PHYSICAL REVIEW A VOLUME 38, NUMBER 12 DECEMBER 15, 1988

Intruder states and incomplete model spaces in multireference coupled-cluster theory: The $2p^2$ states of Be

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(Received 1 August 1988)

The open-shell coupled-cluster (CC) method is applied to the excited $2p^2$ states of Be. With the $2s^2$ and $2p^2$ configurations included in the model (P) space, the CC equations prove very difficult to converge. When they do converge, very large (>5) excitation amplitudes are observed, and the second ^1S corresponds to the intruder $2s3s$ configuration, rather than the desired $2p^2$. The inclusion of $2s3s$ (but not $3s^2$) in the model space, which thereby becomes incomplete, improves convergence significantly, and gives energies in very good agreement with values known from other sources.

I. INTRODUCTION

Open-shell or multireference many-body perturbation theory[1-6] (MBPT) and coupled-cluster (CC) methods[7-24] start out with the selection of a low-dimensional model (or P) space, in which an effective Hamiltonian is defined. The effect of the complementary Q space is taken into account while calculating the matrix elements of the effective Hamiltonian, using an appropriate truncation of the wave operator. The eigenvalues of the effective Hamiltonian approximate some desirable eigenvalues of the physical Hamiltonian.

Most derivations of the multireference MBPT and CC, starting with Brandow,[1] 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."[25] 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 nonvalence orbitals) lie close to or even within the energy range spanned by the P space. This situation leads to the so-called "intruder states,"[26] which destroy the convergence of the expansion. A clever way of circumventing the problem in low-order (up to third order) MBPT has been devised by Freed and co-workers.[27] They arbitrarily assigned the same energy to all valence orbitals, and managed to obtain very good results for a variety of atoms and molecules. Their method is equivalent to a different partitioning of the Hamiltonian, so that an extra potential term, diagonal and one electron, is included in the perturbation, with effects showing up in higher order only. Pushing the method to higher order may therefore present difficulties, and the stratagem would fail in CC, which entails infinite-order summation of such perturbation terms, so that the extra term would be summed away without any effect on the convergence problem.

A general, incomplete model space MBPT has been proposed by Hose and Kaldor[25] and used in extensive calculations.[28] A similar CC method has been described by Jeziorski and Monkhorst.[16] Significant theoretical progress has been made in recent years in understanding incomplete model spaces.[13,19,29-31] The number of applications has also increased considerably.[19,32-35] The main interest in CC applications with incomplete model spaces has been aimed at calculating one-electron excitation energies,[32,33] 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 "quasicomplete" model spaces.[13,30] Sinha *et al.*[36] have shown that the energy calculation for the particular case of a $1h$-$1p$ space is operationally equivalent to the complete-space procedure. The first applications of a more general type of incomplete model spaces appeared recently.[34,35]

The $2p^2$ levels of the Be atom provide a good test case for the study of the intruder state problem. These levels are strongly perturbed, with the ^1D lying below the ^3P. The ^1S level has never been observed,[37,38] and extensive CI calculations[39] indicate that it lies just above the $2s$ ionization limit. The $2s3s$ ^1S lies below all the $2p^2$ states, thus acting as an intruder state and causing severe convergence problems. Salomonson *et al.*[12] 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[12] converged easily for the C^{2+} ion.

Various strategies for solving the problem are discussed in this work. They include the application of averaging and projection techniques for iterating the CC equations within the complete model space, and the addition of the intruder $2s3s$ configuration to the model space, which thereby becomes incomplete. All the calculations are carried out in finite basis sets, as our main interest involves molecular applications; this should not, however, affect the conclusions.

II. METHOD

The basic method used in previous work[32,34] follows Lindgren's[12] choice of a normal-ordered wave operator,

$$\Omega=\{\exp(S)\}=1+S+\tfrac{1}{2}\{S^2\}+\cdots . \tag{1}$$

S is the excitation operator describing *connected* single, double, . . . , excitations,

$$S=S_1+S_2+\cdots$$

$$=\sum_{i,j}\{a_i^\dagger a_j\}s_j^i+\tfrac{1}{2}\sum_{i,j,k,l}\{a_i^\dagger a_j^\dagger a_l a_k\}s_{kl}^{ij}+\cdots , \tag{2}$$

where $s_j^i, s_{kl}^{ij}, \ldots$, are excitation amplitudes, and the curly brackets denote normal order with respect to a reference (core) determinant. The summation is carried over connected terms only. The equations determining the excitation amplitudes for a complete model space may be derived from

$$[S,H_0]=\{QV\Omega-\Omega V_{\rm eff}\}_{\rm conn} , \tag{3}$$

$$V_{\rm eff}=V\Omega , \tag{4}$$

where H_0 and V result from the partitioning of the Hamiltonian in the usual way,

$$H=H_0+V . \tag{5}$$

Mukherjee[29] has shown that a similar formulation may be derived for 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[29]

$$[S,H_0]^{(k)}_{m\text{-op}}=\{V\Omega-\Omega V_{\rm eff}\}^{(k)}_{m\text{-op,conn}} , \tag{6}$$

$$\{\Omega V_{\rm eff}\}^{(k)}_{m\text{-cl}}=\{V\Omega\}^{(k)}_{m\text{-cl}} . \tag{7}$$

Two differences between Eqs. (6) and (7) on the one hand and (3) and (4) on the other hand 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 $V_{\rm eff}$ are implicit [Eq. (7)] rather than explicit [Eq. (4)]. 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 $V_{\rm eff}$ 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.

III. APPLICATION TO Be

All calculations were carried out in the 6-311G basis of Krishnan *et al.*,[40] 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, 0.085 (the spherically symmetric 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. Single and double virtual excitations are included in the summation (2), giving the CCSD approximation,

$$S\simeq S_1+S_2 . \tag{8}$$

The reference state for the calculation must have closed shells. Be^{2+} is used here, with orbital energies of $-5.667\,19$, $-0.665\,74$, $-0.519\,25$, $-0.265\,96$, and $-0.227\,97$ hartree for the 1s, 2s, 2p, 3s, and 3p orbitals, respectively. The first three may be compared with the numerical Hartree-Fock values of Salomonson *et al.*,[12] $-5.667\,17$, $-0.666\,09$, and $-0.519\,45$ hartree. A complete model space calculation, with the valence orbitals 2s and 2p, was tried first. It should be observed that the orbital energy spectrum does not lead one to expect any problems, as the 2s and 2p are well separated from all the rest. The coupled-cluster equations were solved in the usual manner, first for the core (Be^{2+}) 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 nth iteration and its output in a 3:1 ratio), and repeated use of the reduced linear equations (RLE) method.[41] 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, corresponding to the $2p^2\rightarrow 2s3s$ excitation. Other very large amplitudes (>1) were found for $2s^2\rightarrow 2s3s$, $2s^2\rightarrow 2s4s$, and $2p^2\rightarrow 2s4s$. These large amplitudes result from the inversion of atomic level ordering relative to that predicted by orbital energies.

As mentioned above, core (Be^{2+}) orbitals are used. To

TABLE I. Total energies with Be^{2+} and Be orbitals (hartree).

		Be^{2+} orbs	Be orbs
Be^{2+}	Hartree-Fock	$-13.610\,377$	
	correlated	$-13.625\,730$	$-13.625\,953$
Be^{+}		$-14.292\,476$	$-14.292\,170$
Be	Hartree-Fock		$-14.571\,942$
	correlated	$-14.633\,618$	$-14.633\,315$

TABLE II. Be ionization potentials and excitation energies (eV).

		Expt.[a]	Be orbs	Be^{2+} orbs[b]	Be^{2+} orbs[c]
Be^+	^2S *IP*	18.206	18.128	18.142	18.142
	$^2S \rightarrow (2p)^2P$	3.959		3.971	3.971
	$^2S \rightarrow (3s)^2P$	10.939			10.900
Be	^1S *IP*	9.320	9.283	9.283	9.283
	$^1S \rightarrow (2p)^3P$	2.725	2.821	2.721	2.721
	$^1S \rightarrow (2p)^1P$	5.277	5.406	5.323	5.323
	$^1S \rightarrow (3s)^3S$	6.457	6.473		6.432
	$^1S \rightarrow (3s)^1S$	6.779	6.840	(6.802)[d]	6.765
	$^1S \rightarrow (2p^2)^1D$	6.997		7.075	7.075
	$^1S \rightarrow (2p^2)^3P$	7.402		7.403	7.403
	$^1S \rightarrow (2p^2)^1S$	9.505[e]		(6.802)[d]	9.520

[a] References 37 and 38.

[b] $(2s,2p)$ complete model space.

[c] With the $2s3s$ configuration added to the model space.

[d] This value formally belongs to the $(2p^2)^1S$ state. However, because of the very large $2p^2 \rightarrow 2s3s$ excitation amplitude, it actually describes the $(2s3s)^1S$ state.

[e] Not observed experimentally. This is the evaluated value of Ref. 39.

assess the effect of using these orbitals for Be states, another set of calculations was performed with Be atom Hartree-Fock orbitals, with the $2s$ orbital serving as a valence hole. Table I shows that the change in the total energies of the ground state of Be and its ions is 3×10^{-4} hartree or less, indicating that the summation inherent in the CCSD method takes care of the difference in orbital description. Another worthwhile observation is that the Be energy obtained with Be^{2+} orbitals and a single reference state is $-14.633\,468$ hartree, so that the inclusion of the $2p^2$ configuration in the model space is not necessary if one is only interested in the ground state.

The more interesting results of the calculation are the ionization potentials and excitation energies. The values obtained with the complete model space described above are shown and compared with experiment[37,38] in Table II. As can be expected from the excitation amplitudes, the second ^1S state corresponds to $2s3s$ rather than $2p^2$; it is not possible to obtain the $2p^2\,{}^1S$ 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 $3s^2$ as well led to divergence). Equations (6) and (7), rather than (3) and (4), were used to derive the detailed expressions for the excitation amplitudes. Convergence was somewhat faster (90 iterations), and the largest excitation amplitude $(2s3s \rightarrow 2s4s)$ was 0.49. All states of interest came out in their proper places (Table II), giving very good agreement with experiment.

IV. SUMMARY AND CONCLUSION

The open-shell coupled-cluster method has been applied to the $2p^2$ states of Be. The $2s3s$ states, which lie in zero order well above the $2p^2$, are pulled below them by correlation effects. The $2s3s\,{}^1S$ level appears as an intruder state, with the result that the coupled-cluster equations for a model space including the $2s^2$ and $2p^2$ configurations are extremely difficult to converge; when they do converge, very large excitation amplitudes appear, and the eigenvalue of the ^1S effective Hamiltonian approximates the $2s3s$ rather than the $2p^2$ energy. An incomplete model space, which includes the $2s3s$ configuration in addition to $2s^2$ and $2p^2$, gives much faster convergence and good agreement with excitation energies known from experiment or from extensive configuration interaction studies.

ACKNOWLEDGMENT

This work was supported in part by the U.S.–Israel Binational Science Foundation.

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