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A TEST OF MULTICONFIGURATIONAL COUPLED-CLUSTER THEORY ON $Be(^1S) + H_2(X\,^1\Sigma_g^+) \rightarrow BeH_2(^1A_1)$

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A perpendicular C_{2v} insertion of Be into H_2 is explored via our multiconfiguration coupled-cluster method within the double-excitation (CCMC-T_2) model. This straight-line path, which encompasses the fragment geometry (Be and H_2), the equilibrium geometry (linear BeH_2) and a transition-state geometry of BeH_2, requires several configurations to achieve a qualitatively correct zeroth-order description of the ground state. The path is identical to that used by Shepard et al. in their single-configuration coupled-cluster study of this same system. It is demonstrated that the CCMC-T_2 model is theoretically and computationally viable and that the resultant coupled-cluster energies parallel the reference-wavefunction energies. When the reference wavefunction ceases to incorporate the dominant configurations, the coupled-cluster wavefunction correspondingly represents the state poorly.

1. Introduction

Calculations of potential energy surfaces of uniform accuracy over a wide range of nuclear geometries are essential when such surfaces are used in dynamics studies. So-called size-consistent (SC) methods [1] are therefore desirable for such applications. Rayleigh–Schrödinger perturbation theory and coupled-cluster theories satisfy the SC requirements stressed by Pople et al. [1]. However the introduction of finite (truncated) approximations to the effective hamiltonians arising in the above theories is not sufficient to guarantee the desired uniform accuracy unless the zeroth-order wavefunctions of these theories are qualitatively correct (in the sense described below) over the relevant geometries.

An example, which forms the subject matter of the present paper, involves the perpendicular (C_{2v}) insertion of (^1S) Be into ($X\,^1\Sigma_g^+$) H_2 which has been investigated by Shepard et al. [2]. The BeH_2 molecule is chosen to lie in the *YZ* plane with the Be atom at the origin and with the *Z* axis the C_2 rotation axis. The path of insertion defined *arbitrarily* in ref. [2], can be described by the straight line $r = 2.54 - 0.46\,R$ (in au), where r is the H–H separation and R is the Be to center of H_2 distance. The geometries at which calculations have been performed are given in table 1. Although this constrained path is *not* any actual reaction path, it covers a wide range of geometries over which (as is shown later) at least six configurations, $1a_1^2 2a_1^2 3a_1^2$, $1a_1^2 2a_1^2 1b_2^2$, $1a_1^2 2a_1^2 1b_1^2$, $1a_1^2 2a_1 3a_1 1b_2^2$, $1a_1^2 2a_1 3a_1 1b_2 2b_2$ are required to achieve a qualitatively correct (zeroth-order) description of the ground state. As shown in more detail in section

Table 1
The perpendicular insertion path of Be into H_2. Be located at (0, 0, 0)

Point	Coordinates of H_2 (x, y, z) (bohr)
A	(0, ±2.54, 0.0)
B	(0, ±2.08, 1.0)
C	(0, ±1.62, 2.0)
D	(0, ±1.39, 2.5)
E	(0, ±1.275, 2.75)
F	(0, ±1.16, 3.0)
G	(0, ±0.93, 3.5)
H	(0, ±0.70, 4.0)
I	(0, ±0.70, 8.0)
J	(0, ±0.70, 20.0)

3.1, these *essential* configurations include the $1s_{\mathrm{Be}}^2 2s_{\mathrm{Be}}^2 1\sigma_{\mathrm{g,H_2}}^2$, $1s_{\mathrm{Be}}^2 2p_{\mathrm{Be}}^2 1\sigma_{\mathrm{g,H_2}}^2$, $1s_{\mathrm{Be}}^2 2s_{\mathrm{Be}}^2 1\sigma_{\mathrm{u,H_2}}^2$ "reactant" configurations as well as the $1s_{\mathrm{Be}}^2\sigma_{\mathrm{BeH,a_1}}^2$-$\sigma_{\mathrm{BeH,b_2}}^2$ configuration of BeH_2. They do not represent high-level electron correlation effects; they provide the qualitatively correct descriptions of the bonds in reactants and products as well as the well-known quasidegeneracy effects in Be($2s^2$, $2p^2$). This example thus presents a good testing ground for multidimensional-reference theories such as the multiconfigurational coupled-cluster (CCMC) method developed earlier in our laboratory [3,4]. Shepard et al. [2] have been successful in describing different parts of this BeH_2 ground-state ($^1A_1$) energy surface using different single-configuration reference functions for different ranges of R, in their so-called coupled-cluster singles and doubles (CCSD) calculations. However, such an approach involves making an arbitrary choice of which reference configuration to use for which range of R values and for what R value to change from one reference configuration to the other.

Recently, we developed a multiconfiguration coupled cluster (CCMC) theory which admits a multiconfiguration (MC) reference wavefunction [3,4]

$$\Phi = \sum_K C_K X_K, \tag{1}$$

in which the $\{X_K\}$ are the configurations and the C_K are their expansion coefficients. Our method is applicable to both closed- and open-shell systems and is cast in terms of the generators of the unitary group [5]. We describe in section 2 the particular approximation of our CCMC method used here and in section 3 the results of our calculations using this approximation on the BeH_2 system are discussed.

2. CCMC method: summary and justification of the $T \approx T_2$ approximation

In ref. [3], we assumed that one has available a MC reference wavefunction $\Phi(\boldsymbol{C}, \boldsymbol{X})$ of the general form shown in eq. (1) but where the configurations X_K contain *all* possible arrangements of N electrons in the valence orbitals. The valence orbitals occupied in Φ are denoted by Greek letters α, β,... while the italic subscripts p, q, r, s... designate the orbitals unoccupied in Φ. Within this notation, the so-called cluster operators are expressed in terms of unitary generators

$$e_{ij} = \sum_\mu a_{i\mu}^+ a_{j\mu},$$

$$e_{ijkl} = e_{ij}e_{kl} - \delta_{jk}e_{il},$$

$$T = \sum_s T_s, \tag{2a}$$

with

$$T_1 = \sum_{r,\alpha} t_{r\alpha} e_{r\alpha}, \tag{2b}$$

$$T_2 = \tfrac{1}{2} \sum_{r\alpha s\beta} t_{r\alpha s\beta} e_{r\alpha s\beta}, \text{ etc.} \tag{2c}$$

Following the conventional coupled-cluster development, $\exp(T)$ is the operator which, when acting on Φ, gives the correlated wavefunction Ψ

$$\Psi = e^T \Phi, \tag{3}$$

which obeys the Schrödinger equation $(H - E)\Psi = 0$. The unknown $\boldsymbol{t}$ amplitudes and the $\boldsymbol{C}$ coefficients in Φ are calculated in our CCMC method from the equations

$$\langle \Phi_{r\alpha s\beta\ldots} | \tilde{H} | \Phi \rangle = 0 \tag{4}$$

and

$$\langle X_L | \tilde{H} | \Phi \rangle = EC_L, \tag{5}$$

where $\tilde{H}$ is the so-called effective hamiltonian,

$$\tilde{H} = e^{-T} H e^T, \tag{6}$$

and the $|\Phi_{r\alpha s\beta\ldots}\rangle = e_{r\alpha s\beta\ldots}|\Phi\rangle$ are singly, doubly, etc. excited configurations relative to the MC reference Φ. Given $\boldsymbol{C}$ and $\boldsymbol{t}$ amplitudes, the total energy can be calculated from

$$E = \langle \Phi | \tilde{H} | \Phi \rangle. \tag{7}$$

In the earlier publication [4], we demonstrated the generality of our method through its application to various closed- and open-shell systems: $H_2(^1\Sigma_g^+)$, $Li(^2S)$, $HeH_2(^1A_1)$, and $CH_2(^3B_1, {}^1A_1)$, with no restrictions on the configurations included in the reference symmetries. These applications were carried out within the approximation $T \approx T_1 + T_2$ and with the commutator expansion for $\bar{H}$ truncated after the second commutators (see below). It was found that when an MC SCF reference function is used for Φ, the t amplitudes in T_1 are small (because the MC SCF procedure has produced nearly optimal orbitals) and that the contributions from the three-particle density matrix elements in the t-determining equations [eq. (4)] can be offset by increasing the size of the function space X_K used in Φ. Hence, it was found that T_1 could essentially be neglected if an MC SCF reference state were employed.

In this paper we explore the approximation $T \approx T_2$ within the structure of our CCMC method with an MC SCF reference function. Within such a coupled-cluster approximation, some simplifications occur. Because of the MC SCF reference function, the t amplitudes occurring in T_1 are expected to be negligible whenever the non-linear couplings between T_1 and T_2 are small. This fact arises due to generalized Brillouin theorems (GBT) [6], $\langle \Phi_{r\alpha} | H | \Phi \rangle = 0$. Secondly, the matrix elements

$$\langle \Phi_{r\alpha s\beta} | [[[H, T_2], T_2], T_2] | \Phi \rangle \equiv 0 \qquad (8)$$

and matrix elements of all higher commutators vanish identically. Since one is justified in neglecting T_1 because an MC SCF reference is employed, the t-determining equations [eq. (4)] can be written *exactly* as

$$\langle \Phi_{r\alpha s\beta} | H + [H, T_2] + \tfrac{1}{2}[[H, T_2], T_2] | \Phi \rangle = 0. \qquad (9)$$

The above two properties, also arise in the coupled-pair many-electron theory CP MET of Čižek [7].

Given this choice of the description of Φ and the truncation ($T \approx T_2$) of the cluster operator which logically follows, we now turn to examine the results of applying the CCMC method to the $^1A_1$ BeH_2 potential energy surface.

3. Calculations and results

3.1. Construction of the MC SCF reference function

It is essential to first examine the multiconfigurational wavefunction of BeH_2 along the reaction path defined in ref. [2], which we simply accept as a path on which to evaluate our CCMC method in comparison to the single-configuration based CC method of ref. [2]. Three qualitatively different types of geometries arise along the path: the fragment geometry $R \to \infty$, $r = 1.4$ au, the linear equilibrium geometry, $R = 0$, $r = 2.54$ au and the "transition-state" geometry. (We use the term transition state loosely here. It is taken to be the geometry at which the energy along the path reaches its maximum.)

At the fragment geometry, the valence molecular orbitals can be labeled as follows: $1a_1 = Be(1s)$, $2a_1 = Be(2s)$, $3a_1 = \sigma_g(H_2)$, $1b_2 = \sigma_u(H_2)$, $2b_2 = Be(2p_y)$, $1b_1 = Be(2p_x)$. The first dominant configuration $1a_1^2 2a_1^2 3a_1^2$ thus corresponds to $Be(^1S) + H_2(^1\Sigma_g^+)$, which is a product of the restricted Hartree–Fock configurations for the ground states of Be and H_2. At the linear equilibrium geometry, the other dominant configuration (in terms of C_{2v} symmetry) is $1a_1^2 2a_1^2 1b_2^2$ which involves the two Be–H σ-bonding orbitals $2a_1$ and $1b_2$. At the transition-state geometry these two configurations $1a_1^2 2a_1^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2$ become quasidegenerate. However, these two chemically intuitive configurations are found to be not sufficient to produce an *accurate* description of the $^1A_1$ surface particularly at this transition-state geometry [☆]. Other configurations ($1a_1^2 2a_1 3a_1 1b_2 2b_2$, both singlet and triplet coupled, $1a_1^2 2a_1^2 1b_1^2$ and $1a_1^2 2a_1 3a_1 1b_2^2$) which can be thought of as describing correlation among the two Be–H σ bond pairs, are found to have configuration weights of ≈ 0.20, 0.12 and 0.10, respectively, near the transition-state geometry (see fig. 1). To obtain a more accurate description of the wavefunction it is therefore best to include all of these configurations in defining the zeroth-order (reference) function along the reaction path.

[☆] In particular, the two configurations ($1a^2 2a_1^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2$) are not adequate at the transition-state geometry (E) as can be seen through the following facts. The 2C MC SCF ground-state energy of -15.5385 hartree is well above the correct energy of the first excited ($^1A_1$) state (E(FCI) $= -15.5540$ hartree). Hence, unless proper precautions are taken, the coupled-cluster procedure can converge to the first excited state when starting from the 2C MC SCF reference wavefunction.

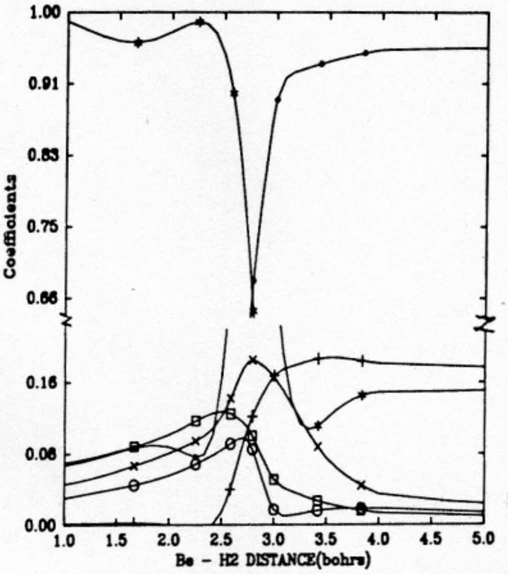

Fig. 1. Comparative weights of the six dominant configurations in the reference MC SCF wavefunction, for the $^1A_1$ ground state of BeH_2. ● $1a_1^2 2a_1^2 3a_1^2$; $_*$ $1a_1^2 2a_1^2 1b_2^2$; + $1a_1^2 2a_1^2 1b_1^2$; ○ $1a_1^2 2a_1 3a_1 1b_2^2$; □ $1a_1^2 2a_1 3a_1 1b_2 2b_2(s)$; × $1a_1^2 2a_1 3a_1 1b_2 2b_2$.

We described in earlier publications [8] systematic selection procedures for obtaining the dominant configurations at any particular geometry of an MC SCF wavefunction. The procedure involves performing, at several chosen geometries, a "dynamic" selection (i.e., selection of configurations with changing orbitals) of configurations based on their energy contributions. After performing such a selection at several geometries one then takes the union of all such selected configurations. The dominant configurations at the fragment $Be + H_2$, equilibrium BeH_2, and transition-state geometries were obtained using such a selection procedure. The resultant reference wavefunction which was used in our subsequent CCMC calculation consisted of all $^1A_1$ configurations arising from placing the four valence electrons in the orbital space $2a_1$, $3a_1$, $1b_1$, $1b_2$, and $2b_2$ with $1a_1^2$ frozen. The magnitudes of the configuration amplitudes belonging to these important configurations are shown as functions of R in fig. 1.

In all of the calculations reported here, the $1a_1$ orbital, which is essentially of Be(1s) character, never participates in the bonding and can be shown to have a negligible (≈ 0.1 kcal/mol) and constant (independent of geometry) correlation energy contribution [☆]. Thus the $1a_1^2$ orbital occupancy is frozen for all of the calculations reported here. In particular, the full CI (FCI) results, which define the exact energies within our limited basis set, involve the frozen $1a_1^2$ orbital occupancy. The basis set consists of contracted gaussian orbitals and is identical to that used by Shepard et al [2].

3.2. Resulting CC energies

Fig. 2 provides a comparison of our MC SCF energy with the energies of the two SCF functions, $1a_1^2 2a_1^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2$, which are the most dominant in Φ as well as with the full configuration interaction (FCI) energy. As mentioned earlier, use of a CC method in which the reference wavefunction is qualitatively correct (i.e., contains all of the dominant configurations) can potentially lead to quantitatively correct results. This point is demonstrated by comparing the potential energy curves of fig. 2 to those of fig. 3 in which the corresponding CC energies are depicted for the various reference functions.

Figs. 2 and 3 illustrate that the coupled-cluster energies are qualitatively parallel to the energies of their respective reference wavefunctions. In particular, the single reference configuration ($1a_1^2 2a_1^2 1b_2^2$), which dissociates to ground-state $Be(1s^2 2s^2)$ and excited $H_2(\sigma_u^2)$, yields a CC energy curve which also converges to a correlated ground state of $Be(^1S)$ and excited $H_2(^1\Sigma_g^+)$ as $R \to \infty$. Analogous problems arise in attempting to follow the CC energy based upon the other dominant $1a_1^2 2a_1^2 3a_1^2$ configuration past the transition state to $R = 0$. Note that single-configuration based CC energies lie below the full CI energies (see fig. 3). Because CC methods are non-variational, they can indeed yield energies lower than the correct full CI energy.

The energies of our CCMC calculations are shown in table 2 where the errors (ΔE) relative to the full CI energies can be seen. The notation

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[☆] We compared the results with those of a complete-space CI calculation in which the $1a_1$(Be 1s) orbital was also correlated.

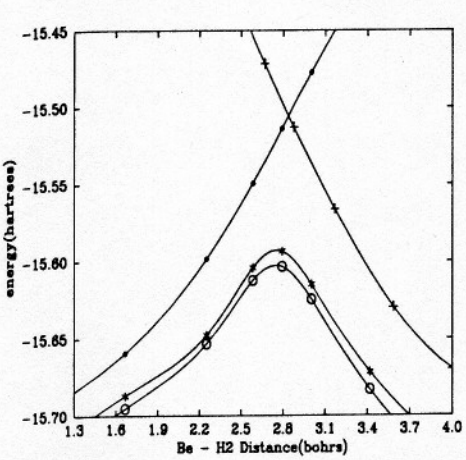

Fig. 2. Comparison of reference wavefunctions' energies for the ${}^1A_1$ ground state of BeH_2. ● $1a_1^2 2a_1^2 1b_2^2$; + $1a_1^2 2a_1^2 3a_1^2$; * 18-MC SCF; ○ FCI.

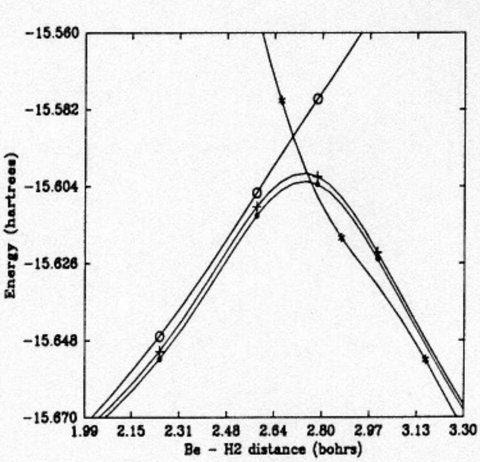

Fig. 3. Comparison of CCMC-T_2 energies for various reference functions (○ $1a_1^2 2a_1^2 1b_2^2$; * $1a_1^2 2a_1^2 3a_1^2$; + 18-MC SCF) with FCI (●) energy for the ${}^1A_1$ ground state of BeH_2.

labeling the molecular geometries along the reaction path is that used in ref. [2]. The resultant CCMC potential energy curve is quite parallel to the corresponding FCI curve and lies within ≈ 1.6 kcal/mol of this "exact" (FCI) curve. Shepard et al. have also calculated [2] CC energies for these same geometries based on using single-configuration reference functions in the CC method. For the range of R values over which each of their two separate reference configurations remain applicable, they also find the CC energies to be very close (±4 kcal/mol) to the FCI values.

When using the MC SCF reference function in the BeH_2 calculations reported here, we found all of the t_2-amplitudes to be relatively small ($\leqslant 0.2$). For the three limiting geometries (A, E, and J) we also included the T_1-operators to provide a check on our $T \approx T_2$ approximation. The T_1 contributions (E_{T_1} and $E_{T_1-T_1}$; see ref. [3]) were found to be $\leqslant 10^{-5}$ hartree or $\leqslant 0.1$ kcal/mol at all of these three geometries.

Table 2
Comparison of CCMC-T_2 energies with SCF and MC SCF reference functions

Point	E(SCF I) [a)] (hartree)	ΔE (kcal/mol)	E(SCF II) [b)] (hartree)	ΔE (kcal/mol)	E(18-MC SCF) (hartree)	ΔE (kcal/mol)	E_{FCI} [c)]
A			−15.780903	−1.3	−15.778544	0.8	−15.778836
B			−15.737141	−0.1	−15.736382	0.3	−15.736918
C	−15.370999	190.9	−15.671348	1.9	−15.673008	0.9	−15.674505
D	−15.526684	60.3	−15.616804	3.6	−15.619949	1.6	−15.622579
E	−15.599198	2.2	−15.584198	11.6	−15.600295	1.4	−15.602629
F	−15.632368	−4.7	−15.552464	45.5	−15.622955	1.1	−15.624785
G	−15.701875	−5.6	−15.474740	137.3	−15.691787	0.7	−15.692965
H	−15.735454	0.6			−15.736625	0.1	−15.736471
I	−15.762241	0.2			−15.762344	0.2	−15.762634
J	−15.762239	0.3	−15.3652992	250.0	−15.762372	0.2	−15.762703

[a)] SCF I refers to the reference configuration $1a_1^2 2a_1^2 3a_1^2$.
[b)] SCF II refers to the reference configuration $1a_1^2 2a_1^2 1b_2^2$.
[c)] The E_{FCI} refers to a complete CI energy in which the $1a_1$ orbital has been kept frozen.

4. Conclusions

The CCMC method with $T \approx T_2$, which can be viewed as an extension of the CP MET to multi-configuration reference functions, is computationally viable. Inclusion of the T_1 operators is made essentially unnecessary through the use of an MC SCF reference function. When included, T_1 yields a miniscule improvement in energy at the expense of the much larger computational effort needed to evaluate matrix elements of $[[H,T_1],T_2]$. The inclusion of T_1 operators also causes the commutator expansion of the effective hamiltonian $\bar{H}$ to go beyond the second commutator level [cf. eq. (9)] as a result of which quartic equations for the t amplitudes should be treated. That the CCMC-T_2 approximation avoids these complications is a strong point in its favor.

Finally it has been observed that the energies calculated via the single-configuration CC and CCMC methods tend to parallel the energies of the respective reference functions. When the reference function ceases to be a good representation to the state under consideration, so does the correlated CC wavefunction. In general, it is wise to use well tested procedures for selecting important configurations at crucial geometries to build a reference function which contains the essential electronic configurations at all geometries. Use of this MC reference function will then yield a CCMC energy surface which can be trusted for all geometries.

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