\hat{H}_1^{(1)}=[\hat{H}+[\hat{H},T_2],\tau_{\nu_1}], \tag{47}$$

$$\hat{H}_1^{(2)}=[[\hat{H},T_3],\tau_{\nu_1}], \tag{48}$$

$$\hat{H}_{2\pm}^{(1)}=[\hat{H},\tau_{\nu_{2\pm}}], \tag{49}$$

$$\hat{H}_{2\pm}^{(2)}=[[\hat{H},T_2],\tau_{\nu_{2\pm}}], \tag{50}$$

$$\hat{H}_3^{(2)}=[[\hat{H},T_2],\tau_{\nu_1}]. \tag{51}$$

The CC3 Jacobian can be divided into a CCSD part and a triples part. Here we will only examine the triples part since the CCSD part has already been described in Ref. 8. The triples part of the CC3 Jacobian consists of the terms

$$\mathbf{A}_3^{\mathrm{CC3}}=\begin{pmatrix} 0 & 0 & 0 & \langle\mu_1|[H,\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2+}|\hat{H}_1^{(2)}|\mathrm{HF}\rangle & 0 & 0 & \langle {}^{(3)}\mu_{2+}|[\hat{H},\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle {}^{(3)}\mu_{2-}|\hat{H}_1^{(2)}|\mathrm{HF}\rangle & 0 & 0 & \langle {}^{(3)}\mu_{2-}|[\hat{H},\tau_{\nu_3}]|\mathrm{HF}\rangle \\ \langle\mu_3|\hat{H}_3^{(2)}|\mathrm{HF}\rangle & \langle\mu_3|[\hat{H},\tau_{\nu_{2+}}]|\mathrm{HF}\rangle & \langle\mu_3|[\hat{H},\tau_{\nu_{2-}}]|\mathrm{HF}\rangle & \langle\mu_3|[F,\tau_{\nu_3}]|\mathrm{HF}\rangle \end{pmatrix}. \tag{52}$$

E. Triples CC3 triplet excitation specific terms

The individual contributions that are obtained from the linear transformation $\mathbf{A}_3^{\mathrm{CC3}}\mathbf{R}$ are given in Table I where we have introduced the ${}^{(3)}R_1$ operator containing the single excitation trial vector,

$${}^{(3)}R_1=\sum_{ck}\ {}^{(3)}R_k^c T_{ck}, \tag{53}$$

and the ${}^{(+)}R_2$ and ${}^{(-)}R_2$ operators containing the double excitation trial vectors,

$$\begin{aligned} {}^{(+)}R_2&=\sum_{c>d,k>l}\ {}^{(+)}R_{kl}^{cd}(T_{ck}E_{dl}+T_{dl}E_{ck}) \\ &=\frac{1}{4}\sum_{ckdl}\ {}^{(+)}R_{kl}^{cd}(T_{ck}E_{dl}+T_{dl}E_{ck}) \\ &=\frac{1}{2}\sum_{ckdl}\ {}^{(+)}R_{kl}^{cd}\,T_{ck}E_{dl}, \end{aligned} \tag{54}$$

$$\begin{aligned} {}^{(-)}R_2&=\sum_{ck>dl}\ {}^{(-)}R_{kl}^{cd}(T_{ck}E_{dl}-T_{dl}E_{ck}) \\ &=\frac{1}{2}\sum_{ckdl}\ {}^{(-)}R_{kl}^{cd}(T_{ck}E_{dl}-T_{dl}E_{ck}) \\ &=\sum_{ckdl}\ {}^{(-)}R_{kl}^{cd}T_{ck}E_{dl}. \end{aligned} \tag{55}$$

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TABLE V. Triplet excitation energies in mE_h for Be_2 in the aug-cc-pVTZ basis set. The coupled cluster results are the error compared to FCI.

	CCS	CC2	CCSD	CC3	FCI
$1\,^3\Sigma_g^+$	31.9	6.66	−4.79	−2.83	155.708
$2\,^3\Sigma_g^+$	29.9	12.4	0.57	0.20	196.295
$1\,^3\Pi_u$	39.7	12.8	2.05	0.38	111.032
$2\,^3\Pi_u$	−62.6	−55.8	−13.9	−5.84	116.714
$1\,^3\Sigma_g^-$	—	—	−29.1	−13.6	133.134
$1\,^3\Sigma_u^+$	36.0	14.7	4.19	1.66	41.011
$2\,^3\Sigma_u^+$	27.2	11.1	0.55	0.10	182.569
$1\,^3\Pi_g$	31.8	11.3	0.96	0.24	51.721

The operator $^{(3)}R_3$ containing the triples amplitudes has been defined in Eq. (25).

The triples trial vector amplitudes may explicitly be determined from the eigenvalue equation as a function of the single and double trial vector amplitudes:

$$
\begin{aligned}
{}^{(3)}R_{ijk}^{abc} = \frac{1}{2(\epsilon-\epsilon_{ijk}^{abc})} P_{jk}^{bc}\tilde{P}_{jk}\Bigg(& \sum_d t_{ik}^{ad}\hat{g}_{cjbd}^{(1)} + \sum_d t_{jk}^{bd}\hat{g}_{aicd}^{(2)} \\
& + \sum_d t_{ki}^{bd}\hat{g}_{cjad}^{(2)} - \sum_l t_{il}^{ac}\hat{g}_{bklj}^{(3)} - \sum_l t_{jl}^{bc} g_{ailk}^{(4)} \\
& - \sum_l t_{kl}^{ba}\hat{g}_{cjli}^{(4)} + \sum_d {}^{(+)}R_{kj}^{db}\hat{g}_{cdai} - \sum_l {}^{(+)}R_{lj}^{cb}\hat{g}_{ailk} \\
& + \sum_d \left({}^{(-)}R_{ki}^{cd}\hat{g}_{bjad} + {}^{(-)}R_{ik}^{ad}\hat{g}_{cjbd}\right) \\
& + \sum_l \left({}^{(-)}R_{lk}^{ac}\hat{g}_{bjli} + {}^{(-)}R_{li}^{ba}\hat{g}_{cjlk}\right)\Bigg),
\end{aligned}
\tag{56}
$$

where

$$\hat{g}_{ckbd}^{(1)} = \hat{g}_{\bar{c}dbk} - \hat{g}_{\bar{c}kbd} - \hat{g}_{c\bar{k}bd}, \tag{57}$$

$$\hat{g}_{ckbd}^{(2)} = \hat{g}_{\bar{b}dck} - \hat{g}_{\bar{c}kbd} - \hat{g}_{c\bar{k}bd}, \tag{58}$$

$$\hat{g}_{cklj}^{(3)} = \hat{g}_{cj\bar{l}k} - \hat{g}_{ck\bar{l}j} - \hat{g}_{\bar{c}klj}, \tag{59}$$

$$\hat{g}_{cklj}^{(4)} = \hat{g}_{ck\bar{j}l} - \hat{g}_{ck\bar{l}j} - \hat{g}_{\bar{c}klj}. \tag{60}$$

Here the two types of R_1 transformed integrals are given by

$$\hat{g}_{pqr\bar{k}} = \sum_a {}^{(3)}R_k^a g_{pqra}, \tag{61}$$

$$\hat{g}_{\bar{a}pqr} = -\sum_k {}^{(3)}R_k^a g_{kpqr}. \tag{62}$$

In the initial implementation we explicitly construct both the T_3 and the R_3 amplitudes and keep them in memory. The eigenvalue equation is solved by folding the triples amplitudes into the singles and doubles space. This approach gives the correct operation count $\mathcal{O}(N^7)$ where N is the number of orbitals. The large memory requirements limits the size of the systems that can be investigated.

The explicit coupling of the triplet excitation space gives a significant saving in the operation count compared to a spin–orbital approach. In Table I we note that the terms (II) and (III) are identical except for the perturbation operators. These terms are therefore only calculated once. The scaling of the leading terms is thus V^4O^3 for (II)/(III), (IV), (V) and (VII), whereas (VI) and (VIII) scales as $3V^4O^3$ and $2V^4O^3$, respectively. The construction of the T_3 amplitudes scales as V^4O^3 and therefore the total operation count for the CC3 model is $10\,V^4O^3$ in leading order. In the spin–orbital approach for example the coupling between the doubles and triples scales as $\frac{9}{2}V^4O^3$ which is significant larger than the $2V^4O^3$ that is obtained with an explicit spin coupled triplet excitation space. In addition to this, savings may also be obtained due to the fact that triplet and singlet excitation energies can be calculated independently.

III. SAMPLE CALCULATIONS FOR THE Be_2 AND CH_2 SYSTEMS

We have calculated the triplet excitation energies in the coupled cluster models CCS, CC2, CCSD and CC3 for the Be_2 and the CH_2 systems. In Table II the total energies of the reference states are given in the various wavefunction and basis set calculations. The FCI energies were obtained using the LUCIA program,[32] whereas the CC excitation energies were obtained using a local version of the DALTON program.[33]

A. Be_2

For Be_2 we used an inter-nuclear distance of $4.56a_0$, which in Ref. 19 was calculated to be the equilibrium distance for the ground state. The correlation-consistent basis sets aug-cc-pVXZ were used with the cardinal number X being either D or T.[34–37] In the calculations we have frozen the $1s$ orbital on both Be atoms.

The excitation energies for Be_2 using the various CC models and FCI are presented in Tables III and V using the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. Furthermore the weights for each excitation level in the FCI wavefunction as well as the single excitation weight in the

TABLE VI. Weight of various excitation levels in the FCI wavefunction for excited states in Be_2, and the weight ($\%T_1$) of the single excitations in the coupled cluster calculations.

	$1\,^3\Sigma_g^+$	$2\,^3\Sigma_g^+$	$1\,^3\Pi_u$	$2\,^3\Pi_u$	$1\,^3\Sigma_g^-$	$1\,^3\Sigma_u^+$	$2\,^3\Sigma_u^+$	$1\,^3\Pi_g$
1	82.2	82.7	84.9	28.0	0.00	88.5	80.7	86.3
2	7.42	11.2	5.18	66.7	93.0	5.99	12.9	7.53
3	10.1	5.87	9.78	4.21	5.22	5.41	5.98	5.94
4	0.22	0.35	0.20	1.11	1.74	0.15	0.42	0.22
$\%t_1$(CC2)	99.5	99.2	99.8	98.1	—	99.6	99.2	99.4
$\%t_1$(CCSD)	98.1	98.0	99.3	72.3	0.00	99.0	97.9	98.3
$\%t_1$(CC3)	97.9	97.5	99.2	68.6	0.00	98.8	97.2	98.0

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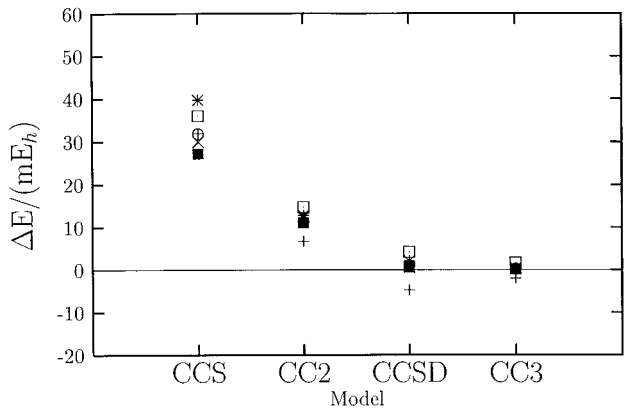


FIG. 1. The deviation from the FCI result in the coupled cluster hierarchy calculations for single excitation dominated excitation energies in the Be_2 molecule using the aug-cc-pVTZ basis set. Results for $1\,^3\Sigma_g^+(+)$, $2\,^3\Sigma_g^+(\times)$, $1\,^3\Pi_u(*)$, $1\,^3\Sigma_u^+(\boxdot)$, $2\,^3\Sigma_u^+(\blacksquare)$ and $1\,^3\Pi_g(\odot)$.

different coupled cluster models are given in Table IV and VI. From the weights it is seen that the excitations belongs to three different groups. Most states are single excitation dominant, one state is a mixture of single and double excitations with the double excitation component being the dominant and finally we have one excitation that has no single excitation contribution. For this last excitation the CCS and CC2 results are not given, since the excitation energy is not correct even to first order in the fluctuation potential. In Figs. 1 and 2 the results for the aug-cc-pVTZ basis are displayed for the single and double excitation dominated excitations, respectively. For the single replacement dominant excitations we obtain a systematic improvement toward the FCI result at each level in the coupled cluster hierarchy. This is in accordance with the fact that single replacement dominant excitations are correct through first, second, second and third order in the fluctuation potential for CCS, CC2, CCSD and CC3, respectively, and that CCSD benefit from the inclusion of all terms in the singles and doubles space. For the double replacement dominant excitations the excitation energy is correct through first order in CCSD and

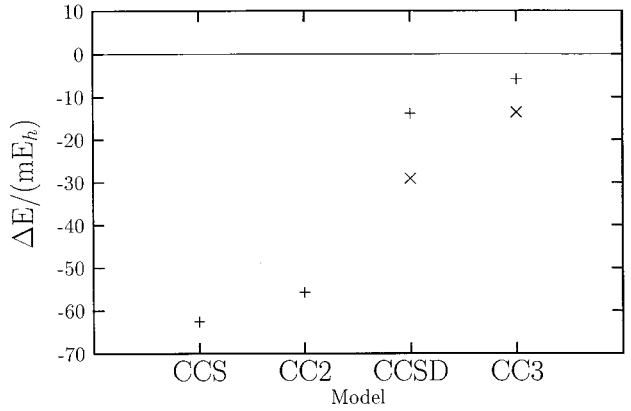


FIG. 2. The deviation from the FCI result in the coupled cluster hierarchy calculations for double excitation dominated excitation energies in the Be_2 molecule using the aug-cc-pVTZ basis set. Results for $2\,^3\Pi_u(+)$ and $1\,^3\Sigma_g^-(\times)$.

TABLE VII. Triplet excitation energies in mE_h for CH_2 in the aug-cc-pVDZ basis set. The coupled cluster results are the error compared to FCI.

	CCS	CC2	CCSD	CC3	FCI
$1\,^3A_1$	11.1	−4.15	−0.38	−0.25	234.76
$2\,^3A_1$	−4.23	−6.26	−1.06	-0.23	302.42
$3\,^3A_1$	12.3	−4.11	0.44	0.18	361.76
$1\,^3B_1$	—	—	−67.8	−23.8	235.57
$2\,^3B_1$	6.13	−6.76	−2.12	0.43	283.03
$1\,^3B_2$	−17.9	−5.43	−1.27	−0.42	−0.298 86
$2\,^3B_2$	14.2	−2.90	0.44	0.44	308.08
$1\,^3A_2$	−4.82	−0.14	−0.13	0.03	176.16

through second order in CC3 and improvements in accordance with this is seen for the double excitation dominant excitations in Tables III and V.

It should be noted that the percent single excitation in the excitation vector is very similar in CC2, CCSD and CC3 and more than 97. In the FCI calculations the weight of the single excitations for the single excitation dominant states is only between 75 and 86%. This emphasizes that the dynamical correlation is very similar for the ground and excited states. It is also worth noting that the states with a large double excitation component cannot be indentified in CC2 but first at the CCSD level. It should be noted that the errors in the various CC models are quite similar using the aug-cc-pVDZ and the aug-cc-pVTZ basis sets.

B. CH_2

For CH_2 we used a C_{2v} geometry with the coordinates in atomic units C(0,0,0) and H($\pm$1.644403,0,1.32313). The correlation consistent basis set aug-cc-pVDZ[34–37] was used and the 1*s* orbital on C was frozen to the canonical orbital.

In Table VII the excitation energies are presented for the CH_2 radical whereas the weights for each excitation level in the FCI wavefunction as well as the single excitation weights in the different CC models are presented in Table VIII. From the weights it is seen that all excitation energies except the $1\,^3B_1$ are single excitation dominated. The CCS and CC2 excitation energies are not listed for the $1\,^3B_1$ state since these excitation energies are not even correct through first order. From Table VII it can be seen that we obtain an improvement when we traverse through the CC hierarchy, though the CCS excitation energies are closer to the FCI

TABLE VIII. Weight of various excitation levels in the FCI wavefunction for excited states in CH_2, and the weight ($\%T_1$) of the single excitations in the coupled cluster calculations.

	$1\,^3A_1$	$2\,^3A_1$	$3\,^3A_1$	$1\,^3B_1$	$2\,^3B_1$	$1\,^3B_2$	$2\,^3B_2$	$1\,^3A_2$
1	89.7	91.3	88.1	1.59	89.2	93.4	82.5	91.2
2	6.31	4.65	7.82	92.6	6.84	3.07	13.3	4.99
3	3.71	3.82	3.78	4.40	3.75	3.42	3.81	3.59
4	0.22	0.17	0.25	1.35	0.22	0.11	0.37	0.15
5	0.03	0.04	0.04	0.04	0.03	0.03	0.04	0.03
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\%t_1$(CC2)	98.9	99.2	98.8	—	98.9	99.6	98.8	99.5
$\%t_1$(CCSD)	98.6	98.9	98.4	32.9	97.3	99.3	98.4	98.9
$\%t_1$(CC3)	98.3	98.8	98.0	20.0	97.3	99.2	97.8	98.8

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values for the states $2\,^3A_1$ and $2\,^3B_1$ than the corresponding CC2 excitation energies. The single excitation dominated excitation energies for CH_2 have in general a little smaller errors than for Be_2, whereas the double excitation dominated excitation energies have a little larger errors than for the beryllium dimer. The $1\,^3B_2-1\,^1A_1$ splitting has an error that is of the same size as the numerical value of the excitation energy, though the error is only $0.42mE_h$. As for Be_2 we see that the $\%t_1$ in CC2, CCSD and CC3 are very similar for the single excitation dominated excitation energies, whereas the FCI calculations show a weight of the single excitations between 83 and 93%.

IV. CONCLUDING REMARKS

We have presented the development of the triplet excitation energies in the CC3 model using an explicit triplet spin coupled excitation space. Sample calculations on the Be_2 and CH_2 systems has been performed in a coupled cluster hierarchy using the CCS, CC2, CCSD and CC3 models and the results has been compared to FCI. Most of the calculated triplet excitation energies are single excitation dominated. The precision of the coupled cluster models are improved at each level in the hierarchy, and at the CC3 level the triplet single excitation dominated excitation energies are quite close to the FCI results. The precision of the double excitation dominated triplet excitation energies in the CC3 model is seen to be comparable to the precision of the CC2 single excitation dominated excitation energies, which is predicted by theory since these excitation energies are for both cases correct to second order in the fluctuation potential.

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