

The second-order approximate coupled cluster singles and doubles model CC2

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Abstract

An approximate coupled cluster singles and doubles model is presented, denoted CC2. The CC2 total energy is of second-order Møller–Plesset perturbation theory (MP2) quality. The CC2 linear response function is derived. Unlike MP2, excitation energies and transition moments can be obtained in CC2. A hierarchy of coupled cluster models, CCS, CC2, CCSD, CC3, CCSDT etc., is presented where CC2 and CC3 are approximate coupled cluster models defined by similar approximations. Higher levels give increased accuracy at increased computational effort. The scaling of CCS, CC2, CCSD, CC3 and CCSDT is N^4 , N^5 , N^6 , N^7 and N^8 , respectively where N is the number of orbitals. Calculations on Be, N_2 and C_2H_4 are performed and results compared with those obtained in the second-order polarization propagator approach SOPPA.

1. Introduction

Calculation of molecular properties are usually more demanding than calculation of the total molecular energy. The molecular properties we discuss may all be obtained from molecular response functions, i.e. transition moments, excitation energies, frequency-dependent polarizabilities and similar spectroscopic parameters. The main goal is to construct models that give results close to the full configuration interaction (FCI) results with a computational effort that is as small as possible. Accuracy of total energies does not assure accuracy of molecular properties. We present models constructed with emphasis on the calculation of molecular properties rather than only on total energies. Furthermore we

emphasize the importance of developing hierarchies of models where properties can be determined at still higher levels of electron correlation. The possibility to perform series of calculations within a hierarchy of models allows an estimate of the accuracy based on an analysis of convergence trends. The application range of the models is increased if the accuracy and computational effort can be chosen in accordance with the given problem.

The most commonly used non-variational methods are many-body perturbation theory (MBPT) and coupled cluster (CC) theory. They have in many respects proven successful in obtaining both correlation energies and molecular properties. Second-order Møller–Plesset (MP2) and coupled cluster singles and doubles (CCSD) have been widely used and

scale as N^5 and N^6 where N is the number of orbitals. Perturbational approaches are in general slowly convergent towards the FCI limit. Coupled cluster methods include all higher-order terms within a given excitation manifold due to the exponential Ansatz, and as a consequence the convergence towards FCI is significantly improved compared to the perturbational approaches. The non-approximated coupled cluster models only provide a feasible hierarchy for small systems due to their fast increasing computational cost: CCSD(N^6), CCSDT(N^8), etc., where the number in parentheses denotes the scaling with the number of orbitals. The CCS model has not been used apart from the fact that for excitation energies CCS is equivalent to the single excited CI (CIS) approach. CCS scales as N^4 . Models in between CCSD and CCSDT in accuracy and computational cost have been designed, and especially the perturbative correction in the CCSD(T) model [1] has been used successfully in obtaining static molecular properties. CCSD(T) scales as N^7 .

A variety of molecular properties have been calculated at the CCSD level using coupled cluster linear response (CCLR) [2–7] theory and the equation of motion [8] (EOMCC) coupled cluster approach. Excitation energies within EOMCC are identical to CCLR excitation energies whereas transition moments and polarizabilities differ, the most important difference being that the EOMCC approach does not scale correctly with system size for these properties [6,7]. The success of CCSD for calculation of molecular properties may be ascribed to several facts. The energy is correct to third order, and contains all singles and doubles contributions to infinite order. Particularly important for properties are the singles which give an approximate orbital relaxation. In this Letter we present a second-order coupled cluster model CC2 as an approximation to CCSD. We approximate the doubles equations to the form occurring in first order but with the singles retained to provide an approximate description of orbital relaxation. This gives a N^5 model with an energy comparable to MP2.

The CC2 model described in this Letter and the CC3 model introduced in Ref. [9] is based on the same philosophy in approximating the CCSD and CCSDT models respectively. From the CC2 and CC3 [10] response functions dynamic molecular

properties as well as excitation energies and transition moments can be obtained. By including these two models among the non-approximated coupled cluster models we obtain a hierarchy as follows: CCS(N^4), CC2(N^5), CCSD(N^6), CC3(N^7), CCSDT(N^8), etc. where the computational effort increase by a factor N in each step. Energies and properties increase in accuracy at each level in this hierarchy with a convergence towards the FCI limit that is unique to the coupled cluster approach.

Aiga et al. [11] derived frequency-dependent polarizabilities for the MP2 model, where the orbitals are allowed to relax to the perturbation. Although these polarizabilities and the related ones of Rice and Handy [12] may be used to calculate frequency-dependent polarizabilities, the poles are equal to Hartree–Fock poles. As pointed out by Aiga et al. the function for the polarizability includes second-order poles (order refers here to order of poles not order in the fluctuation potential) due to products of Hartree–Fock poles. This structure is not compatible with the structure of the true linear response function, and excitation energies and transition moments can not be identified in MP2. A second-order model which gives a response function compatible with the true response function and with a N^5 operation count is the second-order polarization propagator approximation (SOPPA) [13]. From the SOPPA linear response function excitation energies and transition moments can be identified which are correct through second order in the fluctuation potential. Since SOPPA is based on an expansion of an expectation value it does not include corrections due to the non-fulfillment of the Hellmann–Feynman theorem. In CC2 we can identify excitation energies and transition moments as poles and residues of the CC2 linear response function. The CC2 response function is based on a quasi energy and therefore includes corrections due to the non-fulfillment of the Hellmann–Feynman theorem. The CC2 poles are correct through second order.

Head-Gordon et al. [14] presented a doubles correction to CIS excitation energies denoted CIS(D). This excitation energy model can be described as a kind of non-iterative CC2. We shall investigate the differences between the iterative and non-iterative models in forthcoming publications. The approach of Head-Gordon only allows excitation energies to be

identified. Another approach closely related to coupled cluster is the quadratic configuration interaction approach QCI of Pople et al. [15]. The QCI singles and doubles (QCISD) model involves a N^6 operation count and significant computational savings relative to CCSD are not obtained. In Ref. [16] a comparison of QCISD and CCSD excitation energies is presented. A hierarchy of models have been introduced in the expectation value coupled cluster method [17] XCC and in the unitary coupled cluster method [18] UCC. The disadvantage of the XCC and UCC approaches is that the cluster equation contains infinitely many terms in contrast to usual coupled cluster theory. The second-order model in these approaches XCC(2) gives the MP2 model. Watts and Bartlett [19,20] have presented calculations of excitation energies using coupled cluster methods where triple excitations have been taken into account in approximate ways. In Refs. [10,21] we presented detailed comparisons of excitation energies calculated within the CCSDT-1a model and our CC3 model.

Among the variational methods used in calculating correlated properties is the multi-reference configuration interaction (MRCI) method [22] and second-order perturbation theory with a complete active space reference [23] (CASPT2). The strategy in obtaining CASPT2 and MRCI excitation energies is different from the one in response function methods since explicit calculations of the excited states are performed.

2. The CC2 model

The CCSD energy is determined from

$$E = \langle \text{HF} | H \exp(T_1 + T_2) | \text{HF} \rangle, \quad (1)$$

where the CCSD cluster amplitudes are obtained from the CCSD amplitude equations

$$\langle \mu_i | \exp(-T_1 - T_2) H \exp(T_1 + T_2) | \text{HF} \rangle = 0 \\ i = 1, 2, \quad (2)$$

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

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

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

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

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

For an optimized Hartree–Fock reference the doubles enter in first order in the fluctuation potential, and singles and triples in second order. The CCSD energy is correct through third order. To obtain an energy correct through second order it is sufficient to include the first order doubles amplitudes as in MP2. The fact that the singles appears in second order is solely due to the use of Hartree–Fock orbitals. If non-optimized orbitals were used, this is not the case. The singles respond to external perturbations to zeroth order in U . To obtain a balanced description of properties other than the total energy, we will use a coupled cluster strategy where we assign the singles to be zeroth order in U . We therefore approximate the CCSD equations as follows. The singles equations are retained in their original form, but the doubles equations are approximated to be correct through first order only, with the singles treated as zeroth-order parameters. The doubles equation thus becomes

$$\langle \mu_2 | [F, T_2] + \hat{H} | \text{HF} \rangle = 0. \quad (7)$$

Eqs. (7) and (4) define the CC2 model in the absence of external perturbations. The T_1 transformed operators in Eq. (3) provide a convenient tool for retaining the singles in the equations. In Ref. [24] equations are given for the CCSD amplitude equations in terms of t_2 amplitudes and integrals of the T_1 transformed Hamiltonian and an integral direct algorithm for implementing these equations is described. The CC2 equations are a subset of the CCSD equations and a CC2 integral direct implementation follows immediately from the above. The doubles equations in CC2 give an MP2 like expression, but with transformed integrals. Since only N^5 terms occur in the singles equations, it is clear that CC2 is an iterative N^5

model. The CC2 model is in no sense a complete solution in the space of singles and doubles as CCSD, and does not include all singles and doubles terms to infinite order. The CC2 energy is expected to be of the same quality as the MP2 energy. The purpose of including the singles in the CC2 model is not to improve the energy, but to make it possible to derive response functions in a form compatible with the structure of the exact response function, such that excitation energies and transition moments can be defined.

We therefore immediately proceed to the case where the system described by $H_0 = F + U$ is perturbed by a time-dependent one electron perturbation

$$H = H_0 + V^t, \quad (8)$$

where we write

$$V^t = - \sum_{i=-n}^n \sum_x V^x \epsilon_x(\omega_i) \exp(-i\omega_i t). \quad (9)$$

In the time-dependent case we obtain the cluster equations from projection of the coupled cluster time-dependent Schrödinger equation onto the chosen excitation manifold. We will derive general frequency-dependent response functions, and we therefore will not allow the orbitals to relax explicitly. This would in addition to the correlated poles in the response function give Hartree–Fock poles as well as product poles. Features which are inconsistent with the structure of the true response function. Instead of using explicitly relaxed orbitals we apply a double perturbation expansion of the cluster equations. That is instead of treating $F + V^t$ as the zeroth-order problem as in the orbital relaxed case we keep F as the zeroth-order problem perturbed by the two distinct perturbations U and V^t . The crucial importance of the singles for calculating accurate properties is clearly exposed in such an analysis since the singles are zeroth-order in U , and first order in the one-electron perturbation V . Treating the singles as zeroth-order parameters give an alternative way of describing orbital relaxation and allow the determination of molecular properties from frequency-dependent response functions.

Approximating the doubles equations to first order in U and keeping all terms in V^t , the equations

for the time evolution of the CC2 parameters in the presence of external perturbations are

$$\langle \mu_1 | \hat{H} + [\hat{H}, T_2] | \text{HF} \rangle = i \partial t_{\mu_1} / \partial t, \quad (10)$$

$$\langle \mu_2 | [F + \hat{V}, T_2] + \hat{H} | \text{HF} \rangle = i \partial t_{\mu_2} / \partial t. \quad (11)$$

The discussion above is restricted to one-electron perturbations. The case of two-electron perturbations is more involved and the CC2 response function can not be expected to describe two-electron perturbations well. Geometrical derivatives should be calculated using energy derivative techniques for CC2 or MP2. In Section 3 we derive the CC2 linear response function based on Eqs. (10) and (11).

3. Response theory for the CC2 model

In Ref. [10] we discussed different approaches for the derivation of coupled cluster response functions and described a strategy applicable for approximate coupled cluster models. This strategy was applied to derive the linear response function for the CC3 model. The same strategy can straightforwardly be used to obtain response functions for the CC2 model. It is based on the quasi energy approach described in detail by Sasagane et al. [25] and applied to the derivation of expressions for MP2 frequency-dependent properties in Ref. [11]. We give here only a very short and compact exposition of the derivation of CC2 response functions and refer to Ref. [10] for a more detailed discussion. The CC2 quasi energy with the CC2 amplitude equations Eqs. (10) and (11) as time-dependent constraints can be written in terms of a quasi energy Lagrangian

$$\begin{aligned} L = & \langle \text{HF} | H \exp(T_1 + T_2) | \text{HF} \rangle \\ & + \sum_{\mu_1} \tilde{t}_{\mu_1} \left(\langle \mu_1 | \hat{H} + [\hat{H}, T_2] | \text{HF} \rangle - i \partial t_{\mu_1} / \partial t \right) \\ & + \sum_{\mu_2} \tilde{t}_{\mu_2} \left(\langle \mu_2 | [F + \hat{V}^t, T_2] + \hat{H} | \text{HF} \rangle - i \partial t_{\mu_2} / \partial t \right). \end{aligned} \quad (12)$$

This Lagrangian includes all the information necessary to derive CC2 response functions. A derivation

similar to the one in Ref. [10] determines the CC2 linear response function as

$$\begin{aligned} \langle\langle A, B \rangle\rangle_{\omega} = & P(A(-\omega), B(\omega)) \\ & \times \left\{ \langle \text{HF} | [A, T_1^B(\omega)] \right. \\ & + \frac{1}{2} [[H_0, T_1^A(-\omega)], T_1^B(\omega)] | \text{HF} \rangle \\ & + \sum_{\mu_1} \tilde{t}_{\mu_1}^{(0)} \langle \mu_1 | [\hat{A}, T^B(\omega)] \\ & + \frac{1}{2} [[\hat{H}_0, T^A(-\omega)], T^B(\omega)] | \text{HF} \rangle \\ & + \sum_{\mu_2} \tilde{t}_{\mu_2}^{(0)} \langle \mu_2 | [\hat{A}, T_2^B(\omega)] \\ & + [[\hat{A}, T_1^B(\omega)], T_2^{(0)}] \\ & \left. + \frac{1}{2} [[\hat{H}_0, T_1^A(-\omega)], T_1^B(\omega)] | \text{HF} \rangle \right\}, \end{aligned} \quad (13)$$

where we have used the abbreviation $V^A = A$. The operator $P(A(-\omega), B(\omega))$ symmetrizes with respect to A and B and related frequency indices. The t amplitude responses are obtained from

$$(\omega \mathbf{1} - \mathbf{A}) t^A(\omega) = \xi^A \quad (14)$$

and the zeroth-order multipliers are determined from

$$\tilde{t}^{(0)} \mathbf{A} = \boldsymbol{\eta}^{(0)}, \quad (15)$$

where we have introduced the CC2 Jacobian

$$A_{\mu, \nu_i} = \begin{pmatrix} \langle \mu_1 | [\hat{H}, \tau_{\nu_1}] \exp(T_2^{(0)}) | \text{HF} \rangle & \langle \mu_1 | [\hat{H}, \tau_{\nu_2}] | \text{HF} \rangle \\ \langle \mu_2 | [\hat{H}, \tau_{\nu_1}] | \text{HF} \rangle & \delta_{\mu\nu} \omega_{\mu_2} \end{pmatrix}. \quad (16)$$

The right hand sides are defined as

$$\eta_{\nu_i}^{(0)} = - \langle \text{HF} | [\hat{H}_0, \tau_{\nu_i}] | \text{HF} \rangle \quad (17)$$

and

$$\xi^A = \begin{pmatrix} \langle \mu_1 | \hat{A} + [\hat{A}, T_2^{(0)}] | \text{HF} \rangle \\ \langle \mu_2 | [\hat{A}, T_2^{(0)}] | \text{HF} \rangle \end{pmatrix}. \quad (18)$$

Excitation energies and transition moments may be determined as poles and residues of the linear response function. The poles are according to Eq. (14) at plus and minus the eigenvalues of the Jaco-

bian. That is CC2 excitation energies are determined as

$$\mathbf{A} \mathbf{S}_k = \omega_k \mathbf{S}_k. \quad (19)$$

In Ref. [10] we analyzed excitation energies in orders of the fluctuation potential in coupled cluster theory from considerations of the orders of the various blocks in the coupled cluster Jacobian. A similar analysis can be performed for the CC2 model. In CC2 the doubles amplitudes are correct to first order and the singles to second order. The single–single block is thus correct to second order in CC2. The doubles affect the singles spectrum in second order whereas triples enter in third order. In CC2 the double–single and single–double blocks are correct to first order due to the fact that the lowest-order coupling to the singles spectrum is retained in CC2. This ensures that the CC2 single replacement dominated excitation energies are correct through second order.

In coupled cluster theory the deexcitation manifold occurs in an indirect form from the left hand projection manifold. As a consequence we do not have direct coupling of the excitation and deexcitation spectrum in the response function. This rather technical point is important, since for other non-variational models as MP2 [11] and Brueckner coupled cluster theory [26] this coupling causes second-order poles in the expressions for the frequency-dependent polarizabilities. Due to the special coupled cluster structure we do not have second-order poles even though we have products of first-order responses. Restricting ourselves to considering only excitation operators we thus avoid this type of problems. In contrast to MP2 we can identify excitation energies and transition moments.

4. A hierarchy of coupled cluster models

In Ref. [10] an alternative derivation of many-body perturbation theory was presented using a coupled cluster parametrization of the exact wavefunction. Based on this we have in this Letter introduced the CC2 model and in Ref. [10] the CC3 model. The same type of approximations were used to define the CC2 and CC3 models. The CC2 model is intermediate between the truncated coupled cluster models

Table 1

Coupled cluster models given in terms of defining equations. H is the total Hamiltonian $H = H_0 + V'$ where V' is a one-electron general time-dependent perturbation. H_0 is further divided into $H_0 = F + U$ where F is the Fock operator and U is the fluctuation potential. The equations are for the non-orbital relaxed perturbed case. For the unperturbed or explicit orbital relaxed case V' is put to zero. The T_1 transformed operators of Eq. (3) is used

CCS	$\langle \mu_1 \hat{H} \text{HF} \rangle = i \partial t_{\mu_1} / \partial t$
CC2	$\langle \mu_1 \hat{H} + [\hat{H}, T_2] \text{HF} \rangle = i \partial t_{\mu_1} / \partial t$ $\langle \mu_2 \hat{H} + [F + \hat{V}', T_2] \text{HF} \rangle = i \partial t_{\mu_2} / \partial t$
CCSD	$\langle \mu_1 \hat{H} + [\hat{H}, T_2] \text{HF} \rangle = i \partial t_{\mu_1} / \partial t$ $\langle \mu_2 \hat{H} + [\hat{H}, T_2] + \frac{1}{2} [[\hat{H}, T_2], T_2] \text{HF} \rangle = i \partial t_{\mu_2} / \partial t$
CC3	$\langle \mu_1 \hat{H} + [\hat{H}, T_2] \text{HF} \rangle = i \partial t_{\mu_1} / \partial t$ $\langle \mu_2 \hat{H} + [\hat{H}, T_2] + \frac{1}{2} [[\hat{H}, T_2], T_2] \text{HF} \rangle = i \partial t_{\mu_2} / \partial t$ $\langle \mu_3 [F + \hat{V}', T_3] + [\hat{H}, T_2] + \frac{1}{2} [[\hat{V}', T_2], T_2] \text{HF} \rangle = i \partial t_{\mu_3} / \partial t$
CCSDT	$\langle \mu_1 \hat{H} + [\hat{H}, T_2 + T_3] \text{HF} \rangle = i \partial t_{\mu_1} / \partial t$ $\langle \mu_2 \hat{H} + [\hat{H}, T_2 + T_3] + \frac{1}{2} [[\hat{H}, T_2], T_2] \text{HF} \rangle = i \partial t_{\mu_2} / \partial t$ $\langle \mu_3 [\hat{H}, T_2 + T_3] + \frac{1}{2} [[\hat{H}, T_2], T_2] + [[\hat{H}, T_2], T_3] \text{HF} \rangle = i \partial t_{\mu_3} / \partial t$

CCS and CCSD, and the CC3 is intermediate between CCSD and CCSDT in accuracy and in computational cost. The approach for defining these approximate coupled cluster models may be expressed as follows. Consider a coupled cluster model truncated at excitation level n , $n > 1$. The CC n model is defined from introducing approximations in the n -tuple coupled cluster equations: the cluster equations for the n -tuple excitation manifold are approximated to the form entering in lowest non-vanishing order, with the singles treated as zeroth-order parameters. We thus restrict ourselves to the form entering in order $n - 1$ in perturbation theory. The singles are included to provide approximate orbital relaxation in two senses: relaxation to the correlation, and relaxation to external perturbations. The cluster equations up to level n are left unaltered. The hierarchy of coupled cluster methods becomes

CCS, CC2, CCSD, CC3, CCSDT, etc.

The equations defining these models are given in Table 1. The equations are given in the time-depen-

Table 2

Features of coupled cluster models and related models

Model	Energy correct to order	Single excitations correct to order ^a		Double excitations correct to order ^a		Dynamic response function correct to order ^b	Scaling	Amplitudes ^c	Iterative
		Energy	T.M.	Energy	T.M.				
CCS	1	1	0			0	4	t_1	yes
CC2	2	2	1			1	5	t_1, t_2	yes
CCSD	3	2	2	1	1	2	6	t_1, t_2	yes
CC3	4	3	3	2	2	3	7	$t_1, t_2, (t_3)$	yes
CCSDT	4	4	3	2	2	3	8	t_1, t_2, t_3	yes
RPA	1	1	1			1	4	t_1 ^d	yes
MP2	2					2	5	t_1, t_2 ^d	no
SOPPA	e	2	2			2	5	t_1, t_2 ^d	no
CCSDT-1a ^f	4	2	2	2	2	2	7	$t_1, t_2, (t_3)$	yes
CCSD(T)	4					g	7	$t_1, t_2, (t_3)$	no

^a Non-iterative models do not have corresponding excitation energies. For a discussion of the orders of excitation energies in CCSD, CC3 and CCSDT-1a, see Ref. [10]

^b Non-orbital relaxed. If orbital relaxation is included, the static response function will formally be correct to the same order as the total energy, but will in this case contain spurious Hartree–Fock poles.

^c The amplitudes in parentheses do not need to be stored in optimization of the reference and in solving eigenvalue equations and linear response equations.

^d In RPA, MP2 and SOPPA the t_1 vector actually refers to orbital rotation vectors.

^e SOPPA does not have a corresponding energy. The correlation coefficients are MP2 correlation coefficients.

^f In Ref. [19] CCSDT-1a excitation energies were presented. In Ref. [10] a detailed comparison was made with CC3.

^g A dynamic response function for CCSD(T) is not well defined.

dent case with an external perturbation V' present. The unperturbed equations for optimizing the reference energy are easily obtained neglecting the time-differentiation terms and all V' terms. The most important features of the various coupled cluster models are summarized in Table 2. We comment only briefly on the characteristics of the various models. Some are well known, and other will be commented on in more detail in later papers. In Refs. [9,10] many of the characteristics of the CC3 model are described in more detail.

CCS is the coupled cluster singles model. For an optimized Hartree–Fock state the wave function is already optimal due to the Brillouin theorem. Excitation energies in the CCS model are equivalent to those obtained in single configuration interaction (CIS) or the Tamm Dancoff approximation (TDA). The linear response function and transition moments differ however due to the non-variational nature of the coupled cluster approach. We have described CC2 in the previous sections. CCSD is the most commonly used coupled cluster model. CCSD is a complete solution in the singles and doubles space and as such the energy in CCSD is correct through third order and includes all higher-order singles and doubles terms. CC3 is an approximate CCSDT model constructed using the same type of criteria used in the construction of the CC2 model. In CC3 the singles and doubles equations of CCSDT are unaltered and the triple equation is approximated to the form occurring in second order, but with the singles treated as zeroth-order parameters. The next step is CCSDT which is the complete solution in the space

of singles, doubles and triples. The hierarchy is extendable to yet higher levels, but the applicability for practical purposes is significantly reduced at each step. In this hierarchy the accuracy of energies and properties are increased at each level. In Table 2 this is indicated in terms of order in the fluctuation potential. It should be recalled that a unique feature of coupled cluster theory is the summation to infinite order of certain types of terms. For example as seen in Table 2 single replacement dominated excitations in CCS are correct to first order, in CC2 to second order, in CCSD to second order but with complete inclusion of all singles and doubles terms, in CC3 to third order with all singles and doubles terms completely included, and in CCSDT to third order with complete treatment of all singles, doubles and triples terms. The features of the coupled cluster properties in Table 2 refers to the case where orbital relaxation is not introduced. Introducing orbital relaxation gives polarizabilities at the order of the corresponding energy. However it is not possible to identify excitation energies and transition moments in any rigorous sense from such an approach as discussed before. In the non-orbital relaxed form CC2 formally lacks one second-order term, that is included in the orbital relaxed form. Features of some related models are also given in Table 2.

5. Calculations

We present calculations of excitation energies for Be, N_2 and C_2H_4 and compare our results with the

Table 3
Singlet excitation energies for Be in eV from various coupled cluster and polarization propagator calculations ^a

Excitation	RPA	CCS (CIS-TDA)	CC2	CCSD	CC3	SOPPA ^b	CCD- PPA ^b	CCSD- PPA ^b	FCI ^c	% t_1 (CCSD)
¹ P	4.80	5.049	5.206	5.318	5.3144	4.90	5.28	5.30	5.3140	94
¹ S	6.12	6.131	6.519	6.772	6.7653	6.47	6.87	6.89	6.7645	95
¹ D				7.153	7.0969				7.0863	45
¹ P	6.72	6.770	7.187	7.464	7.4601	7.10	7.51	7.53	7.4597	95
¹ D	6.94	6.939	7.427	8.058	8.0359	7.39	7.79	7.81	8.0323	82
¹ S	7.26	7.265	7.733	8.078	8.0733	7.72	8.16	8.18	8.0728	97
¹ P	7.48	7.496	7.964	8.306	8.3009	7.95	8.38	8.40	8.3004	96
¹ D	7.59	7.586	8.080	8.547	8.5365	8.08	8.53	8.55	8.5350	93

^a Calculated using the [9s9p5d] basis set of Ref. [28] with the $x^2 + y^2 + z^2$ components of the d-functions included as in the polarization propagator calculations.

^b Polarization propagator excitation energies from Ref. [27].

^c FCI results from Ref. [28].

Table 4
N₂ excitation energies in eV and ground state energies in au ^a

	RPA	CCS	CC2	CCSD	CC3	SOPPA ^b	Exp. ^c
¹ Π _u	15.37	15.63	14.11	13.74	13.48	13.83	13.4
¹ Σ _u ⁺	16.45	16.67	14.39	14.63	14.39	14.30	14.4
¹ Δ _u	8.86	9.14	11.08	10.68	10.53	10.54	10.3
¹ Σ _u ⁻	8.02	8.58	10.54	10.27	10.16	10.05	9.9
¹ Π _g	9.85	10.10	9.65	9.62	9.55		
¹ Σ _u ⁺	14.49	15.31	15.65	15.70	15.14		
G.s. E.	-108.985177	-108.985177	-109.402101	-109.394480	-109.413431	-109.394689	

^a Basis set and geometry as in Ref. [29]. Basis set is [11s7p2d/6s5p2d] and $R_{NN} = 2.067$ au.

^b SOPPA results from Ref. [29] The ground state energy given is the MP2 energy.

^c Experimental results taken from Ref. [29].

ones obtained with other models. In Ref. [21] and in a forthcoming publication excitation energies are presented for the hierarchy of CCS, CC2, CCSD, CC3 and comparison made with FCI results.

In Ref. [27] several singlet excitation energies were calculated for Be using SOPPA and with the same basis set as in the FCI calculations in Ref. [28]. We have performed the corresponding CCS, CC2, CCSD and CC3 excitation energy calculations. The results are given in Table 3. The CC2 and SOPPA excitation energies are of similar quality for all excitations except the lowest. SOPPA excitation energies have a mean (max) error of 0.41 (0.64) eV whereas the corresponding CC2 results are 0.34 (0.58). SOPPA uses first-order correlation coeffi-

cients from a MP2 calculation. Using instead coupled cluster doubles (CCD) amplitudes or CCSD amplitudes the so called CCDPPA and CCSDPPA propagators are obtained. It should be emphasized that molecular properties are still only correct to second order, but the calculation of the correlation coefficients scales as N^6 . The errors of the CCS-DPPA results are 0.1(0.22) eV, the CCDPPA are of same magnitude. CCSD gives a mean (max) error of 0.009 (0.02) eV excluding the lowest ¹D excitation that is double electron replacement dominated. CC3 has a mean error of 0.001 eV for the same excitations. The differences between SOPPA and CC2 excitation energies are less than 0.05 eV except for the lowest state. These differences are small com-

Table 5
C₂H₄ singlet excitation energies in eV. Ground state energies in au ^a

	RPA	CCS	CC2	CCSD	CC3 ^b	CASPT2 ^c	Exp. ^d
¹ B _{3u}	7.07	7.09	7.14	7.29	7.23	7.17	7.11
¹ B _{1g}	7.66	7.67	7.78	7.95	7.90	7.85	7.80
¹ B _{2g}	7.82	7.83	7.82	7.99	7.94	7.95	7.90
¹ B _{1u}	7.33	7.67	7.86	7.98	7.87	8.40	8.01
¹ A _g	8.14	8.16	8.23	8.46	8.42	8.40	8.29
¹ B _{3u}	8.54	8.55	8.58	8.79	8.75	8.66	8.62
¹ A _u	8.74	8.74	8.77	9.02	8.99	8.94	
¹ B _{3u}	8.79	8.79	8.84	9.08	9.04	9.03	8.90
¹ B _{2u}	8.96	8.97	9.07	9.27	9.22	9.18	9.05
¹ B _{1u}	8.94	8.97	9.03	9.31	9.27	9.31	9.33
E _{tot}	-78.064796	-78.064796	-78.388064	-78.411268	-78.425041		

^a Basis set and geometry as in Ref. [30] Basis set is an atomic natural orbital type (ANO) where (14s9p4d/8s4p) is contracted to [4s3p2d/3s2p] and where a set of diffuse (2s2p1d) is added on carbon. The geometry is $r_{CC} = 1.339$ Å, $r_{CH} = 1.086$ Å and $\angle HCH = 117.6$.

^b CC3 results from Ref. [10].

^c CASPT2 results from Ref. [30].

^d Experimental data from the compilation in Ref. [30].

pared to the overall error relative to FCI. Concerning the lowest state it should be noticed that a similar difference is observed between CCS and RPA results. This difference is due to an overestimation of the coupling between the excitation and the deexcitation manifolds for RPA and SOPPA. It is well known that RPA and SOPPA can be unstable for small excitation energies. All excitation energies are increased from CCS to CC2 and again to CCSD. CCSD overshoots FCI for all excitations whereas CC2 undershoots. The excitation energies are decreased slightly going from CCSD to CC3 and are correct to three decimals in CC3 for single replacement dominated excitations.

In Ref. [29] SOPPA calculations were presented for several excitation energies of N_2 . We have performed RPA, CCS, CC2 and CCSD calculations using the same basis set and geometry, see Table 4. The CC3 results are from Ref. [10]. The differences between CC2 and SOPPA are more pronounced than for Be. A similar trend can be observed for CCS relative to RPA. The large change in the excitation energies going from CCSD to CC3 indicates the large correlation contributions for this molecule. SOPPA is closer to CC3 and experiment than CC2 for three out of four excitations. With the large correlation effects in mind this may be fortuitous. In absolute values the differences between CC2 and CC3 are of order 0.3–0.5 eV. Relative to CCSD differences of 0.3–0.4 eV occurs. The CC3 results are within 0.1–0.3 eV of the experimental values. The effect of extending the basis set needs to be further investigated to be more conclusive concerning comparison with experiment. With respect to the total energies we notice that for N_2 MP2 and CC2 differ by more than 8 mhartree, whereas the difference between MP2 and CCSD is less than 1 mhartree. CC3 is again almost 20 mhartree lower than CCSD.

In Ref. [30] CASPT2 calculations were reported for several excitation energies in ethylen. We have performed the CCS, CC2 and CCSD calculations using the same basis set and geometry. In Table 5 we give the results together with the CC3 results from Ref. [10]. From the convergence in the hierarchy CCS, CC2, CCSD and CC3 and the small difference between CCSD and CC3 for all excitations, it is evident that the CC3 results are close to the exact results within this basis. The CC2 results are within

0.25 eV of CC3 for all excitations. CASPT2 results are within 0.1 eV of CC3 for all excitations except for the lowest $^1B_{1u}$ state. CC2 is close to CC3 for this state. It should be noticed that all excitation energies are increased from CCS to CC2 and again to CCSD, whereas the CC3 results are decreased relative to CCSD.

6. Conclusion

Several models exist which in some sense can be denoted second-order. We have introduced a second-order approach denoted CC2 based on an approximation to CCSD. The CC2 model is similar to MP2 in the sense that CC2 has a corresponding total energy correct through second order and CC2 properties are obtained as quasi energy derivatives and include Hellmann–Feynman corrections. In contrast SOPPA is not obtained as a quasi energy derivative and does not include Hellmann–Feynman correction terms. CC2 is similar to SOPPA in the sense that single replacement dominated excitation energies can be identified and are correct through second order. The poles in MP2 are only of first-order quality and product poles are present. The poles inherent in CC2 are correct to second order and the pole structure is compatible with the pole structure of the exact response function. In this sense CC2 combines the attractive features of MP2 and SOPPA. The CC2 model can in a loose sense be considered as an approximate orbital relaxed MP2 approach. However, the CC2 model is founded in coupled cluster theory and comes about as an approximation to CCSD.

A hierarchy of coupled cluster models is introduced, and in Table 2 and in Section 4 we described how properties are obtained with increasing accuracy at each step in this hierarchy. Benchmark calculations may provide the error bounds of the models within this hierarchy, and error estimates may be obtained from analyzing converging trends. The role of CC2 in a hierarchy of coupled cluster based methods is an important aspect of this model. A computationally tractable hierarchy like the CC described in this Letter will in many cases enhance the possibility to perform predictive calculations and provide error bounds on the calculated properties. The range of

coupled cluster methods for property calculations is significantly extended by introducing a N^5 model as CC2 and a N^7 model like CC3. We thereby obtain a unique possibility for extending our calculations toward the exact results. In benchmark calculation on excitation energies of BH, CH₂ and Ne we have observed significant reductions of the error relative to FCI in each step in the hierarchy. Similar quality is obtained in CC2 and SOPPA excitation energies. A more thorough comparative analysis with SOPPA will be presented in future applications. The wide applicability of the coupled cluster models will be demonstrated in forthcoming calculations on larger molecules using integral direct techniques.

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