

Calculations of the ground states of BeH and BeH⁺ without the Born-Oppenheimer approximation

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Non-Born-Oppenheimer variational calculations employing explicitly correlated Gaussian basis functions have been performed for the ground states of the beryllium monohydride molecule (BeH) and its ion (BeH⁺), as well as for the beryllium atom (Be) and its ion (Be⁺). An approach based on the analytical energy gradient calculated with respect to the Gaussian exponential parameters was employed. The calculated energies were used to determine the ionization potential of BeH and the dissociation energies of BeH and BeH⁺. Also, the generated wave functions were used to compute various expectation values, such as the average interparticle distances and the nucleus-nucleus correlation functions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2736699]

I. INTRODUCTION

The paradigm of the potential energy surface of a molecular system (the potential energy curve for a diatomic molecule) has been widely accepted and used by both theoreticians and experimentalists. When the Born-Oppenheimer (BO) approximation¹ is assumed regarding the separability of the electronic and nuclear motions, one can use various available methods for quantum mechanical molecular calculations to determine the total electronic energy of the system. This, augmented with the Coulombic repulsion energy calculated for the stationary positions of the nuclei, provides a numerical point for the potential energy surface (PES). Thus, the PES is, in a way, an artificial creation that results from an approximate treatment of the coupling between the electronic and nuclear motions. The question is whether we can liberate ourselves from the PES concept in molecular quantum calculations. The work we have been doing for the last decade on molecular calculations without assuming the BO approximation indicates that this is possible, at least for small molecular systems. An interesting aspect of such calculations is that such concepts as the chemical bonds, the molecular structure expressed in terms of interatomic distances and angles between bonds, the dipole, quadrupole, and higher electrical moments, etc. have different representations when the wave function simultaneously and equivalently depends on the coordinates of the nuclei and the electrons.

Calculating the electronic energy of a molecule for fixed positions of the nuclei is much easier than calculating the energy of the system without assuming the Born-Oppenheimer approximation. Including simultaneously in the wave function the electronic and nuclear coordinates on equal footing leads to complications that do not appear in the calculation of the electronic wave function. The complications result from the strong correlation effects in the motion of the nuclei. These effects are much larger than the corresponding effects for the electrons because the nuclei are

much heavier than the electrons, and the probability of finding two nuclei in one point in space is virtually zero in contrast to the electrons, whose wave functions usually significantly overlap. Also, the relative motion of the electrons and the nuclei is highly correlated because the electrons closely follow the nuclei due to the strong attraction. The large nuclear and electronic correlation effects make the one-particle approximation completely inadequate in describing a molecular system without assuming the BO approximation. Instead, one needs to use a wave function that includes components that explicitly depend on the distances between the particles forming the system (nuclei and electrons). Such components are usually called explicitly correlated functions.

The approach used here that does not assume the BO approximation from the very beginning assures that when there is a breakdown of this approximation, the non-BO effects are properly accounted for. Such an assurance does not always hold for a calculation that accounts for the non-BO effects with the first-order perturbation approach because in the case of a BO breakdown, the perturbation may be too large to be handled with the perturbation theory method. This, however, does not mean that the perturbation approach cannot be applied. There have been successful applications of this method, for example, in the recent works by Gauss *et al.*,² Temelso *et al.*,³ and Gindensperger *et al.*⁴ A problem may only appear at BO-breakdown regions, which are much less likely to be present in the ground state than in excited states of a molecule.

While the molecular electronic calculations that assume the BO approximation are numerous, the calculations where it is not assumed are very scarce. Only recently have such calculations been performed for molecules with more than two electrons (see Refs. 5 and 6 and references therein). By employing the variational method and the analytical derivatives of the energy with respect to the exponential parameters of explicitly correlated Gaussians, we have been able to

achieve a very high accuracy in those calculations. Until very recently we have only been able to calculate diatomic systems, but with the implementation of Gaussians with shifted centers⁵⁻⁷ and, more importantly, Gaussians with complex exponential parameters,⁸ we are trying to extend the scope of the systems that we can calculate to molecules with more than two nuclei.

Essential factors in very accurate non-BO molecular calculations are the use of extended basis sets (several thousand basis functions) and an efficient optimization of the linear and nonlinear parameters contained in them. Such an optimization, in our case, involves multiple calculations of the energy and the energy gradient. The algorithms for such calculations are well suited to computer parallelization, and this feature must be effectively explored in their implementation in order to make such calculations feasible for systems of chemical interest.

In this work we present non-BO calculations on the BeH molecule. This seven-particle problem is the largest neutral molecule we have attempted to calculate with the approach that does not assume the BO approximation. The purpose of the calculations has been to determine the ionization energy (IE) of BeH by subtracting the total non-BO BeH energy from the energy of BeH⁺, which was calculated in this work as well. We also calculated the BeH and BeH⁺ dissociation energies (D_0). Some of these quantities have been experimentally determined with the high-resolution spectroscopy.⁹⁻¹³

II. THE METHOD USED IN THE CALCULATIONS

A non-BO calculation on a molecular system needs to be done in an internal frame of coordinates that excludes the coordinates of the center of mass of the system. Thus, in the first step we transform the total nonrelativistic Hamiltonian by separating the center-of-mass motion, thereby reducing the N -particle problem to an n -pseudoparticle ($n=N-1$) problem described by the internal Hamiltonian \hat{H}_{int} . In this transformation the laboratory Cartesian coordinate system is replaced by a system whose first three coordinates are the laboratory coordinates of the center of mass, \mathbf{r}_0 , and the remaining $3n$ coordinates are the internal Cartesian coordinates. In our approach the origin of the internal coordinate system is placed at one of the nuclei (usually the heaviest one; this nucleus is called the *reference particle*). The other particles (nuclei and electrons) are referred to the reference particle with the Cartesian position vectors \mathbf{r}_i . After separating out from the total Hamiltonian the kinetic energy operator representing the center-of-mass motion, the remaining internal Hamiltonian \hat{H}_{int} has the following form:

$$\hat{H}_{\text{int}} = -\frac{1}{2} \left(\sum_{i=1}^n \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{M_1} \nabla_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i=1}^n \sum_{i < j}^n \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where the prime denotes transposition. The separation of the internal Hamiltonian and the Hamiltonian of the motion

of the center of mass is exact. The internal Hamiltonian [Eq. (1)] describes n pseudoparticles with charges $q_i = Q_{i+1}$ and reduced masses $\mu_i = M_1 M_{i+1} / (M_1 + M_{i+1})$ moving in the central potential of the charge of the reference particle (where Q_i and M_i , $i = 1, \dots, N$, are the charges and the masses of the original particles, respectively; $q_0 = Q_1$ is the charge of the reference nucleus). For BeH $N=7$ and for BeH⁺ $N=6$, and the numbers of the pseudoparticles are $n=6$ and $n=5$, respectively.

In our works concerning non-BO calculations on light diatomic molecular systems with σ electrons,¹⁴⁻²¹ we have shown that the explicitly correlated Gaussians (ECGs) that depend on all interparticle distances in the exponents and on the internuclear distance in the preexponential multipliers very effectively describe nonadiabatic zero-angular-momentum states of those systems. The form of the preexponential multipliers is the internuclear distance \mathbf{r}_1 raised to a non-negative even power, m_k . The ECG function has the following form:

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}] = r_1^{m_k} \exp[-\mathbf{r}'\bar{A}_k\mathbf{r}], \quad (2)$$

where the symbol \bar{A}_k denotes the Kronecker product $A_k \otimes I_3$, and I_3 is the 3×3 identity matrix. The symmetric matrix A_k unique for each basis function must be positive definite. This is achieved by representing this matrix as a product of a lower triangular matrix L_k and its transpose: $A_k = L_k L_k'$. The total internal wave function that includes the spin has to be antisymmetric with respect to permuting the labels of the electrons. Since the Hamiltonian is independent of the spin, the spin coordinates can be integrated out in the calculations of the Hamiltonian matrix elements. With that, the spatial part of the nonrelativistic wave function has to have a certain symmetry with respect to the electron permutations. This is implemented by means of operators \hat{P} , which represent different permutations of electrons. Their action on the Gaussians transforms the exponential parameters in the following way:

$$\hat{P}\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(T_p' A_k T_p \otimes I_3)\mathbf{r}], \quad (3)$$

where T_p is a certain permutation matrix that transforms the internal coordinates. For more details on implementation of the permutational symmetry in our calculations, we refer the reader to our previous works.^{5,6}

In calculating the dissociation energies of BeH and BeH⁺ we also needed the non-BO atomic energies of Be and Be⁺. The basis functions used in those calculations excluded the preexponential multiplier,

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}]. \quad (4)$$

For BeH, each L_k matrix included $n(n+1)/2=21$ independent parameters. For BeH⁺ that number was 15. For each of the basis function these parameters were optimized using the variational method. The variational minimization of the energy was performed with respect to both linear expansion coefficients and the nonlinear parameters of the basis functions, i.e., the basis set exponent matrices L_k and, in the case

TABLE I. Convergence of the total energies for Be⁺, Be, BeH⁺, and BeH, as well as the ionization energy of BeH [IE(BeH)= $E(\text{BeH}^+) - E(\text{BeH})$] and dissociation energies of BeH and BeH⁺ [$D_0(\text{BeH}) = E(\text{Be}) + E(\text{H}) - E(\text{BeH})$, $D_0(\text{BeH}^+) = E(\text{Be}^+) + E(\text{H}) - E(\text{BeH}^+)$]. The total energies are shown in a.u., while the ionization potential and the dissociation energies are given in cm⁻¹.

Basis size	$E(\text{Be}^+)$	$E(\text{Be})$	$E(\text{BeH}^+)$	$E(\text{BeH})$	IE(BeH)	$D_0(\text{BeH})$	$D_0(\text{BeH}^+)$
500	-14.323 863 04	-14.666 426 04	-14.935 110 43	-15.235 538 80	65 936.40	15 228.23	24 475.71
1000	-14.323 863 42	-14.666 433 83	-14.935 710 49	-15.239 801 97	66 740.37	16 162.18	24 607.33
1500	-14.323 863 47	-14.666 434 94	-14.935 837 80	-15.240 969 49	66 968.67	16 418.18	24 635.26
2000	-14.323 863 48	-14.666 435 25	-14.935 885 72	-15.241 451 43	67 063.92	16 523.88	24 645.77
2500	-14.323 863 48	-14.666 435 36	-14.935 908 00	-15.241 703 44	67 114.34	16 579.17	24 650.66
3000	-14.323 863 49	-14.666 435 40	-14.935 920 08	-15.241 862 35	67 146.57	16 614.03	24 653.31
3500	-14.323 863 49	-14.666 435 42	-14.935 927 82	-15.241 965 25	67 167.45	16 636.61	24 655.01
4000	-14.323 863 49	-14.666 435 44	-14.935 933 05	-15.242 034 48	67 181.50	16 651.80	24 656.16

of BeH and BeH⁺, the powers m_k . In the minimization with respect to L_k 's we used the analytically calculated gradients of the Rayleigh quotient,

$$E(\{L_k\}, \{c_k\}) = \min_{\{L_k, c_k\}} \frac{c' H(\{L_k\}) c}{c' S(\{L_k\}) c},$$

with respect to the linear c_k and the nonlinear parameters $\{L_k\}$. In the above expression $H(\{L_k\})$ and $S(\{L_k\})$ are the Hamiltonian and overlap matrices, respectively. Both are functions of the nonlinear parameters of the basis functions. c is a column vector whose components are c_k 's. The use of the analytical gradients in the optimization of the nonlinear parameters significantly reduces the computational time needed for the calculations and is one of the key factors in achieving high accuracy. The range of the preexponential powers, $\{m_k\}$, used was 0–200. The power of each function was optimized when the function was added to the basis set.

The masses of Be and H nuclei we used in the calculations were equal to 16 424.2037 a.u. (⁹Be isotope) and 1836.152 672 61 a.u., respectively.

III. RESULTS

The results of the calculations are summarized in Tables I and II. In the first table we present the results for the total non-BO ground state energies of Be⁺, Be, BeH⁺, and BeH, and their behavior as the basis set size increases. For each system the largest basis set used contained 4000 functions. In the calculations we incrementally grow the basis set for each system from a relatively small size basis obtained by a semi-random selection to finally reach the size of 4000. At the initial stage of this process, when the basis was relatively small, we performed a simultaneous optimization of all exponential parameters of the Gaussians. After the size of 500 was reached, the optimization process involved an approach where only one function at a time was optimized with the gradient procedure. This approach was applied to all basis functions each time the basis was increased by 10 until we reached the size of 2500. Starting with 2500 basis functions, we performed such a cycle each time 20 new functions were added to the basis set.

As seen from the results shown in Table I, the energy convergence is not uniform for all the systems. As can be expected, the energy for the atomic systems (Be⁺ and Be) converges much faster than for the diatomic systems (BeH⁺

and BeH). With 4000 basis functions the energies of Be⁺ are essentially converged within ten significant figures shown in the table. For Be the number of converged significant figures is 9. At the same time, the convergence of the BeH⁺ and BeH energies does not go beyond six to seven figures for BeH⁺ and five to six significant figures for BeH. Out of the four calculations, the BeH calculation was the most computationally demanding and required at least an order of magnitude more CPU time than the BeH⁺ calculation. The results presented in this work required almost one year of continuous calculations performed on a parallel computer system with 32 dedicated processors. At this point the continuation of this effort would be impractical. However, in the future, when faster computers become available, the accuracy of the present calculations can be further improved. As we show next, with 4000 functions in the basis set for each of the systems, some properties can already be calculated quite accurately.

The properties that one can directly calculate from the total energies shown in Table I are the IE of BeH and the dissociation energies for BeH and BeH⁺ corresponding to the lowest-energy products. Those are the neutral Be and H atoms for the first system and Be⁺ and H for the second system [$D_0(\text{BeH}) = E(\text{Be}) + E(\text{H}) - E(\text{BeH})$, $D_0(\text{BeH}^+) = E(\text{Be}^+) + E(\text{H}) - E(\text{BeH}^+)$]. When non-BO energies are used in calculating IE and D_0 's, these quantities include the changes of the zero-point vibrational energies that occur in the process. Thus, they cannot be directly compared with the differences between energies calculated for the equilibrium geometries of the systems (the D_e dissociation energies). Since almost all quantum mechanical calculations are performed by assuming the Born-Oppenheimer approximation, authors of experimental works often do not report the D_0 energies, but they employ sophisticated algorithms where, based on the rovibrational transitions, they determine the D_e 's that can be directly compared with the calculations. For example, in the most recent work on BeH and its isotopomers by Le Roy *et al.*,¹³ only the equilibrium quantities (D_e and r_0) are reported. They are $D_e = 17\,590.00(\pm 200)$ and $r_e = 1.342\,394(\pm 0.000\,001\,2)$ Å. Also Coxon and Colin¹⁰ in their work on the BeH⁺ and BeH only report the D_e dissociation energies. Their results are $17\,426 \pm 100$ and $26\,285 \pm 100$ cm⁻¹, respectively. Our D_0 dissociation energies for BeH⁺ and BeH obtained with 4000 basis functions are 16 651.80 and 24 656.15 cm⁻¹, respectively (see Table I).

TABLE II. Various expectation values computed with different basis sets. All numbers are in a.u.

System	Quantity	500	1000	2000	3000	4000
Be ⁺	$\langle r_{\text{Be-e}}^{-1} \rangle$	2.657 798 0	2.657 798 0	2.657 798 0	2.657 798 0	2.657 798 0
	$\langle r_{e-e}^{-1} \rangle$	1.081 950 0	1.081 949 8	1.081 949 8	1.081 949 8	1.081 949 8
	$\langle r_{\text{Be-e}} \rangle$	1.033 861 9	1.033 862 8	1.033 862 8	1.033 862 8	1.033 862 8
	$\langle r_{e-e} \rangle$	1.755 785 6	1.755 787 5	1.755 787 4	1.755 787 4	1.755 787 4
	$\langle r_{\text{Be-e}}^2 \rangle$	2.169 576 4	2.169 587 3	2.169 587 1	2.169 587 2	2.169 587 2
	$\langle r_{e-e}^2 \rangle$	4.358 501 4	4.358 523 7	4.358 523 4	4.358 523 5	4.358 523 5
	$\langle \delta(\mathbf{r}_{\text{Be-e}}) \rangle$	11.693 664	11.697 017	11.698 496	11.698 637	11.698 790
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.527 170 1	0.526 970 9	0.526 962 7	0.526 944 2	0.526 859 9
Be	$\langle r_{\text{Be-e}}^{-1} \rangle$	2.106 704 9	2.106 707 0	2.106 707 3	2.106 707 3	2.106 707 3
	$\langle r_{e-e}^{-1} \rangle$	0.729 073 8	0.729 074 4	0.729 074 4	0.729 074 4	0.729 074 4
	$\langle r_{\text{Be-e}} \rangle$	1.493 195 1	1.493 195 0	1.493 194 4	1.493 194 4	1.493 194 4
	$\langle r_{e-e} \rangle$	2.545 434 9	2.545 442 2	2.545 442 4	2.545 442 6	2.545 442 6
	$\langle r_{\text{Be-e}}^2 \rangle$	4.061 988 1	4.062 038 5	4.062 038 8	4.062 039 6	4.062 039 7
	$\langle r_{e-e}^2 \rangle$	8.809 205 3	8.809 341 7	8.809 346 4	8.809 349 3	8.809 349 7
	$\langle \delta(\mathbf{r}_{\text{Be-e}}) \rangle$	8.831 099 0	8.837 271 5	8.838 616 1	8.839 539 9	8.839 512 4
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.268 117 1	0.267 773 5	0.267 635 3	0.267 629 0	0.267 625 9
BeH ⁺	$\langle r_{\text{Be-H}}^{-1} \rangle$	0.399 923 8	0.399 921 8	0.399 914 4	0.399 916 3	0.399 913 1
	$\langle r_{\text{Be-e}}^{-1} \rangle$	2.101 823 9	2.101 884 4	2.101 896 7	2.101 899 9	2.101 900 5
	$\langle r_{\text{H-e}}^{-1} \rangle$	0.608 295 0	0.608 374 8	0.608 402 8	0.608 412 2	0.608 409 5
	$\langle r_{e-e}^{-1} \rangle$	0.765 422 2	0.765 426 9	0.765 424 6	0.765 424 8	0.765 422 7
	$\langle r_{\text{Be-H}} \rangle$	2.513 946 9	2.512 940 4	2.512 797 2	2.512 761 6	2.512 782 2
	$\langle r_{\text{Be-e}} \rangle$	1.418 580 3	1.418 409 3	1.418 397 5	1.418 393 8	1.418 399 2
	$\langle r_{\text{H-e}} \rangle$	2.188 670 3	2.188 248 6	2.188 225 3	2.188 215 9	2.188 242 2
	$\langle r_{e-e} \rangle$	2.192 320 1	2.192 219 7	2.192 255 2	2.192 259 3	2.192 276 0
	$\langle r_{\text{Be-H}}^2 \rangle$	6.353 808 1	6.346 166 5	6.344 964 1	6.344 722 1	6.344 828 9
	$\langle r_{\text{Be-e}}^2 \rangle$	3.450 284 0	3.450 021 8	3.450 234 8	3.450 279 3	3.450 337 3
	$\langle r_{\text{H-e}}^2 \rangle$	5.492 949 9	5.490 562 5	5.490 589 2	5.490 590 1	5.490 762 6
	$\langle r_{e-e}^2 \rangle$	6.096 960 5	6.097 448 0	6.098 075 2	6.098 192 8	6.098 332 0
	$\langle \delta(\mathbf{r}_{\text{Be-H}}) \rangle$	1.34×10^{-8}	2.07×10^{-9}	6.35×10^{-9}	2.34×10^{-9}	1.02×10^{-9}
	$\langle \delta(\mathbf{r}_{\text{Be-e}}) \rangle$	8.704 308 6	8.710 822 1	8.735 147 3	8.736 294 0	8.745 846 8
	$\langle \delta(\mathbf{r}_{\text{H-e}}) \rangle$	0.094 644 5	0.095 992 3	0.096 785 3	0.098 111 7	0.098 130 8
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.266 275 2	0.265 910 7	0.265 366 0	0.265 257 0	0.265 068 2
BeH	$\langle r_{\text{Be-H}}^{-1} \rangle$	0.390 804 2	0.390 819 8	0.390 711 8	0.390 654 1	0.390 609 4
	$\langle r_{\text{Be-e}}^{-1} \rangle$	1.760 411 1	1.760 673 5	1.760 767 5	1.760 770 8	1.760 767 1
	$\langle r_{\text{H-e}}^{-1} \rangle$	0.543 635 5	0.543 844 4	0.543 811 3	0.543 757 8	0.543 718 2
	$\langle r_{e-e}^{-1} \rangle$	0.588 928 8	0.588 904 1	0.588 812 4	0.588 754 2	0.588 721 5
	$\langle r_{\text{Be-H}} \rangle$	2.581 691 8	2.574 818 1	2.572 984 4	2.572 893 1	2.573 026 2
	$\langle r_{\text{Be-e}} \rangle$	1.748 138 4	1.748 405 8	1.749 015 9	1.749 426 9	1.749 634 9
	$\langle r_{\text{H-e}} \rangle$	2.653 207 7	2.651 012 0	2.651 123 8	2.651 557 7	2.651 852 7
	$\langle r_{e-e} \rangle$	2.828 844 9	2.830 448 8	2.832 054 1	2.832 913 9	2.833 328 7
	$\langle r_{\text{Be-H}}^2 \rangle$	6.724 173 7	6.671 153 7	6.655 136 1	6.653 450 9	6.653 722 7
	$\langle r_{\text{Be-e}}^2 \rangle$	4.920 246 7	4.931 627 7	4.940 783 3	4.945 395 3	4.947 572 6
	$\langle r_{\text{H-e}}^2 \rangle$	8.833 119 1	8.820 386 6	8.823 108 7	8.827 108 7	8.829 386 0
	$\langle r_{e-e}^2 \rangle$	10.321 047	10.346 657	10.366 107	10.375 353	10.379 558
	$\langle \delta(\mathbf{r}_{\text{Be-H}}) \rangle$	6.27×10^{-7}	1.58×10^{-7}	3.93×10^{-8}	1.16×10^{-8}	9.74×10^{-9}
	$\langle \delta(\mathbf{r}_{\text{Be-e}}) \rangle$	6.850 831 9	6.919 339 8	6.959 969 4	6.969 805 7	6.976 104 4
	$\langle \delta(\mathbf{r}_{\text{H-e}}) \rangle$	0.079 389 8	0.081 664 1	0.083 062 7	0.083 623 6	0.084 126 4
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.163 373 2	0.161 638 1	0.160 381 7	0.160 258 0	0.160 092 3

For the IE our result is $67\,181.50\text{ cm}^{-1}$, while the result obtained by Coxon and Colin¹⁰ was $66\,333 \pm 100\text{ cm}^{-1}$.

As mentioned above, the level of the convergence of the energies for Be⁺, Be, BeH⁺, and BH is not uniform. Obviously, atomic systems require fewer basis functions than diatomics, and systems with more particles require more functions than systems with fewer particles. These trends allow us to relate the IE and D_0 results we obtained in the calcu-

lations to the complete-basis-set values. For example, since the BeH energy is less converged with 4000 basis functions than the BeH⁺ energy, our IE should be considered as a lower bound to the complete-basis-set IE. The same applies to $D_0(\text{BeH})$ and $D_0(\text{BeH}^+)$.

Having calculated the non-BO wave functions for Be⁺, Be, BeH⁺, and BH for different numbers of basis functions, we used them to calculate some common expectation values

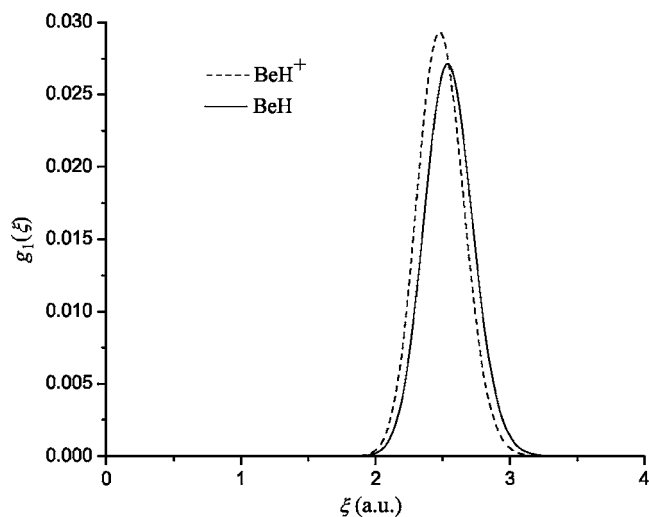


FIG. 1. Be–H correlation function for BeH and BeH⁺.

to see how they converge with the increase of the basis set size and how they change from system to system. The results for the expectation values are summarized in Table II. As one can see, the convergence with the size of the basis set is again much faster for the atomic systems than for the diatomic systems. For example, the average nuclear distances in BeH and BeH⁺ are converged to only five digits. As expected, the average internuclear distance in BeH (2.573 026 2 a.u.) is longer than the distance in BeH⁺ (2.512 782 2 a.u.). The former can be compared with the experimental equilibrium distance r_e of 2.536 837 a.u.^{22,23}

In a non-BO calculation the structure of a molecular system can only be determined through expectation values of the geometrical parameters. One can also plot the nucleus-nucleus correlation function. For BeH and BeH⁺ this distribution is calculated as

$$g_1(\xi) = \langle \Psi(\mathbf{r}) | \delta(\mathbf{r}_1 - \xi) | \Psi(\mathbf{r}) \rangle \\ = \int_{-\infty}^{\infty} |\Psi(\xi, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_2, \dots, d\mathbf{r}_n, \quad (5)$$

where $\delta(\mathbf{r}_1 - \xi)$ is the three-dimensional Dirac delta function. The above correlation function is equivalent to the density of the proton in the reference frame of the Be nucleus. The BeH and BeH⁺ nucleus-nucleus correlation functions are compared in Fig. 1. The correlation functions are spherically symmetric and depend only on the absolute value of ξ . As expected, the BeH⁺ nucleus-nucleus correlation function is slightly narrower and more peaked than for BeH, and its maximum is located slightly closer to the origin in agreement with the average BeH⁺ internuclear distance being slightly shorter than the BeH distance.

IV. SUMMARY

In this work we have performed very accurate non-BO calculations of the ground states of the Be⁺, Be, BeH⁺, and

BeH systems. Up to 4000 explicitly correlated Gaussian functions were used in expanding the wave function for each system. The Gaussian expansions were extensively optimized in terms of both the linear and nonlinear parameters. The present calculations are by far the most accurate ever performed for all these systems.

The calculated energies were used to determine the ionization energy of BeH and the BeH and BeH⁺ dissociation energies. The values for these quantities obtained in the calculations should be considered lower bounds to the complete-basis-set values. Apart from the energies, we also calculated some expectation values, as well as the nucleus-nucleus correlation functions. Those quantities provide the characterization of the ground state wave functions and describe the structures of the systems.

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