

The Fock space coupled cluster method: theory and application*

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Summary. The Fock space coupled cluster method and its application to atomic and molecular systems are described. The importance of conserving size extensivity is demonstrated by the electron affinities of the alkali atoms. Two types of intruder states are discussed, one attributable to the orbital energy spectrum and the other caused by two-electron interactions. They are illustrated by the excited states of Li_2 and by 1S states of Be, respectively. It is shown how both problems may be solved using incomplete model spaces. The selection of the model space in a moderately dense spectrum is discussed in connection with N_2 excited states.

Key words: Coupled cluster method – Intruder states – Incomplete model spaces – Electronic transition energies

1. Introduction

The coupled-cluster (CC) method [1–4], originally designed for closed-shell systems, has been extended to include open-shell systems, which cannot be described adequately by a single determinant [5–22]. The basic approach of the multireference method is to define an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. The effect of the complementary Q space is taken into account in the calculation of the effective Hamiltonian matrix elements, using an appropriate truncation of the wave operator. Two different approaches are commonly used. Most applications to date follow the state-universal or Fock space approach, with simultaneous calculation of many states having different numbers of valence electrons. The state-specific or Hilbert space method, on the other hand, treats a manifold of states with a constant number of valence electrons. The selection of the model space plays a crucial role in both methods. Intruder states, which spoil the convergence of the calculation, occur frequently. Careful construction of the model space may alleviate the problem. In particular, so-called incomplete model spaces are useful in many cases.

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A detailed formal discussion of open-shell coupled cluster theories may be found in a recent review by Mukherjee and Pal [23]. A brief description of the Fock space method is presented below, followed by a summary of recent atomic and molecular applications. Only a few examples are described at any length. These were selected for pedagogical reasons, to demonstrate such points as the importance of size extensivity, criteria for selecting the model space, or the intruder state problem and its solution.

2. The Fock space coupled cluster method

2.1. Formalism

The Hamiltonian H of the system is separated in the conventional way into H_0 , with known eigenfunctions, and a perturbation V :

$$H = H_0 + V \quad (1)$$

$$H_0|\alpha\rangle = E_0^\alpha|\alpha\rangle. \quad (2)$$

A d -dimensional model space P and its complement Q are defined by projection operators:

$$P = \sum_{\alpha \in P} |\alpha\rangle\langle\alpha|, \quad Q = 1 - P. \quad (3)$$

There will usually be d eigenfunctions of H with major components in the model space:

$$H\Psi^a = E^a\Psi^a, \quad (4)$$

$$P\Psi^a = \Psi_0^a, \quad a = 1, 2, \dots, d \quad (5)$$

where Ψ_0^a are linear combinations of $|\alpha\rangle$, $\alpha \in P$. The wave operator transforms the model functions into exact ones:

$$\Omega\Psi_0^a = \Psi^a, \quad a = 1, 2, \dots, d. \quad (6)$$

Intermediate normalization is assumed:

$$\langle\Psi^a|\Psi_0^a\rangle = \langle\Psi_0^a|\Psi_0^a\rangle = 1. \quad (7)$$

The key equation in Lindgren's [10] derivation is the generalized Bloch equation:

$$[\Omega, H_0]P = V\Omega P - \Omega P W P, \quad (8)$$

where W is the effective interaction:

$$W = V\Omega. \quad (9)$$

Alternatively, one may rewrite Eq. (8) as:

$$[\chi, H_0]P = QWP - \chi P W P, \quad (10)$$

where the correlation operator χ is defined by:

$$\Omega = 1 + \chi. \quad (11)$$

The energies of interest are obtained by diagonalizing the effective Hamiltonian in the model space:

$$H_{\text{eff}}\Psi_0^a = E^a\Psi_0^a, \quad (12)$$

where

$$H_{\text{eff}} = PH\Omega P = P(H_0 + W)P. \quad (13)$$

The correlation operator χ includes single, double, \dots , virtual excitations and may be written as:

$$\chi = C_1 + C_2 + \dots = \sum_{ij} \{a^\dagger a_j\} s_j^i + \frac{1}{2} \sum_{ijkl} \{a^\dagger a^\dagger a_l a_k\} s_{kl}^{ij} + \dots \quad (14)$$

$s_j^i, s_{kl}^{ij}, \dots$, are excitation amplitudes, and the curly brackets denote normal order with respect to a reference (core) determinant. *All* terms, connected as well as disconnected, are included in Eq. (14). The operator used in CCM is the excitation operator S , related to Ω by:

$$\Omega = \{\exp(S)\} = 1 + S + \frac{1}{2}\{S^2\} + \dots \quad (15)$$

S is obtained by summing the rhs of Eq. (14) over *connected* terms only. Perturbative or non-perturbative schemes for calculating the excitation operator and correlation energies may be derived from either of the following two equations, which include connected terms only [10]:

$$[S, H_0] = (QV\Omega - \chi PV\Omega)_{\text{conn}}, \quad (16)$$

or

$$[S, H_0] = W_{\text{op,conn}} - (\chi W_{\text{cl}})_{\text{conn}}. \quad (17)$$

$W_{\text{op,conn}}$ describes all connected diagrams which have some open (non-valence) lines, corresponding to $P \rightarrow Q$ transitions. W_{cl} diagrams, with no external non-valence lines, describe $P \rightarrow P$ transitions. The latter also appear in the effective Hamiltonian, which may be written as:

$$H_{\text{eff}} = PH_0P + W_{\text{cl}}. \quad (18)$$

The second term in Eq. (16) or (17) gives rise to the so-called *folded diagrams*.

The Fock space approach is valence universal, meaning that one S operator is used for a manifold of states which may have different numbers of valence electrons. The operator may be partitioned according to the number of valence electrons:

$$S = S^{(0)} + S^{(1)} + S^{(2)} + \dots \quad (19)$$

Haque and Mukherjee [17] have shown that partial decoupling of the equations occurs if normal order is assumed, as the equations for $S^{(n)}$ involve only $S^{(m)}$ elements with $m \leq n$. This decoupling is helpful in reducing the computational effort, and is used routinely in our calculations.

The H_{eff} or W_{cl} diagrams (see Eq. (18)) may be separated into core and valence parts:

$$H_{\text{eff}} = H_{\text{eff}}^{\text{core}} + H_{\text{eff}}^{\text{val}}, \quad (20)$$

where the first term on the rhs consists of diagrams without any external lines. The eigenvalues of $H_{\text{eff}}^{\text{val}}$ will then give directly the transition energies from the core, with correlation effects included for both core and valence electrons. The physical significance of these energies depends on the nature of the model space. Thus, electron affinities may be calculated by constructing a model space with valence particles only [24, 25], ionization potentials are given using valence holes [26, 27], and both types are included for the purpose of getting excitations out of a closed-shell system [28–31].

2.2. Structure of the model space

Most derivations of the coupled-cluster equations, as well as the original open-shell many-body perturbation theory (MBPT) of Brandow [32], depend on a particular choice of the model space. The orbitals are classified as core, valence, or particles (unoccupied). The core orbitals are always occupied, and all possible distributions of the remaining electrons in the valence orbitals give rise to determinants included in the P space (there may also be valence holes, i.e. unoccupied core orbitals, but the situation is not fundamentally different). Such model spaces have been called “complete” [33]. This recipe is appropriate when the open-shell orbitals are close in energy, which is not the case for most atomic and molecular excited states. It is often impossible to select valence orbitals so that no Q space determinants (with one or more non-valence orbitals) lie close to or even within the energy range spanned by the P space. Thus, if we were to describe the $1s2s\ ^1S$ state of He by designating the $1s$ and $2s$ orbitals as valence, the P space would include the $1s^2$, $1s2s$ and $2s^2$ determinants, but exclude the various $1sns$ terms lying within its energy span. The situation leads to the so-called “intruder states” [34], which destroy the convergence of the expansion.

A general, incomplete model space MBPT has been proposed by Hose and Kaldor [33] and used in extensive calculations [35]. A similar CC method has been described by Jeziorski and Monkhorst [14]. Significant theoretical progress has been made in recent years in understanding incomplete model spaces [23, 36–38]. While our main interest here is in the Fock space approach, it should be mentioned in passing that a general Hilbert space formalism has recently been presented by Meissner, Kucharski and Bartlett [39]. The number of applications has also increased considerably [24–31]. A substantial number of CC applications with incomplete model spaces have been aimed at calculating one-electron excitation energies [28–31], where a natural choice of P determinants involves one hole and one particle with respect to the closed-shell ground state. This is a special case of “quasi-complete” model spaces [11, 37]. It should be noted that intermediate normalization [Eq. (7)] is not satisfied in general for incomplete model spaces [36]. Sinha et al. [40] have however demonstrated that the energy calculation for the particular case of a $1h-1p$ space is operationally equivalent to the complete-space procedure.

Mukherjee [36] has derived a linked-diagram expansion for Fock space coupled cluster in a general model space. The model space $P^{(m)}$ with m valence electrons is chosen on physical grounds, and may be incomplete. Model spaces $P^{(k)}$, $k < m$, are then constructed by deleting $m - k$ orbitals in all possible ways from the $P^{(m)}$ determinants. An operator is designated k -open if it corresponds to a $P^{(k)} \rightarrow Q^{(k)}$ transition, where $Q^{(k)}$ is the complement of $P^{(k)}$; otherwise it is k -closed. The construction of the $P^{(k)}$ spaces causes all m -closed operators to be k -closed for all $k < m$; m -open operators may however be k -closed (in other words, an orbital change transforming every $P^{(k)}$ determinant to another $P^{(k)}$ function may take some $P^{(m)}$ determinant to a $Q^{(m)}$ term). The basic equations for the k -valence sector are then [36]:

$$[S, H_0]_{m\text{-op}}^{(k)} = \{V\Omega - \Omega W\}_{m\text{-op,conn}}^{(k)} \quad (21)$$

$$\{\Omega W\}_{m\text{-cl}}^{(k)} = \{V\Omega\}_{m\text{-cl}}^{(k)}. \quad (22)$$

Two differences between Eqs. (21)–(22) and (8)–(9) should be noted. The classification of the transitions at the k -valence level into $P \rightarrow P$ and $P \rightarrow Q$ has

to be done according to their effect on m -valence states; and the equations for W are implicit [Eq. (22)] rather than explicit [Eq. (9)]. The former requires some additional, not very difficult, bookkeeping. The latter involves a few diagrams not encountered in complete model spaces, and the solution of a set of equations for W matrix elements. As the new diagrams are relatively simple and the equation system is of low dimension, incomplete model spaces are not more difficult to handle than complete ones.

The necessity of using incomplete model spaces may arise under different circumstances. A glance at the zero-order energies of the states to be investigated (the sum of orbital energies) frequently tells us that a complete model space approach is doomed to diverge, since it generates states in Q space which have energies in the range spanned by P space and significant coupling to P states. These intruder states, owing their existence to the one-electron spectrum, may be expected in most molecular excited state calculations, and are discussed in connection to Li_2 states below. In other cases, the zero-order spectrum may look harmless enough, but the CC equations fail to converge because of strong two-electron interactions giving rise to intruder states, as in the 1S states of the beryllium atom.

3. Applications

A considerable number of applications implementing the methods described above have been reported. Many of them were summarized in receipt reports [41, 42] and will not be discussed here. Applications from our group included the ionization potentials and excitation energies (about ten per system) of Be [28], Ne [28], Mg [29], Ar [29], H_2O [30], N_2 and O_2 [41–44], as well as ionization potentials and electron affinities of the alkali atoms Li, Na, K, Rb, and Cs [25]. Highly satisfactory results were obtained in all cases. More recent applications involve the molecular potential functions of LiH [45], Li_2 [46], and Na_2 [47], the reaction path for deprotonation of NH_4^+ [48], and the geometry and vibrational frequencies of the radicals NO_3 [49], NO_2 [50], N_3 [51] and the corresponding anions. The few examples described below were selected to demonstrate certain features of the method. The importance of size extensivity is shown by the electron affinity calculation for the alkali atoms, the selection of model space for simultaneous treatment of a large number of states is investigated for the N_2 molecule [44], and two types of intruder states are discussed in connection with Li_2 excited states [46] and Be 1S states [52].

3.1. Electron affinities of the alkali atoms: the size-consistency problem

The Hartree–Fock electron affinities of the alkali atoms are negative (the energy of the anion is higher than that of the neutral atom), and correlation is crucial in getting correct values. Configuration interaction (CI) studies [53] with only the valence ns shell correlated gave good electron affinities. Inclusion of core $(n-1)sp$ correlation spoiled the agreement with experiment. This is a manifestation of the size-inconsistency of the CI method [54], characterized by the appearance of unlinked terms in the expansion. The attribution of the error to size inconsistency is supported by the relatively large Davidson corrections, which go only part way toward correcting the results.

Table 1. Electron affinities of alkali atoms (eV)

M =	Li	Na	K	Rb	Cs
M ⁻ orbital energy	0.380	0.319	0.247	0.253	0.188
$E_{HF}(M) - E_{HF}(M^-)$	-0.124	-0.112	-0.085	-0.069	-0.070
CISD, ^a <i>ns</i>		0.541	0.492	0.471	
CISD, ^a <i>ns</i> & $(n-1)sp$ + Davidson corr.				0.232	0.326
				0.365	0.451
CCSD, <i>ns</i>	0.612	0.534	0.491	0.473	0.450
CCSD, <i>ns</i> & $(n-1)sp$	0.610	0.552	0.507	0.497	0.480
expt ^b	0.620	0.546	0.501	0.486	0.472

^a Ref. [53]^b Ref. [55]

The CCSD method was applied to the alkali atoms using moderately large bases, from a set of $5s$, $5p$ and one d contracted Gaussian-type orbitals for Li, to $11s$, $9p$ and $5d$ orbitals for Cs [25]. The M⁺ ion served as the reference closed-shell system. Two sets of calculations were performed, correlating the *ns* electrons with or without the $(n-1)sp$ shell. The results are compared with CI calculations [53] and experiment [55] in Table 1. The main contribution to the electron affinities comes from the $(ns)^2$ correlation, which by itself brings the results to within 0.02 eV of experiment. The inclusion of $(n-1)s$ and p correlation has small effect (<0.03 eV) and gives some improvement, cutting the error of 0.01 eV. No adverse effects result from the inclusion of core-core and core-valence correlation. These results show the advantage of using a size-consistent method for calculating energy differences between systems with different numbers of electrons.

3.2. Li₂ potentials: intruders and incomplete model spaces

Li₂ is a natural choice for testing the CC method, as it is small enough to allow experimentation yet has a wealth of low-lying excited states. Many of the spectroscopic constants are known experimentally [56], and detailed theoretical information is available from a recent calculation by Schmidt-Mink et al. [57], using effective core polarization potentials and configuration interaction in a large basis. From the methodological point of view, the study of Li₂ illustrates the selection of the model space over a wide range of internuclear separations for ground and excited states of singly bound molecules.

The nine lowest states of the molecule were calculated. The basis set includes 74 Gaussian type orbitals, and is described in Ref. [46]. The states of interest may be reached by two different computational routes, either by starting from the Li₂ ground state and exciting one electron, or by adding two electrons to Li₂⁺. The latter route was followed, since Li₂⁺ has a closed shell structure at all separations and dissociates correctly. Adding two electrons in the $2\sigma_g$, $3\sigma_g$, $2\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals will generate all desired states. A complete model space will include determinants with two electrons distributed in all possible ways in these orbitals. A computation based on this model space failed to converge. The orbital energies of Li₂ at $R = 5$ bohr, listed in Table 2, explain the divergence. Determinants such as $1\pi_g^2$, included in the model space, are higher in energy than

Table 2. Orbital energies of Li_2^+ at $R = 5$ bohr (in hartree). Orbitals serving as valence particles are underlined

σ_g	σ_u	π_u	π_g	δ_g	δ_u
-2.9923	-2.9919	<u>-0.3271</u>	<u>-0.2372</u>	-0.1821	-0.0763
<u>-0.4363</u>	<u>-0.3091</u>	-0.1669	-0.1288	-0.0286	...
<u>-0.2837</u>	-0.1568	-0.1148	-0.0772	...	
-0.1907	-0.1382	-0.0986	-0.0125		
-0.1460	-0.0959	-0.0133	...		
-0.1086	-0.0837	...			
-0.0895	-0.0563				
-0.0620	-0.0399				
...	...				

several Q determinants, e.g. $2\sigma_g n\sigma_g$ ($n = 4-8$), which turn into intruder states. An incomplete model space was therefore constructed by selecting determinants according to their zero-order energy. It included functions with at least one $2\sigma_g$ electron, as well as $2\sigma_u 1\pi_u$, 17 determinants in all. The $2\sigma_u^2$ function had to be included for $R > 7$ bohr.

The CCSD potential functions are shown in Fig. 1. Table 3 presents a comparison of the calculated molecular properties of ${}^7\text{Li}_2$ with experiment [56]. The tabulated properties are the dissociation energy D_e , the equilibrium separation R_e , the adiabatic excitation energy T_e , and the vibrational constant ω_e . Excellent agreement is obtained for the experimentally known states, with errors of up to 0.02 eV in D_e and T_e , 0.01 Å in R_e , and 3 cm^{-1} in ω_e . These results are better than any previous *ab initio* calculation.

3.3. The $2p^2$ states of Be: unexpected intruder states

Our interest in the $2p^2$ levels of the Be atom stems from the presence of an intruder state which cannot be predicted from the orbital energy spectrum. These

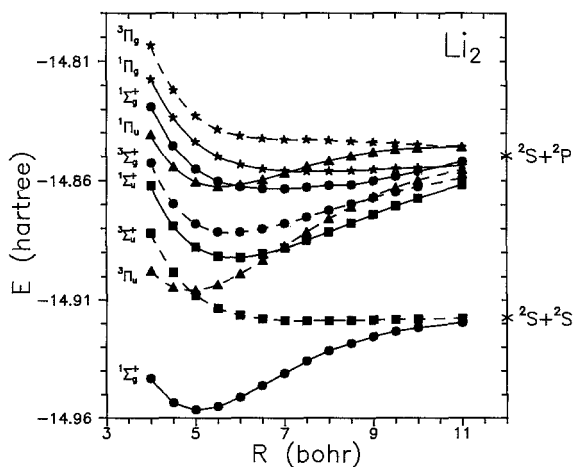
**Fig. 1.** Li_2 potential functions

Table 3. Molecular constants of ${}^7\text{Li}_2$. Experimental values [56] in parentheses

	R_e (Å)	T_e (eV)	D_e (eV)	ω_e (cm $^{-1}$)
$X^1\Sigma_g^+$	2.67 (2.67)	...	1.061 (1.056)	351 (351)
$a^3\Sigma_u^+$	4.05	1.023	0.038	75
$b^3\Pi_u$	2.58 (2.59)	1.375 (1.394)	1.533 (1.510)	349 (346)
$A^1\Sigma_u^+$	3.10 (3.11)	1.750 (1.744)	1.158 (1.160)	257 (256)
${}^3\Sigma_g^+$	3.06	2.032	0.876	252
${}^1\Sigma_g^+$	3.56	2.530	0.378	137
$B^1\Pi_u$	2.94 (2.94)	2.557 (2.534)	0.350 (0.370)	269 (271)
${}^1\Pi_g$	4.02	2.726	0.181	97
${}^3\Pi_g$	repulsive			

levels are strongly perturbed, with the 1D falling below the 3P [58]. The 1S level is a resonance lying just above the $2s$ ionization limit [59]. The $2s3s$ 1S lies below all the $2p^2$ states, thus acting as an intruder state and causing severe convergence problems. Salomonson et al. [10] tried to calculate the Be $2p^2$ levels in the numerical CCD (coupled cluster with double excitations) model, but could not get convergence. All the anomalies disappear for the higher members of the isoelectronic sequence, where the level ordering is as predicted from the independent particle model. Indeed, the numerical CCD model [10] converged easily for the C^{2+} ion.

The calculations reported here were carried out in the 6-311G basis of Kirshnan et al. [60], augmented by diffuse s and p orbitals with exponents $\zeta = 0.0207$ and 0.0069 , with three sets of d orbitals added, $\zeta = 0.765, 0.255, 0.065$ (the spherically symmetrical d combination is left out). This set is expected to provide only a fair description of the $1s$ shell correlation, but a very good representation of the $2s$ and low excited orbitals. The CCSD approximation is employed. Be^{++} is used as the closed-shell reference state, with two electrons added to give the states of the neutral atom. The energies of the $2s$ and $2p$ orbitals are -0.66574 and -0.51925 hartree, well separated from $1s$ on one hand (-5.66719 hartree) and $3s$ and $3p$ on the other hand (-0.26596 and -0.22797 hartree). Unlike the Li_2 case, the Be^{++} one-electron spectrum would indicate using a complete model space calculation, based on $2s$ and $2p$ as valence orbitals. Such a calculation was tried, with the coupled-cluster equations were solved in the usual manner, first for the core (Be^{++}) state, then for one added valence electron, and finally for two valence electrons (Be states). While the first two stages converged rapidly, requiring five iterations each (the convergence criterion is that *all* excitation amplitudes agree to six decimal places), the third stage proved rather difficult. Two techniques were used to achieve convergence: strong damping of the excitation amplitudes in consecutive iterations (the input to the $n + 1$ iteration was taken as a linear combination of the input to the n th iteration and its output in a 3:1 ratio), and repeated use of the reduced linear equations (RLE) method [61]. The latter is essentially solving for the linear combination of excitation amplitude vectors obtained in previous iterations which gives the smallest error when inserted in the CC equations. The RLE equations rapidly become linearly dependent, and when that happens we use their solution as a new starting guess for the CC cycle. Convergence was finally achieved after 195 iterations. The largest excitation amplitude was 5.12, corre-

Table 4. Be ionization potentials and excitation energies (eV)

		Exp ^a	CMS ^b	IMS ^c
Be ⁺	² S IP	18.206	18.141	18.142
	² S → (2p) ² P	3.959	3.971	3.971
	² S → (3s) ² S	10.939	...	10.900
Be	¹ S IP	9.320	9.283	9.283
	¹ S → (2p) ³ P	2.725	2.721	2.721
	¹ S → (2p) ¹ P	5.277	5.232	5.323
	¹ S → (3s) ³ S	6.457	...	6.432
	¹ S → (3s) ¹ S	6.779	(6,802) ^d	6.765
	¹ S → (2p ²) ¹ D	6.997	7.075	7.075
	¹ S → (2p ²) ³ P	7.402	7.403	7.403
	¹ S → (2p ²) ¹ S	9.447	(6,802) ^d	9.520

^a Refs. [58, 59]^b (2s, 2p) complete model space^c Incomplete model space, with the 2s3s configuration added^d This vague formally belongs to the (2p²)¹S state. However, because of the very large 2p² → 2s3s excitation amplitude, it actually describes the (2s3s)¹S

sponding to the 2p² → 2s3s excitation. Other very large amplitudes (> 1) were found for 2s² → 2s3s, 2s² → 2s4s, and 2p² → 2s4s. These large amplitudes result from the inversion of atomic level ordering relative to that predicted by orbital energies.

The ionization potentials and excitation energies calculated in the complete model space described above are shown and compared with experiment [58, 59] in Table 4. As can be expected from the excitation amplitudes, the second ¹S state corresponds to 2s3s rather than 2p²; it is not possible to obtain the 2p²¹S energy this way. Another set of computations was therefore performed, *with the 2s3s configuration moved from Q to P*, forming an incomplete model space (an attempt to include 3s² as well led to divergence). Equations (21)–(22), rather than (8)–(9), were used to derive the detailed expressions for the excitations amplitudes. Convergence was somewhat faster (90 iterations), and the largest excitation amplitude (2s3s → 2s4s) was 0.49. All states of interest came out in their proper places (Table 4), giving very good agreement with experiment. In this case, the intruder problem in the (2s, 2p) complete model space is caused by very strong interaction, two-electron in origin, of the 2s3s determinant with P states.

3.4. N₂ excitation: selection of large model spaces

N₂ has a dense excitation spectrum even at relatively low energies, presenting a challenge both to theoretical evaluation and to interpretation of experimental data. Not all of its low-lying states are well characterized. Orbital excitations of both valence and Rydberg character can mix strongly. A reliable theoretical prediction therefore requires (i) a sophisticated method which includes high-order effects, and (ii) a flexible basis which allows accurate description of both valence and Rydberg excitations. The purpose of our CCSD calculation [44] was to obtain relatively high excitations, and 35 levels with energies up to 15 eV above the ground state were reported and compared with the best available experimental and theoretical values. The details of the calculations are described

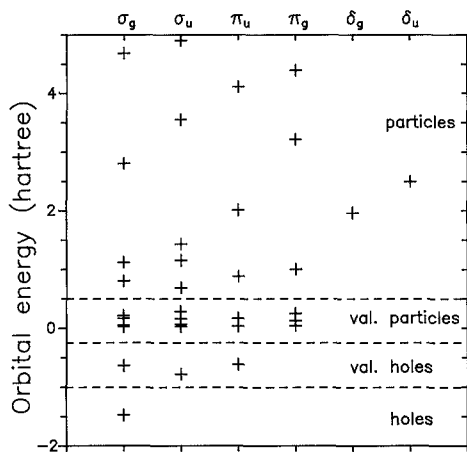


Fig. 2. Hartree-Fock orbital energies of N_2 at $R = 2.074$ bohr, arranged by symmetry

in [44]. Here the considerations for model space selection will be discussed and a brief summary of results given.

The Hartree-Fock orbital energy spectrum of N_2 at an internuclear separation of 2.074 bohr is shown in Fig. 2. These energies provide the most obvious (though not always satisfactory) criterion for the selection, and will usually serve for the first trial. Omission of an orbital which should have been included in the valence space due to large contribution to the states of interest will result in very large excitation amplitudes with attendant convergence difficulties, as the Be example shows, so that a warning mechanism against such omissions exists. Another guide in constructing the model space is the desirability of having it span a narrow energy range and be well separated energetically from the Q space, as these features greatly facilitate convergence of the coupled-cluster iterations. Reliable predictions for a considerable number of excited states are sought here, and a rather large model space is therefore in order. The orbital energies of the N_2 system (Fig. 2) led to the following selection: the $2\sigma_u$, $3\sigma_g$, and $1\pi_u$ orbitals served as valence holes; the $4\sigma_g$ - $7\sigma_g$, $3\sigma_u$ - $6\sigma_u$, $2\pi_u$ - $3\pi_u$, and $1\pi_g$ - $3\pi_g$ were valence particles. All other orbitals are holes or particles and take part in Q space virtual excitations, except for the $1\sigma_g$, $1\sigma_u$ and the highest σ orbitals correlating them, which are eliminated altogether. The $2\sigma_g$ orbital was omitted from the valence space because it lies far below the other valence orbitals, and its contribution to the excited states would be sufficiently taken care of by its participation as a hole in virtual excitations. Indeed, it was found that these virtual excitations did not have particularly large amplitudes, justifying the selection a posteriori. The model space includes all determinants with single excitations from a valence hole to a valence particle. It gives rise to a total of 96 states, the higher of which are not meaningful. Only the 35 states with energies under 15 eV are discussed. Their energy spectrum is shown in Fig. 3. A detailed analysis of the excitation amplitudes reveals the complexity of many of the states, which may have mixed valence-Rydberg character and involve excitations of orbitals belonging to different symmetry species. Information regarding specific states is given in [44]. Table 5 compares the 16 excitation amplitudes known experimentally [62-64] with the CCSD results. These are not necessarily the 16 lowest states, as the $^1\Sigma_u^+$ and $^1\Pi_u$ states are more accessible than others, and the highest state listed in Table 5 is in fact the 33rd in our calculations. The

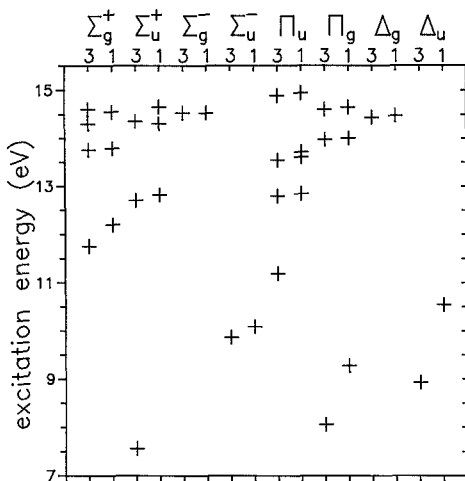


Fig. 3. The 35 excited states of N_2 ($R = 2.074$ bohr) below 15 eV, as given by the coupled cluster method. 3 and 1 on top indicate triplets and singlets, respectively

average error for the lowest eight states is 0.11 eV, better than any previous calculation. The quality of results does not deteriorate at higher energy, the average error for all 16 states being 0.13 eV (no other calculation has reported all of these states). The N_2 application illustrates the feasibility of selecting an appropriate model space even in the case of a relatively dense energy spectrum. It should be noted in passing that the computational effort involved was rather modest, requiring about 15 minutes on the CYBER 180-990 mainframe, with all states obtained in a single calculation.

Table 5. N_2 excitation energies (eV) for experimentally known states

	Exp ^a	CCSD
$A^3\Sigma_u^+$	7.75	7.56
$B^3\Pi_g$	8.04	8.05
$W^3\Delta_u$	8.88	8.93
$a^1\Pi_g$	9.31	9.27
$B^1\Sigma_u^-$	9.67	9.86
$a^1\Sigma_u^-$	9.92	10.09
$w^1\Delta_u$	10.27	10.54
$C^3\Pi_u$	11.19	11.19
$E^3\Sigma_g^+$	12.0	11.75
$a'^1\Sigma_g^+$	12.2	12.20
$c^1\Pi_u$	12.90	12.84
$c'^1\Sigma_u^+$	12.98	12.82
$b^1\Pi_u$	13.24	13.61
$o^1\Pi_u$	13.63	13.71
$b'^1\Sigma_u^+$	14.25	14.31
$e'^1\Sigma_u^+$	14.48	14.65

^a Values fitted in Ref. [64] to experimental spectroscopic constants. $^1\Pi_u$ and $^1\Sigma_u^+$ states from Ref. [63]

4. Summary and conclusion

The open-shell coupled cluster method has been applied to a considerable number of different atomic and molecular systems, with very good results. The applications described above represent rather difficult cases, involving such thorny problems as intruder states, incomplete model spaces and avoided curve crossing. Most of these problems were solved satisfactorily, attesting to the usefulness of the method. In particular, the importance of size extensivity is demonstrated by the case of the alkali atom electron affinities, and examples show that the basic problem of the multireference coupled cluster method, the selection of a model space which will include all the important reference determinants and still lead to convergence of the equations, is solvable in many cases.

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