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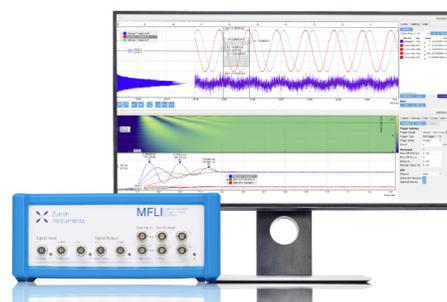
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An analysis and implementation of a general coupled cluster approach to excitation energies with application to the B_2 molecule

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A general scheme is presented for the calculation of excitation energies using the standard coupled cluster hierarchy and a simple implementation is described for the higher standard models. An error analysis is performed to find to what order excitation energies in different coupled cluster models are correct. The analysis includes both the standard coupled cluster hierarchy as well as the approximate models and considers excitations to states that are dominated by one, two, and three electron replacements compared to the reference state. Calculations are presented up to the quadruple excitation level for the open shell B_2 molecule using an excited closed shell state as reference state to emphasize the usefulness of the order analysis. The coupled cluster excitation energies are compared to full configuration interaction results. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379332]

I. INTRODUCTION

For a closed shell ground state molecule coupled cluster (CC) theory can straightforwardly be used to determine the ground and lowest excited states and the properties of these states.¹⁻⁵ The ground state can be determined using the standard set of coupled cluster models CCS (singles), CCSD (singles and doubles),⁶ CCSDT (singles, doubles, and triples),^{7,8} CCSDTQ (singles, doubles, triples, and quadruples),^{9,10} etc., where an improved accuracy is obtained at each level.^{1,2} The excitation energies and the properties of the ground and excited states can also be determined, with improving accuracy, from the coupled cluster response functions for these models.³⁻⁵ The approximate coupled cluster models CC2,^{11,12} CC3,¹³⁻¹⁵ CC4, etc., may also be used to determine the excitation energies and the properties of the ground and excited states and together with the standard coupled cluster models they are often used as a hierarchy, that converges towards the full configuration interaction (FCI) results.

In this paper we will examine the order to which an excitation energy that is one, two or three electron replacement dominated compared to the reference state is correct for a given coupled cluster model. The analysis is an extension of the one by Christiansen *et al.*^{13,16} to general levels of electron replacement and correlation.

Calculations are presented up through the CCSDTQ level. Highly efficient algorithms have previously been described for calculation of excitation energies for the coupled cluster models CC2, CCSD, and CC3 but general algorithms are not available for obtaining excitation energies for the CCSDT and in particular for the CCSDTQ models. We describe in this paper a simple algorithm for calculating exci-

tation energies for these models. The algorithm uses generalized CI technique to evaluate the action of excitation operators on general states and is a simple extension of the general algorithm by Olsen¹⁷ for calculating coupled cluster states. Similar approaches have been suggested in Refs. 18 and 19. Using the present implementation we report the first use of such a program to analyze and predict an excitation spectrum. Previous calculations were restricted to small benchmark calculations using basis sets lacking diffuse functions.

For closed shell molecules, the electronic configurations for the lowest excited states are usually single electron promoted in comparison to the ground state configuration. In a few cases the lowest excited states are dominated by a configuration where two electrons are promoted. When electronic configurations for excited states are compared they often differ by two and in some cases even by three electrons or more. Therefore, when an excited closed shell state is used as the reference state in a coupled cluster response function calculations, states that are double and even triple excited with respect to the reference state will often be encountered among the lowest excitation energies. Standard restricted coupled cluster models can be applied for open shell ground state molecules only if an excited closed shell state is used as reference state. To investigate the performance of the standard coupled cluster models for excitation energies that are dominated by higher excitation levels, we report calculations on B_2 which has an $X^3\Sigma_g^-$ open shell ground state. We use the second closed shell state of $^1\Sigma_g^+$ symmetry as the reference state.

In Sec. II we perform an order analysis while Sec. III describes the algorithm that is used to obtain the excitation energies in the CCSDT and CCSDTQ models. In Sec. IV the performance of the order analysis is demonstrated through

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$$\mathbf{A} = \begin{pmatrix} & S & D & T & Q & P & H & \cdots \\ S & d(0)+o(1) & o(1) & o(1) & 0 & 0 & 0 & \cdots \\ D & o(1) & d(0)+o(1) & o(1) & o(1) & 0 & 0 & \cdots \\ T & o(2) & o(1) & d(0)+o(1) & o(1) & o(1) & 0 & \cdots \\ Q & o(3) & o(2) & o(1) & d(0)+o(1) & o(1) & o(1) & \cdots \\ P & o(4) & o(3) & o(2) & o(1) & d(0)+o(1) & o(1) & \cdots \\ H & o(5) & o(4) & o(3) & o(2) & o(1) & d(0)+o(1) & \cdots \\ \vdots & \ddots \end{pmatrix}, \quad (18)$$

where we explicitly have written the singles (S), doubles (D), triples (T), quadruples (Q), quintuples (P), and hexuples (H) terms. In the Jacobian $d(0)$ denotes the zero-order diagonal elements consisting of the orbital energy differences and $o(n)$ is the lowest nonvanishing order of the Jacobian matrix element.

To find to what order an excitation energy in Eq. (4) is correct, we need to know to what order the right and left eigenvectors are correct. We therefore expand the Jacobian \mathbf{A} , the trial vectors \mathbf{R} , \mathbf{L} , and the excitation energy ω in orders of the fluctuation potential

$$\mathbf{A} = \sum_{k=0}^{\infty} \mathbf{A}^{(k)}, \quad (19)$$

$$\mathbf{R} = \sum_{k=0}^{\infty} \mathbf{R}^{(k)}, \quad (20)$$

$$\mathbf{L} = \sum_{k=0}^{\infty} \mathbf{L}^{(k)}, \quad (21)$$

$$\omega = \sum_{k=0}^{\infty} \omega^{(k)}. \quad (22)$$

We further assume intermediate normalization. Recognizing that $\mathbf{L}^{(0)} = \mathbf{R}^{(0)}$ we therefore have

$$(\mathbf{L}^{(0)})^T \mathbf{R}^{(0)} = 1, \quad (23)$$

$$(\mathbf{L}^{(k)})^T \mathbf{R}^{(0)} = (\mathbf{L}^{(0)})^T \mathbf{R}^{(k)} = 0. \quad (24)$$

To determine the right eigenvectors we rearrange Eq. (1) as

$$(\mathbf{A}^{(0)} - \omega^{(0)}) \mathbf{R}^{(k)} = \sum_{l=1}^k (\omega^{(l)} \mathbf{R}^{(k-l)} - \mathbf{A}^{(l)} \mathbf{R}^{(k-l)}). \quad (25)$$

The first term on the right-hand side $\omega^{(l)} \mathbf{R}^{(k-l)}$ is just a constant times lower order contributions. If we only want to find the lowest order in which an excitation level can be nonzero, we can neglect this term, since it contributes only to the same excitation levels as the lower order correction vectors. The first term on the right-hand side in Eq. (25) will therefore be neglected in the following analysis.

For an i excitation dominated excitation energy the right correction vector to first order can be analyzed using

$$(\omega_{\mu_x} - \omega^{(0)}) R_{\mu_x}^{(1)} = -\langle \mu_x | [V, R_i^{(0)}] | \text{HF} \rangle \quad (26)$$

which can be different from zero for $i-2 \leq x \leq i+1$ using Eq. (12). To second order for an i excitation dominated right correction vector we have

$$(\omega_{\mu_x} - \omega^{(0)}) R_{\mu_x}^{(2)} = -\langle \mu_x | [[V, R_i^{(0)}], T_2] + [V, R_{i-2}^{(1)} + R_{i-1}^{(1)} + R_i^{(1)} + R_{i+1}^{(1)}] | \text{HF} \rangle. \quad (27)$$

Using Eqs. (12) and (13) it is seen that we have nonvanishing terms for $i-4 \leq x \leq i+2$. Continuing in this fashion it can be shown that the n th order correction for an i excitation dominated right correction vector has nonvanishing contributions when $i-2n \leq x \leq i+n$. This is summarized in Table I for single, double, triple, quadruple, and quintuple excitation dominated excitation energies.

The left eigenvectors can be found from Eq. (2) which may be rearranged as

$$\mathbf{L}^{(k)} (\mathbf{A}^{(0)} - \omega^{(0)}) = \sum_{l=1}^k (\mathbf{L}^{(k-l)} \omega^{(l)} - \mathbf{L}^{(k-l)} \mathbf{A}^{(l)}). \quad (28)$$

TABLE I. The order, in the fluctuation potential, in which different excitation components enter in the right vector.

Excitation vector component	S	D	T	Q	P	H
Single replacement dominated	0	1	2	3	4	5
Double replacement dominated	1	0	1	2	3	4
Triple replacement dominated	1	1	0	1	2	3
Quadruple replacement dominated	2	1	1	0	1	2
Quintuple replacement dominated	2	2	1	1	0	1
Hextuple replacement dominated	3	2	2	1	1	0

TABLE II. The order, in the fluctuation potential, in which different excitation components enter in the left vector.

Excitation vector component	<i>S</i>	<i>D</i>	<i>T</i>	<i>Q</i>	<i>P</i>	<i>H</i>
Single replacement dominated	0	1	1	2	2	3
Double replacement dominated	1	0	1	1	2	2
Triple replacement dominated	2	1	0	1	1	2
Quadruple replacement dominated	3	2	1	0	1	1
Quintuple replacement dominated	4	3	2	1	0	1
Hexuple replacement dominated	5	4	3	2	1	0

This equation is very similar to Eq. (25) for the right vectors. We note that the lowest order in which an excitation level enter is independent of the first term on the right-hand side in Eq. (28). Thus as in the equations for the right correction vector this term will be neglected in the following analysis.

For an *i* excitation dominated excitation energy the first order analysis gives

$$L_{\nu_x}^{(1)}(\omega_{\nu_x} - \omega^{(0)}) = - \sum_{\mu_i} L_{\mu_i}^{(0)} \langle \mu_i | [V, \tau_{\nu_x}] | \text{HF} \rangle. \quad (29)$$

This can be nonzero if $i-1 \leq x \leq i+2$ which is seen from Eq. (12). To second order we need to analyze the equation

TABLE III. The order, in the fluctuation potential, in which contributions from the various blocks of the Jacobian enter in the excitation energies for single, double, triple, and quadruple electron dominated excitations.

	Dominating excitation			
	Single	Double	Triple	Quadruple
$L_S A_{SS} R_S$	0	2	3	5
$L_S A_{SD} R_D$	2	2	4	5
$L_D A_{DS} R_S$	2	2	3	5
$L_D A_{DD} R_D$	2	0	2	3
$L_S A_{ST} R_T$	3	3	3	5
$L_T A_{TS} R_S$	3	4	3	5
$L_D A_{DT} R_T$	4	2	2	4
$L_T A_{TD} R_D$	3	2	2	3
$L_T A_{TT} R_T$	3	2	0	2
$L_S A_{SQ} R_Q$	-	-	-	-
$L_Q A_{QS} R_S$	5	5	5	5
$L_D A_{DQ} R_Q$	5	3	3	3
$L_Q A_{QD} R_D$	5	3	4	3
$L_T A_{TQ} R_Q$	5	4	2	2
$L_Q A_{QT} R_T$	5	3	2	2
$L_Q A_{QQ} R_Q$	5	3	2	0
$L_S A_{SP} R_P$	-	-	-	-
$L_P A_{PS} R_S$	6	7	6	7
$L_D A_{DP} R_P$	-	-	-	-
$L_P A_{PD} R_D$	6	5	5	5
$L_T A_{TP} R_P$	6	5	3	3
$L_P A_{PT} R_T$	6	5	3	4
$L_Q A_{QP} R_P$	7	5	4	2
$L_P A_{PQ} R_Q$	6	5	3	2
$L_P A_{PP} R_P$	6	5	3	2
Hexuple and higher	$o(8)$	$o(6)$	$o(5)$	$o(3)$

$$L_{\nu_x}^{(2)}(\omega_{\nu_x} - \omega^{(0)}) = - \sum_{\mu_i} L_{\mu_i}^{(0)} \langle \mu_i | [[V, \tau_{\nu_x}], T_2] | \text{HF} \rangle + \sum_{\mu_i}^{(1)} \langle \mu_i^{(1)} | [V, \tau_{\nu_x}] | \text{HF} \rangle, \quad (30)$$

where

TABLE IV. An order analysis of excitation energies for different coupled cluster models in terms of the fluctuation potential. The excitations are divided into single, double, triple, and quadruple replacement dominated excitation energies. The scaling is given as a function of the number of orbitals *N*.

Model	Amplitudes included		Scaling	Order through which the excitation energy is correct			
	all	partially		Single	Double	Triple	Quadruple
CCS	S		N^4	1			
CC2	S	D	N^5	2	0		
CCSD	SD		N^6	2	1		
CC3	SD	T	N^7	3	2	0	
CCSDT	SDT		N^8	4	2	1	
CC4	SDT	Q	N^9	5	3	2	0
CCSDTQ	SDTQ		N^{10}	5	4	2	1
CC5	SDTQ	P	N^{11}	6	5	3	2
CCSDTQP	SDTQP		N^{12}	7	5	4	2

$$\begin{aligned} \sum_{\mu_i^{(1)}} \langle \mu_i^{(1)} | &= \sum_{\mu_{i-1}} L_{\mu_{i-1}}^{(0)} \langle \mu_{i-1} | + \sum_{\mu_i} L_{\mu_i}^{(0)} \langle \mu_i | \\ &+ \sum_{\mu_{i+1}} L_{\mu_{i+1}}^{(0)} \langle \mu_{i+1} | + \sum_{\mu_{i+2}} L_{\mu_{i+2}}^{(0)} \langle \mu_{i+2} |. \end{aligned} \quad (31)$$

This may be nonzero if $i-2 \leq x \leq i+4$. To n th order nonzero contributions can be obtained when $i-n \leq x \leq i+2n$. This is summarized in Table II.

Using the analysis of the right and left vectors together with the order analysis of the Jacobian we can determine to what order the different contributions to the excitation energy is correct. This is summarized in Table III where lines have been drawn to separate the terms that enter in the different standard models. From Table III we can determine to what order an excitation energy of an excitation level is correct in different coupled cluster models. The results are given in Table IV for the models CCS, CC2, CCSD, CC3, CCSDT, CC4, CCSDTQ, CC5, and CCSDTQP.

To illustrate how the results of Table IV are obtained for the standard coupled cluster models let us as an example consider to what order a double excitation dominated excitation energy is correct in the CCSDTQ model. The CCSDTQ model includes all terms of quadruple or lower excitation level, i.e., the terms in Table III up to and including $L_Q A_{QQ} R_Q$. The lowest order at which terms enter beyond the CCSDTQ model for a double excitation dominated excitation energy is 5, where, e.g., the term $L_P A_{PD} R_D$ contributes. Therefore CCSDTQ is correct through fourth order for a double excitation dominated excitation energy.

The analysis of the approximate models CC2, CC3, CC4, CC5, etc., is a little different. These models are defined such that approximations are introduced only at the highest cluster amplitude level and at this level only the lowest order correction terms are included. For example, in the CC4 model the quadruples terms of the CCSDTQ model is only kept to lowest order whereas no approximations are introduced in the terms that refer to lower excitation levels, i.e., the terms that only contain single, double, and triple excitations. A double dominated excitation will therefore be correct through third order in CC4 since only the lowest order coupling to the quadruples is correct, for example, the fourth order contributions in the $L_D A_{DD} R_D$, $L_Q A_{QD} R_D$, $L_Q A_{QT} R_T$, and $L_Q A_{QQ} R_Q$ terms are not described correct. A more detailed analysis and an implementation of the CC4 and CC5 models have not yet been performed.

III. LINEAR TRANSFORMATIONS WITH THE COUPLED CLUSTER JACOBIAN MATRIX

The eigenvalue problem defining the excitation energies, Eq. (1), is typically solved iteratively where in each iteration, the Jacobian times a vector \mathbf{x} is calculated

$$j_\mu = \sum_\nu \langle \text{HF} | \hat{\tau}_\mu^\dagger \exp(-\hat{T}) [\hat{H}, \hat{\tau}_\nu] \exp(\hat{T}) | \text{HF} \rangle x_\nu. \quad (32)$$

Highly efficient algorithms have been advanced for constructing the linear transformation of Eq. (32) for the coupled

cluster models CCSD, CC2, and CC3. In the present context, where coupled cluster operator manifolds including quadruple or higher excitations may be included, a more general approach may be used. In Ref. 20, it was demonstrated how the standard coupled cluster vector function

$$f_\mu = \langle \text{HF} | \hat{\tau}_\mu^\dagger \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \text{HF} \rangle \quad (33)$$

may be calculated for arbitrary choices of the excitation manifold using ideas and algorithms developed in the context of configuration interaction theory. For example, the vector $\exp(\hat{T})|\text{HF}\rangle$ is explicitly constructed as an expansion in terms of Slater determinants by expanding $\exp(\hat{T})$ in powers of \hat{T} and using generalized CI techniques to evaluate the action of \hat{T} on a general vector. Although the initial version of these codes are rather slow, their generality allows the testing of the importance of various excitation levels. We will now describe, how the algorithms for the calculation of the coupled cluster vector function can be generalized to the evaluation of Eq. (32), thereby allowing the evaluation of the linear transformation with the coupled cluster Jacobian for very general types of coupled cluster expansions.

The calculation of Eq. (32) is preceded by a calculation of the following vector:

$$|a\rangle = \exp(\hat{T})|\text{HF}\rangle, \quad (34)$$

where \hat{T} is the final cluster operator for the reference state. The vector $|a\rangle$ is stored on disc and used in all the subsequent evaluations of the linear transformations, Eq. (32). We will shortly return to the spaces in which the above vectors should be evaluated. For a given vector \mathbf{x} the linear transformation is obtained by separately calculating the two terms of the commutator in Eq. (32). The first term

$$j_\mu^1 = \sum_\nu \langle \text{HF} | \hat{\tau}_\mu^\dagger \exp(-\hat{T}) \hat{H} \hat{\tau}_\nu \exp(\hat{T}) | \text{HF} \rangle x_\nu \quad (35)$$

is obtained in the following steps:

- (1) $|d\rangle = \sum_\nu x_\nu \hat{\tau}_\nu |a\rangle$;
- (2) $|e\rangle = \hat{H} |d\rangle$;
- (3) $|f\rangle = \exp(-\hat{T}) |e\rangle$;
- (4) $j_\mu^1 = \langle \text{HF} | \hat{\tau}_\mu^\dagger |f\rangle$.

The construction of $|d\rangle$ from $|a\rangle$, the construction of $|f\rangle$ from $|e\rangle$ and the evaluation of the general transition density $\langle \text{HF} | \hat{\tau}_\mu^\dagger |f\rangle$ follows the algorithms discussed in Ref. 20. Similarly the evaluation of $|e\rangle$ from $|d\rangle$ is a direct CI linear transformation.

The second part of the commutator in Eq. (32) is obtained as

$$j_\mu^2 = \sum_\nu \langle \text{HF} | \hat{\tau}_\mu^\dagger \exp(-\hat{T}) \hat{\tau}_\nu \hat{H} \exp(\hat{T}) | \text{HF} \rangle x_\nu = E_{cc} x_\nu, \quad (36)$$

where E_{cc} is the total energy of the ground state. As a final step, the Jacobian times vector product is obtained by subtracting \mathbf{j}^2 from \mathbf{j}^1 .

TABLE V. Ground and reference state energies.^a

	CISDTQ ^b	FCI	CISDTQ	CCSD	CC3	CCSDT	CCSDTQ
$X^3\Sigma_g^-$	-49.297 000 45	-49.276 778 91	-49.273 988 86				
$2^1\Sigma_g^+$	-49.226 179 10	-49.200 902 13	-49.200 145 55	-49.200 739 92	-49.196 806 70	-49.200 569 12	-49.200 885 98

^aaug-cc-pVDZ basis unless stated otherwise.^baug-cc-pVTZ basis.

The vectors $|a\rangle$, $|d\rangle$, $|e\rangle$, and $|f\rangle$ are obtained as Slater-determinant expansions, and must in general be evaluated in spaces that are larger than the space spanned by $|\text{HF}\rangle, \hat{\tau}_\mu|\text{HF}\rangle$. From the definition of \mathbf{j}^1 it is seen that $|f\rangle$ should be evaluated in the space spanned by $|\text{HF}\rangle, \hat{\tau}_\mu|\text{HF}\rangle$. As \hat{T} only contains excitation operators, $|e\rangle$ can be restricted to the same space. However, as $|e\rangle$ is obtained from $|d\rangle$ by applying the Hamiltonian operator, $|d\rangle$ must be evaluated in a larger space, containing all Slater determinants in $\Sigma_{\nu\chi\nu}\hat{\tau}_\nu|a\rangle$ that may be brought into the space $|\text{HF}\rangle, \hat{\tau}_\mu|\text{HF}\rangle$ by the single and double replacement operators in \hat{H} . The construction of \mathbf{j}^2 is straightforward and needs no explanation.

The need to use extended CI spaces for $|a\rangle, |d\rangle$ means that the present algorithm has a significantly higher operation count and requires significantly more disc space than conventional coupled cluster algorithms. If the number of occupied orbitals is O and the number of virtual orbitals is V , the operation count for the CCSDT expansion scales as O^5V^5 for the current algorithm, whereas it scales as O^3V^5 for the standard approach. Furthermore for the CCSDT wave function it is necessary to obtain and manipulate Slater determinant expansions containing up to fivefold excitations. The current implementation is therefore ineffective and is only intended for testing the importance of higher excitations in small molecules using small basis sets. However, CCSDT and CCSDTQ excitation energies may be calculated for diatomic molecules in the aug-cc-pVDZ basis using the present approach. These calculations are significantly larger than previous reported calculations using general algorithms.^{18,19}

IV. SAMPLE CALCULATION OF B_2

A. Computational considerations

The ground state of the B_2 molecule has triplet symmetry $X^3\Sigma_g^-$ and the open shell electronic configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2$. The first state of $^1\Sigma_g^+$ symmetry has the same electronic configuration as the triplet ground state whereas the second state of $^1\Sigma_g^+$ symmetry has the closed shell electronic configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2$, which is doubly excited relative to the ground state configuration. We use this state as the reference state in the coupled cluster response function calculations. The B_2 calculations are carried out at the ground state equilibrium internuclear distance of 1.59 Å,²⁰ and the augmented correlation consistent basis set aug-cc-pVDZ was used.²¹ The augmented correlation consistent basis set aug-cc-pVTZ²¹ was used to estimate the basis set saturation.

In the CC3 calculations of the reference state we found that when the CCSD state was used as a start guess we obtained a solution that had a large admixture of other electronic configurations and an energy of $-49.215\,159\,09$ a.u. However, when we calculated the CC3 reference state directly we obtained a state with the expected dominant electronic configuration and an energy of $-49.196\,806\,70$ a.u. The CC3 excitation energies are calculated using this state as the reference state. It was only in the CC3 calculations that two solutions were encountered. In the calculations that used the standard models only one state was obtained and this state always had the expected configuration dominance. Table V summarizes the total energy for the $X^3\Sigma_g^-$ ground

TABLE VI. FCI excitation energies relative to the $2^1\Sigma_g^+$ state. For the other models it is the differences relative to the FCI excitation energies that are given. All calculations are carried out using the aug-cc-pVDZ basis set.

State	Occupation	Excitation level	Excitation					FCI
			CCSD	CC3	CCSDT	CCSDTQ	FCI	
$X^3\Sigma_g^-$	$2\sigma_u^2\pi_u^2$	2	0.060 65	0.034 73	0.009 45	0.000 53	-0.075 876 771	
$1^5\Sigma_u^-$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.061 50	^a	0.002 33	-0.000 01	-0.066 409 734	
$1^1\Delta_g$	$2\sigma_u^2\pi_u^2$	2	0.060 13	0.033 19	0.009 26	0.000 51	-0.052 741 328	
$1^3\Pi_u$	$2\sigma_u^2\pi_u^1 3\sigma_g^1$	1	0.004 37	-0.000 80	-0.000 02	-0.000 01	-0.050 486 287	
$1^1\Sigma_g^+$	$2\sigma_u^2\pi_u^2$	2	0.068 46	0.019 89	0.006 33	-0.000 14	-0.039 959 216	
$1^1\Pi_u$	$2\sigma_u^2\pi_u^1 3\sigma_g^1$	1	0.009 16	-0.003 33	-0.000 28	-0.000 01	-0.020 899 842	
$1^3\Delta_u$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.069 49	0.024 80	0.003 30	0.000 00	-0.014 743 256	
$1^3\Sigma_u^-$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.078 19	0.024 07	0.002 51	-0.000 14	-0.007 413 979	
$2^1\Sigma_g^+$	$2\sigma_u^2 3\sigma_g^2$		0.0	0.0	0.0	0.0	0.0	
$1^3\Sigma_u^+$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.064 61	0.023 53	0.004 99	0.000 32	0.000 767 332	
$1^3\Pi_g$	$2\sigma_u^1\pi_u^3$	3	0.025 49	0.016 93	0.019 44	0.002 39	0.003 813 231	

^aNot calculated as it is a quintuplet state.

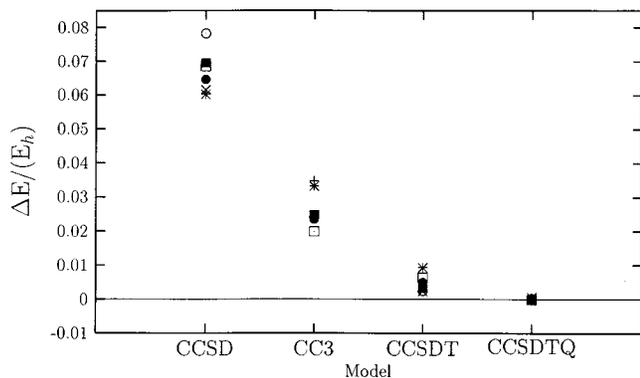


FIG. 1. The deviation of different double excitation dominated excitation energies from the FCI results for different coupled cluster models in B_2 calculations using the aug-cc-pVDZ basis set. Results for $X^3\Sigma_g^-$ (+), $1^5\Sigma_u^-$ (\times), $1^1\Delta_g$ (*), $1^1\Sigma_g^+$ (\square), $1^3\Delta_u$ (\blacksquare), $1^3\Sigma_u^-$ (\odot), and $1^3\Sigma_u^+$ (\bullet).

state and the $2^1\Sigma_g^+$ reference state for different *ab initio* models.

The CCSDT and the CCSDTQ results were obtained using the general CC code of the LUCIA program written by Olsen.^{17,22} Likewise LUCIA was used to calculate the FCI excitation energies. The CCSD and the CC3 excitation energies were obtained with a local version of the DALTON program.²³

B. Convergence of excitation energies for a hierarchy of coupled cluster models

In Table VI the FCI excitation energies are given relative to the $2^1\Sigma_g^+$ state. For the CC hierarchy CCSD, CC3, CCSDT, and CCSDTQ the differences in the excitation energies from the FCI results are also reported in Table VI, as well as the dominant electronic configuration of the states and the excitation level relative to the reference state electronic configuration.

From Table VI it is seen that the considered electronic states fall into three classes having either single, double or triple excitation dominance relative to the reference state. From the analysis in Sec II we will therefore expect the errors for the excitation energies to fall into three different

classes as well. The results in Table VI are in accordance with the order analysis of Table IV. For a given wave function level we have significantly smaller errors for the single excitation dominant states than for the double excitation dominated ones and the largest error is found for the triple excitation dominant state that has an error of $2.4 mE_h$ even at the CCSDTQ level. For excitations of all excitation levels the error decreases when a higher level in the hierarchy is considered. For the single electron replacement dominant excitation energies the decrease is in accordance with previous observations where in average the errors were found to be reduced by about a factor of 3 at each level.^{16,24,25} For two electron replacement dominated excitation energies we observe a similar reduction in the error when increasing the level in the hierarchy. In Fig. 1 we have displayed the errors for the double excitation dominated excitation energies. The figure clearly demonstrates the systematic improvement within the CC hierarchy.

The excitation energies that are correct to the same order in the fluctuation potential also have errors of comparable size. For example, the errors for CCSD single excitation dominated excitation energies are comparable to the errors for CCSDT for double excitation dominated excitation energies which again is similar to the error for the triple excitation dominated excitation energy in CCSDTQ.

When the excitation manifold in the coupled cluster calculations is extended to include triple and quadruple excitations, it is (according to a referee) natural to inquire whether configuration interaction (CI) calculations would provide excitation energies of similar accuracy. In Table VII, we thus report excitation energies relative to FCI using the CISD, CISDT, and CISDTQ expansions. The reference state was identified as the state with the largest weight of the $2\sigma_u^2 3\sigma_g^2$ configuration. For the CISDT calculations, the lowest two $1^1\Sigma_g^+$ states have significant contributions from this configuration and in accordance with the above criterium we used the second state as the reference state. At the CISD level, the spectrum is qualitatively erroneous, predicting all excitation energies to be positive. Comparing the excitation energies in Table VI and Table VII, we note that single, double, and triple replacement excitations all converge significantly faster using the CC hierarchy than using the CI hierarchy.

TABLE VII. FCI excitation energies relative to the $2^1\Sigma_g^+$ state. For the other models it is the differences relative to the FCI excitation energies that are given. All calculations are carried out using the aug-cc-pVDZ basis set.

State	Occupation	Excitation level	Excitation			
			CISD	CISDT	CISDTQ	FCI
$X^3\Sigma_g^-$	$2\sigma_u^2\pi_u^2$	2	0.088 69	0.024 77	0.002 03	-0.075 876 771
$1^5\Sigma_u^-$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.078 55	0.017 91	0.001 04	-0.066 409 734
$1^1\Delta_g$	$2\sigma_u^2\pi_u^2$	2	0.087 25	0.024 47	0.001 96	-0.052 741 328
$1^3\Pi_u$	$2\sigma_u^2\pi_u^1 3\sigma_g^1$	1	0.073 45	-0.004 90	0.002 71	-0.050 486 287
$1^1\Sigma_g^+$	$2\sigma_u^2\pi_u^2$	2	0.091 47	0.032 59	0.003 26	-0.039 959 216
$1^1\Pi_u$	$2\sigma_u^2\pi_u^1 3\sigma_g^1$	1	0.071 46	-0.003 14	0.002 51	-0.020 899 842
$1^3\Delta_u$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.084 11	0.017 03	0.001 27	-0.014 743 256
$1^3\Sigma_u^-$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.094 47	0.017 61	0.001 71	-0.007 413 979
$2^1\Sigma_g^+$	$2\sigma_u^2 3\sigma_g^2$	0	0.0	0.0	0.0	0.0
$1^3\Sigma_u^+$	$2\sigma_u^1\pi_u^2 3\sigma_g^1$	2	0.083 12	0.024 13	0.002 07	0.000 767 332
$1^3\Pi_g$	$2\sigma_u^1\pi_u^3$	3	0.088 68	0.012 83	0.011 91	0.003 813 231

TABLE VIII. Excitation energies with respect to the ground state, $X^3\Sigma_g^-$ (in eV).

State	Excitation level	FCI ^a	Langhoff ^b	Hachey ^c
$X^3\Sigma_g^-$	0	0.00	0.00	0.00
$1^5\Sigma_u^-$	1	0.26	0.21 ^d	0.14 ^f
$1^1\Delta_g$	0	0.63	0.56 ^d	0.64 ^f
$1^3\Pi_u$	1	0.69	0.44 ^d	0.43 ^f
$1^1\Sigma_g^+$	0	0.98	0.91 ^d	0.91 ^f
$1^1\Pi_u$	1	1.50	1.13 ^e	1.22 ^f
$1^3\Delta_u$	1	1.66	1.59 ^e	1.64 ^f
$1^3\Sigma_u^-$	1	1.86	1.79 ^e	1.88 ^f
$2^1\Sigma_g^+$	2	2.06	1.45 ^e	1.40 ^f
$1^3\Sigma_u^+$	1	2.09	2.05 ^e	1.98 ^f
$1^3\Pi_g$	1	2.17	2.05 ^e	2.04 ^f

^aResults using the aug-cc-pVDZ basis set.^bSee Ref. 26.^cSee Ref. 27.^dResults for the $5s4p3d2f1g$ ANO basis set.^eResults for the $4s3p2d1f$ ANO basis set.^fThe basis set is $6s5p2d$.

To understand the superiority of the coupled cluster approach, it is instructive to compare the wave functions of the two approaches. In the coupled approach, the wave function of an excited state is obtained in the form

$$|\text{EX}(\text{CC})\rangle = \sum_{vj} c_{vj} \tau_{vj} \exp(T)|\text{HF}\rangle. \quad (37)$$

We may thus consider the wave function of the excited state as obtained by applying excitations to a contracted reference state $\exp(T)|\text{HF}\rangle$. If the major parts of the correlation are identical in the ground and excited state, as is typical for excitations involving only few electrons, the coupled cluster method provides an accurate description of excited states.

In the CI formalism, the wave functions for an excited state is obtained as

$$|\text{EX}(\text{CI})\rangle = \sum_{vj} c_{vj} \tau_{vj} |\text{HF}\rangle. \quad (38)$$

As the bare Hartree–Fock state here constitutes the reference state, all correlation effects for the excited state must be included through the excitation operators $\sum_{vj} c_{vj} \tau_{vj}$.

The advantage of the CC approach compared to CI is stressed by an order analysis. According to the analysis of the coupled cluster approach in Sec. II, the excitation energy to an n -tuple excited state is correct through second order when up to $n+1$ -fold excitations are included. In the CI approach, the wave function of a n -tuple excited state contains $n+2$ -fold excitations already in first order. In a CI calculation that includes excitations up to level $n+1$, the wave functions are therefore only correct through zero order and the corresponding energy is then correct only through first order.

C. Comparison with other works

Practically no experimental data are available for the energies of the excited states we have calculated for B_2 . Thus, we will only compare our results with other theoretical stud-

ies. In Table VIII we present the FCI results together with multireference configuration interaction (MRCI) calculations of Langhoff and Bauschlicher²⁶ and Hachey *et al.*²⁷ (similar results have been obtained in other works, e.g., Ref. 28). The excitation energies in Table VIII are given relative to the $X^3\Sigma_g^-$ ground state energy. The FCI results are obtained in the aug-cc-pVDZ basis. In the MRCI calculations, as in our work, the core orbitals have been frozen to the canonical Hartree–Fock orbitals. We have verified that the use of frozen core orbitals have very little effect. To investigate basis set saturation we have calculated the excitation energies using the CISDTQ model for both the aug-cc-pVDZ and the aug-pVTZ basis set. The calculation showed only small changes in the excitation energies as a result of increasing the basis set, the largest shift was about 0.09 eV. We therefore expect that the aug-cc-pVDZ FCI results give a good estimate for the vertical excitation energies and have an accuracy of about 0.1 eV.

Comparing the FCI results in Table VIII with the results of Langhoff *et al.* and with Hachey *et al.* we see that the MRCI calculations yield significantly different excitation energies for the $1^3\Pi_u$, $1^1\Pi_u$, and the $2^1\Sigma_g^+$ states. In particular for the $2^1\Sigma_g^+$ state we have large differences between the FCI and the MRCI results. Comparing the electronic configurations for the ground and excited states we recognize that this state is the only one that has an electronic configuration that is doubly excited relative to the ground state configuration, making in particular this state very sensitive to the choice of reference space in the MRCI calculations.

V. CONCLUSION

In this paper we have performed an error analysis of the excitation energies that are calculated using the standard hierarchy CCS, CC2, CCSD, CC3, CCSDT, etc., of coupled cluster theory. The order to which the excitation energies are correct is determined for excitations that are dominated by one, two, three, etc., electron replacement compared to the reference state. To illustrate the performance of the order analysis we have calculated the lowest excitation energies of the open shell system B_2 using a closed shell excited state as the reference state. We have found improvements for excitation energies of all excitation levels at all levels in the hierarchy and have seen that excitation energies that are correct to the same order in the fluctuation potential give errors of comparable size. At the CCSDTQ level the differences compared to FCI are 0.01 and 0.5 mE_h or smaller, for single and double electron replacement excitations, and an error of 2.4 mE_h persists for the triple excitation dominated excitation energy.

Both the order analysis in Table IV and the results in Table VI show that it is generally not feasible to obtain accurate excitation energies for an open shell ground state molecule with the standard coupled cluster models using an excited closed shell state as reference state. This is due to the fact that when an excited closed shell state is used as reference state the lowest electronic states often become double or even triple excitation dominated. As the accuracy of the excitation energies in the standard CC models degrade with the excitation level, the standard models therefore give con-

siderable errors for most of the excitation energies, and the CCSDTQ model, which gives satisfying results for B_2 , is too expensive to be practical for larger molecules. A promising approach for high spin open shell ground state molecules may be to use spin restricted coupled cluster theory.^{29,30}

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