

## Calculated Potential-Energy Curves for CH<sup>+</sup>

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*Ab initio* calculations have been performed for states of CH<sup>+</sup> which arise from atomic C<sup>+</sup>(<sup>2</sup>P) and H(<sup>2</sup>S) - X<sup>1</sup>Σ<sup>+</sup>, A<sup>1</sup>Π, <sup>3</sup>Π, and <sup>3</sup>Σ<sup>+</sup>. Potential curves have been constructed over a wide range of internuclear distances. All computed energies are believed to be within 1 eV of their exact nonrelativistic Born-Oppenheimer value, and all energy differences are believed to have an accuracy of better than 0.3 eV. Results, with known experimental values in parentheses, are R<sub>e</sub>(X<sup>1</sup>Σ<sup>+</sup>) = 2.136 (2.137) a.u.; D<sub>e</sub><sup>0</sup>(X<sup>1</sup>Σ<sup>+</sup>) = 4.11 (4.21) eV; R<sub>e</sub>(A<sup>1</sup>Π) = 2.332 (2.333) a.u.; T<sub>e</sub>(X - A) = 249 70 (241 46) cm<sup>-1</sup>; R<sub>e</sub>(<sup>3</sup>Π) = 2.130 a.u. No evidence is found for a quasibound <sup>3</sup>Σ<sup>+</sup> Rydberg state, although such behavior has been predicted for isoelectronic BH.

### I. INTRODUCTION

It is becoming increasingly apparent that the CH<sup>+</sup> ion plays a significant role in astrophysics.<sup>1</sup> Spin-change scattering of C<sup>+</sup> with H is believed to be an important cooling mechanism in planetary atmospheres and in the interstellar medium. Also, radiative recombination of this species may be an important mechanism in interstellar molecular formation. Although some spectroscopic information exists for the lowest two singlet states, it is not sufficient for an understanding of the astrophysically interesting processes. It is for systems such as this where experimental measurements are unavailable that one would expect quantum theoretical calculations to be most useful. The best previous such calculation on CH<sup>+</sup> was by Moore, Browne, and Matsen.<sup>2</sup> Indeed, recent astrophysical calculations have used these theoretical results, but only after adjusting them to fit certain experimental parameters.<sup>3,4</sup> It is now possible to perform calculations for a system of this size with enough accuracy so that the *ab initio* results can be used directly. This increased capability is due partly to the availability of more advanced computers and partly to more sophisticated algorithms and accumulated experience with such computations.

In order to calculate potential-energy curves or transition energies it is more important to use a method in which the relative errors between calculated points are small rather than a method which produces small absolute errors at each point. Of course, small absolute errors would ensure small relative errors, but it is still not feasible to routinely calculate absolute energies, even for systems as small as CH<sup>+</sup>, to the desired accuracy. The frequently used Hartree-Fock method is particu-

larly poor because it has well-known systematic errors: Singlet states are generally computed less accurately than triplet states, the energy is less accurate at small internuclear distances than at larger distances, and incorrect dissociation to excited atomic states is often predicted. The method of configuration interaction, unlike Hartree-Fock, is capable of approaching the exact energy as the size of the calculation is increased. The convergence is rather slow, but good relative accuracy can be obtained by a proper choice of configurations and molecular orbitals. For a system as small as CH<sup>+</sup>, the absolute errors can also be kept fairly small without exorbitant amounts of computation. The calculations reported here were performed with the ALCHEMY system of programs.<sup>5</sup> ALCHEMY was designed to efficiently handle large-scale Hartree-Fock and configuration-interaction (CI) calculations. The calculations reported here were performed on an IBM 360/195 and required about 10 h of machine time. As computers become larger and faster, the amount of human labor necessary to set up a calculation becomes significant; the rather extensive results reported here actually represent a very modest amount of human effort (excluding the actual programming, of course). With accumulating experience, the choice of basis functions and types of configurations will require even less effort, and results as accurate as the ones reported here should become routinely available.

### II. CALCULATIONS

Approximate solutions to the usual nonrelativistic Born-Oppenheimer Hamiltonian were constructed in the following manner. Self-consistent-field (SCF) wave functions for each state were calculated for the minimum number of configurations needed

TABLE I. Slater-type basis set used in the CI calculations.

	Center	<i>nl</i> values	Exponent(s) used
Σ	C	1 <i>s</i>	(5.55, 9.66)
	C	2 <i>s</i>	(1.4, 2.0, 4.93)
	C	2 <i>p</i>	(1.37, 1.86, 3.05, 6.81)
	C	3 <i>d</i>	(1.24, 2.35)
	C	4 <i>f</i>	(1.85)
	H	1 <i>s</i>	(1.0, 1.7)
	H	2 <i>s</i>	(1.0)
	H	2 <i>p</i>	(1.0, <sup>a</sup> 1.5)
	H	3 <i>p</i>	(1.0 <sup>b</sup> )
	H	3 <i>d</i>	(2.0)
Π	C	2 <i>p</i>	(1.37, 1.86, 3.05, 6.81)
	C	3 <i>d</i>	(1.24, 2.35)
	C	4 <i>f</i>	(1.85)
	H	2 <i>p</i>	(1.0, 1.5)
	H	3 <i>p</i>	(1.0)
	H	3 <i>d</i>	(2.0)
Δ	C	3 <i>d</i>	(1.24, 2.35)
	H	3 <i>d</i>	(2.0)

<sup>a</sup>These functions give the proper large-*R* limit for a hydrogen atom polarized by an ion.

to provide correct dissociation to atoms. For the excited states, single-configuration restricted Hartree-Fock functions are adequate— $^3\Sigma^+1\sigma^22\sigma^23\sigma4\sigma$  and  $^1,^3\Pi1\sigma^23\sigma1\pi$ . For the ground state, two-configuration SCF was performed on  $^1\Sigma^+C_11\sigma^22\sigma^23\sigma^2 + C_21\sigma^22\sigma^24\sigma^2$ . The SCF functions were expanded in terms of Slater-type functions; the basis set used in all calculations is given in Table I. Starting with the SCF functions, CI wave functions were constructed. All configurations were included which had nonvanishing Hamiltonian matrix elements with the SCF function and which could be constructed by replacing occupied SCF orbitals with virtual orbitals. This includes, in effect, all single and double excitation from the SCF configuration (from both configurations for the ground state) with the following exception. Double excitations in which a singlet-coupled pair (e.g.,  $i\sigma\alpha i\sigma\beta$ ) is replaced with a triplet-coupled pair (e.g.,  $m\sigma\alpha n\sigma\beta + m\sigma\beta n\sigma\alpha$ ) have vanishing matrix elements and are not included; this significantly reduces the number of configurations, especially in open-shell states. This choice of configurations can be justified by perturbation theory; these are the only configurations which contribute to the energy through second order.<sup>6</sup> Use of a properly dissociating two-configuration zero-order wave function for the  $^1\Sigma^+$  state allows the higher-than-double excitations to be ignored in a manner which is consistent for all states. Otherwise, at large *R*, single and double excitations from both of the configurations necessary for proper dissociation are important, and

some of these would be triple and quadruple excitations from a single-configuration Hartree-Fock function. The actual number of configurations used for each state was 3370 ( $^1\Sigma^+$ ), 3251 ( $^3\Pi$ ), 3126 ( $^1\Pi$ ), and 2890 ( $^3\Sigma^+$ ). A CI wave function, which includes all single and double excitations, is invariant to unitary transformations of the orbitals which do not mix the occupied with the virtual orbitals. Hence, any convenient set of virtual orbitals can be used, which, with the occupied SCF orbitals, spans the basis set. Normally, the set produced in the SCF calculation was used.

Although our basis set is quite adequate for reaching the SCF limit, there is no guarantee that it is similarly good for a CI calculation, indeed, the dependence of CI wave functions on basis set composition is an area which needs systematic study before calculations such as this can be done routinely. The size of our basis set was chosen so that all single and double replacements could be included without taxing our computing capability. An initial Slater-type basis set was chosen from a consideration of Clementi's<sup>7</sup> optimized C<sup>+</sup> and C basis sets, and the optimized basis set for CH of Cade and Huo.<sup>8</sup> Functions necessary to properly describe the classical long-range behavior—H 2*p* (1.0) and H 3*p* (1.0)—were added.<sup>9</sup> Exponent optimization was done on all states at *R* = 1.5, 2.137, and 8.0 a.u. for the C 1*s* (5.5), C 2*s* (1.4, 2.0), H 2*p* (1.5), and H 3*d* (2.0) orbitals (cf. Table I). From these results, the compromise basis set listed in Table I was chosen and was used in all the CI calculations. It is conservatively estimated that this basis set gives energies within 0.001 a.u. of the SCF limit for all points (except  $^3\Sigma^+$  with *R* less than 2.0 a.u., which will be discussed later). This basis gives an energy 0.00082 a.u. lower than the "near Hartree-Fock" results given by Cade and Huo<sup>8</sup> for  $X^1\Sigma^+$  at *R* = 2.137 a.u. As a final test of this basis set, calculations were done at selected points using a much larger basis set. This basis and the energy improvements obtained are presented in Table II.

The  $^3\Sigma^+$ , unlike the other states, correlates with a Rydberg state in the united-atom limit. The 4*σ* orbital corresponds to H 1*s* at the separated-atom limit but must become a 3*s* orbital as *R* approaches zero. A recent calculation on the isoelectronic BH  $^3\Sigma^+$  shows Rydberg behavior at small *R*, leading to a potential-energy minimum at 2.216 a.u.<sup>10</sup> It can be seen from Table I that our basis set does not contain functions to adequately describe a Rydberg state. We, therefore, undertook a separate set of calculations, within the Hartree-Fock framework, to search for such a state. The basis set was augmented with C 3*s* (0.7, 1.1) and C 3*pσ* (0.7, 1.1) functions, and calculations were done at *R* = 1.75, 2.0, 2.137, 2.25, and 2.5 a.u. We

TABLE II. Results of large basis set SCF calculations used to test the accuracy of the basis set given in Table I.

Centered on C	Basis set (30 $\sigma$ , 17 $\pi$ )	Centered on H
1s(5.025, 9.055)		1s(0.7, 1.3, 2.9)
2s(1.35, 2.14, 3.1)		2s(0.7, 1.3, 2.6)
3s(1.2, 6.1)		2p(1.0, 1.6, 2.6)
2p(1.05, 1.6, 2.8, 3.5, 6.8)		3d(1.5, 3.0)
3p(1.0)		4f(2.0)
3d(1.4, 2.4, 3.8)		
4f(2.0, 4.0)		

SCF results		
R(a.u.) state	E(a.u.)	$\Delta E^a$ (a.u.)
1.5 $^1\Pi$	-37.685 15	0.000 4
1.5 $^3\Pi$	-37.793 64	0.000 2
2.0 $^3\Sigma^+$	-37.468 95	0.000 7
2.0 $^1\Pi$	-37.804 14	0.000 4
8.0 $^3\Sigma^+$	-37.792 76	0.000 07
8.0 $^1\Pi$	-37.792 87	0.000 07

<sup>a</sup>Energy difference between SCF calculation done with this basis set and that done with the (19 $\sigma$ , 11 $\pi$ ) basis given in Table I.

found that there was indeed a rather sudden change in the character of the 4 $\sigma$  orbital near 2.0 a.u.; at larger  $R$  it is decidedly valencelike and at smaller  $R$  it is decidedly Rydberg-like. This change can be monitored in the expectation value  $\langle 4\sigma | r_H | 4\sigma \rangle$  which is given in Table III. The large- $R$  limit for a H 1s orbital is 1.50. The small increases with decreasing  $R$  reflect distortion into the bonding region until about  $R=2.25$  a.u.; the larger increases below 2.137 a.u. reflect the diffuse nature of the Rydberg orbital. The energy gained by including Rydberg basis functions in the SCF calculation is also given

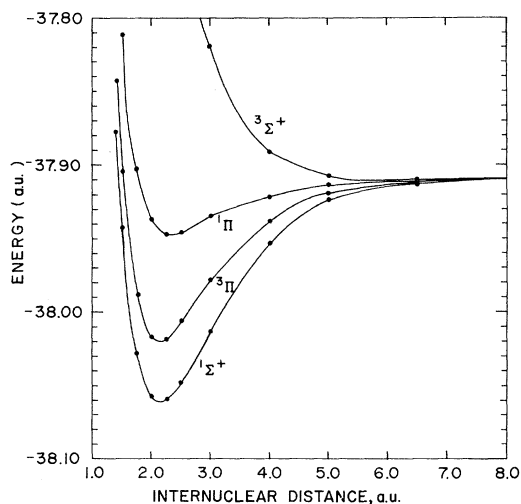


FIG. 1. CI potential-energy curves for states of  $\text{CH}^+$  which dissociate to  $\text{C}^+$  ( $^2P$ ) and  $\text{H}$  ( $^2S$ ).

in Table III. It is seen that for  $R$  greater than 2.0 a.u. the improvement is less than 0.001 a.u., as indicated earlier. Despite the somewhat larger energy gain at smaller  $R$ , we find no evidence for a minimum in the potential curve. We feel that these calculations are accurate enough to eliminate the possibility of a quasibound Rydberg state in the lowest  $^3\Sigma^+$  level of  $\text{CH}^+$ .

The iterative natural orbital scheme proposed by Bender and Davidson<sup>11</sup> has been used very successfully in correlating wave functions. However, it has no formal convergence properties; indeed, upon repeated iteration the energy increases, at which point the procedure is stopped and the lowest energy is the "converged" value. There is a danger that this arbitrary convergence will introduce artificial roughness in a potential surface calculation. Natural orbital iteration was, however, tried at two points to see if significant energy lowering would occur. The natural orbitals of the CI functions were obtained and the CI was repeated using the same configurations but using the natural orbitals in place of the SCF orbitals. In each case the energy *increased*. For  $X^1\Sigma^+$  at  $R=2.25$  a.u. the first iteration caused an increase of 0.000 37 a.u. and the second increased the energy by an additional 0.000 02 a.u. For  $A^1\Pi$  at  $R=1.75$  a.u., one iteration was tried, raising the energy by 0.000 09 a.u. These and other similar results obtained recently imply that the iterative natural orbital method is not effective for improving wave functions of the quality reported here.

### III. RESULTS AND DISCUSSION

The calculated SCF and CI energy values for the lowest  $^1\Sigma^+$ ,  $^3\Pi$ ,  $^1\Pi$ , and  $^3\Sigma^+$  states are given in Tables IV–VII, respectively; the CI potential curves are also presented together in Fig. 1. For the bound states, the CI energy values at  $R=1.75, 2.0,$

TABLE III. Search for Rydberg behavior in the  $^3\Sigma^+$  state. SCF calculations were performed using the basis set given in Table I augmented with C 3s(0.7, 1, 1) and C 2p $\sigma$ (0.7, 1.1) orbitals. (All values are in a.u.)

R(a.u.)	E(a.u.)	$\Delta E^a$	$\langle 4\sigma   r_H   4\sigma \rangle$	$\langle 3\sigma   r_C   3\sigma \rangle^b$
1.75	-37.395 69	0.0045	3.56	1.40
2.0	-37.468 80	0.0006	2.45	1.49
2.137	-37.509 75	0.0002	2.17	1.54
2.25	-37.542 15	...	2.04	1.59
2.5	-37.605 69	0.000 04	1.93	1.68
5.0	-37.788 88 <sup>c</sup>	0.0 <sup>c</sup>	1.54 <sup>c</sup>	1.56 <sup>c</sup>
8.0	-37.792 69 <sup>c</sup>	0.0 <sup>c</sup>	1.50 <sup>c</sup>	1.47 <sup>c</sup>

<sup>a</sup>Energy improvement from SCF result using the basis set given in Table I.

<sup>b</sup>The 3 $\sigma$  orbital correlates with 2p $\sigma$  at both the united-atom and the separated-atom limit.

<sup>c</sup>SCF values using basis set given in Table I. No significant change is expected to occur upon adding Rydberg basis functions.

TABLE IV. CH<sup>+</sup> <sup>1</sup>Σ<sup>+</sup>. Results from two-configuration SCF and 3370-configuration CI calculations (values in a.u.).

<i>R</i>	<i>E</i> (SCF)	<i>C</i> <sub>1</sub> <sup>a</sup>	<i>C</i> <sub>2</sub> <sup>b</sup>	<i>E</i> (CI)	Δ <i>E</i> <sup>c</sup>
1.40	-37.74131	0.998649	-0.051957	-37.87847	0.137
1.50	-37.80510	0.998388	-0.056762	-37.94133	0.136
1.75	-37.89391	0.997404	-0.072010	-38.02816	0.134
2.00	-37.92478	0.995842	-0.091100	-38.05751	0.133
2.137	-37.92856	0.994657	-0.103237	...	...
2.25	-37.92747	0.993459	-0.114186	-38.05899	0.132
2.50	-37.91697	0.989926	-0.141589	-38.04746	0.130
3.00	-37.88369	0.977881	-0.209161	-38.01234	0.129
4.00	-37.82849	0.926629	-0.375976	-37.95308	0.125
5.00	-37.80360	0.848189	-0.529694	-37.92412	0.121
6.50	-37.79421	0.757606	-0.652712	-37.91211	0.118
8.00	-37.79280	0.721929	-0.691967	-37.91023	0.117
20.00	-37.79222	0.707122	-0.707091	-37.90953	0.117

<sup>a</sup>Coefficient of 1σ<sup>2</sup>2σ<sup>2</sup>3σ<sup>2</sup> in two-configuration SCF.<sup>b</sup>Coefficient of 1σ<sup>2</sup>2σ<sup>2</sup>4σ<sup>2</sup> in two-configuration SCF.<sup>c</sup>Difference between two-configuration SCF and full CI.

2.25, 2.5, and 3.0 a.u. were fit to a fourth-degree polynomial and the analytic curves were used to determine the minima. The calculated equilibrium internuclear distances, with known experimental values<sup>12</sup> in parentheses, are  $R_e(X^1\Sigma^+) = 2.136$  (2.137) a.u.,  $R_e(^3\Pi) = 2.130$  a.u., and  $R_e(A^1\Pi) = 2.332$  (2.333) a.u. The corresponding energies are  $E(X^1\Sigma^+) = -38.06067$  a.u.,  $E(^3\Pi) = -38.01863$  a.u., and  $E(A^1\Pi) = -37.94689$  a.u.

The experimental dissociation energy of the ground state is  $D_0^0 = 4.04$  eV.<sup>13</sup> The spectroscopic constants of this state are not very well known,<sup>12</sup> but assuming a zero-point energy equal to one-half  $\omega_e$  leads to an experimental  $D_0^0 = 4.21$  eV. The computed value is 4.11 eV. The other experimentally known energy quantity is the *X* to *A* transition

TABLE V. CH<sup>+</sup> <sup>3</sup>Π. Results from SCF and 3251-configuration CI calculations (all values in a.u.).

<i>R</i>	<i>E</i> (SCF)	<i>E</i> (CI)	Δ <i>E</i> <sup>a</sup>
1.40	-37.73214	-37.84238	0.110
1.50	-37.79365	-37.90412	0.110
1.75	-37.87647	-37.98834	0.112
2.00	-37.90164	-38.01592	0.114
2.25	-37.89934	-38.01687	0.118
2.50	-37.88478	-38.00624	0.121
3.00	-37.84714	-37.97766	0.131
4.00	-37.81174	-37.93699	0.125
5.00	-37.79992	-37.91957	0.120
6.50	-37.79409	-37.91120	0.117
8.00	-37.79282	-37.90954	0.117
9.00	-37.79255	-37.90921	0.117
11.00	-37.79233	-37.90896	0.117
20.00	-37.79219 <sup>b</sup>	-37.90882 <sup>b</sup>	0.117

<sup>a</sup>Difference between SCF and CI energy; i. e., the amount of correlation energy recovered.<sup>b</sup>Extrapolated from 11.0 a.u. results assuming classical long-range behavior.

energy. The computed (and experimental)<sup>12</sup> values are  $T_e = 24\,970$  (24\,145) cm<sup>-1</sup>.

A system which dissociates to an atom and an ion is expected to show a long-range ion induced-dipole attraction which is proportional to  $R^{-4}$ .<sup>14</sup> For CH<sup>+</sup>,

$$E(R) = E_\infty - \alpha_H/2R^4,$$

where  $\alpha_H$  is the polarizability of hydrogen (4.5 a.u.). The computed curves reproduce this behavior quite well as can be seen most dramatically in the large-*R* attractive portion of the otherwise repulsive <sup>3</sup>Σ<sup>+</sup> curve. The energy predicted from the classical long-range interaction is included in Table VII for comparison with the quantum theoretical results. While the SCF energies for all four states approach the same separated-atom limit, the CI results do not (NB the results for  $R = 20.0$  a.u. are essentially the separated-atom limit). The <sup>1</sup>Σ<sup>+</sup> and <sup>3</sup>Σ<sup>+</sup> states have the same CI energy at 20.0

TABLE VI. CH<sup>+</sup> <sup>1</sup>Π. Results from SCF and 3126-configuration CI calculations (all values are in a.u.).

<i>R</i>	<i>E</i> (SCF)	<i>E</i> (CI)	Δ <i>E</i> <sup>a</sup>
1.50	-37.68470	-37.81085	0.126
1.75	-37.77257	-37.90141	0.129
2.00	-37.80372	-37.93657	0.133
2.25	-37.80891	-37.94647	0.138
2.50	-37.80461	-37.94571	0.141
3.00	-37.80039	-37.93410	0.134
4.00	-37.79963	-37.92133	0.122
5.00	-37.79659	-37.91409	0.117
6.50	-37.79375	-37.90956	0.116
8.00	-37.79280	-37.90832	0.116
9.00	-37.79255	-37.90802	0.115
20.00	-37.79219	-37.90762	0.115

<sup>a</sup>Difference between SCF and CI energy; i. e., the amount of correlation energy recovered.

TABLE VII.  $\text{CH}^+ \Sigma^+$ . Results from SCF and 2890-configuration CI calculations (all values in a.u.).

$R$	$E(\text{SCF})$	$E(\text{CI})$	$\Delta E^a$
1.50	-37.28759	-37.39554	0.108
1.75	-37.39117	-37.50866	0.117
2.00	-37.46822	-37.59687	0.129
2.50	-37.60565	-37.73525	0.130
3.00	-37.69487	-37.81998	0.125
4.00	-37.77016	-37.89053	0.120
5.00	-37.78888	-37.90745	0.119
6.50	-37.79283	-37.91049	0.118
	(-37.79347) <sup>b,c</sup>	(-37.91078) <sup>b,d</sup>	
8.00	-37.79269	-37.91011	0.117
	(-37.79276) <sup>b,c</sup>	(-37.91007) <sup>b,d</sup>	
10.00	-37.79242	-37.90976	0.117
	(-37.79243) <sup>b,c</sup>	(-37.90974) <sup>b,d</sup>	
20.00	-37.79222	-37.90953	0.117
	(-37.79222) <sup>b,c</sup>	(-37.90953) <sup>b,d</sup>	

<sup>a</sup>Difference between SCF and CI energy; i.e., the amount of correlation energy recovered.

<sup>b</sup>Classical long-range energy calculated from  $E(R) = E_\infty - \alpha_H/(2R^4)$ ,  $\alpha_H = 4.5 \text{ bohr}^3$ .

<sup>c</sup> $E_\infty = 37.79221$  chosen to fit  $E(\text{SCF})$  at  $R = 20.0 \text{ a.u.}$

<sup>d</sup> $E_\infty = 37.90952$  chosen to fit  $E(\text{CI})$  at  $R = 20.0 \text{ a.u.}$

a.u., but the  $^1\Pi$  state is 0.0007 a.u. and the  $^3\Pi$  state is 0.0019 a.u. (about 0.05 eV) higher. This discrepancy can be explained as follows. Since all calculations included only  $\sigma$ ,  $\pi$ , and  $\delta$  orbitals, and because the  $\delta$  orbitals did not contain any  $f$  basis functions (see Table I), less angular correlation was provided for  $\pi$  than for  $\sigma$  orbitals. The  $\Pi$  states, which have an occupied  $\pi$  orbital, were not, therefore, as well correlated as the  $\Sigma$  states, which do not have occupied  $\pi$  orbitals. Insofar as the  $1\pi$  orbital is essentially a carbon  $2p\pi$  function at all internuclear distances, this deficiency in angular correlation will be constant as a function of  $R$ , and

the  $\Pi$  curves may be uniformly lowered to join the  $\Sigma$  curves at large  $R$ . Such a procedure would eliminate about half the discrepancy between the calculated and experimental  $X$  to  $A$  excitation energy. The difference between the  $^1\Pi$  and  $^3\Pi$  limits is attributed to the method by which certain spin couplings were excluded from the CI. As discussed in Sec. II, double excitations which had zero matrix elements with the dominant configuration because of spin recoupling were excluded. Furthermore, in cases where simple spin-coupling arguments do not lead to a reduction in the spin space, e.g.,  $1\sigma 2\sigma - i\sigma j\sigma$ , it may still be possible to take linear combinations within the complete spin space such that some matrix elements with the dominant configuration vanish identically. This spin recoupling destroys the natural equivalence of singlet and triplet states at large  $R$ . Finally, it should be noted that the energy differences at the separated-atom limit are substantially smaller than the 0.3 eV relative accuracy claimed for these calculations.

Based on these results, it is felt that our estimate of less than 0.3 eV relative error between all computed points is rather conservative.

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<sup>14</sup>See, e.g., Footnote 8 of Ref. 2.