

Non-Born–Oppenheimer calculations of the BH molecule

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Variational calculations employing explicitly correlated Gaussian basis functions have been performed for the ground state of the boron monohydride molecule (BH) and for the boron atom (B). Up to 2000 Gaussians were used for each system. The calculations did not assume the Born–Oppenheimer (BO) approximation. In the optimization of the wave function, we employed the analytical energy gradient with respect to the Gaussian exponential parameters. In addition to the total nonrelativistic energies, we computed scalar relativistic corrections (mass-velocity and Darwin). With those added to the total energies, we estimated the dissociation energy of BH. The non-BO wave functions were also used to compute some expectation values involving operators dependent on the interparticle distances. © 2009 American Institute of Physics.

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I. INTRODUCTION

In the vast majority of quantum mechanical molecular calculations, the Born–Oppenheimer (BO) approximation concerning the separability of the electronic and nuclear motions is assumed. The BO calculations are performed for fixed positions of the nuclei and involve solving the electronic Schrödinger equation. By solving this equation for different geometrical arrangements of the nuclei of the system, the potential energy surface (PES) is generated. The PES can then be used to determine states corresponding to the nuclear motion. If the BO approximation is not assumed, the nuclear and electronic degrees of freedom couple and the wave function describing a particular state of the systems explicitly depends on the coordinates of both the electrons and the nuclei and cannot be represented as a simple product of the electronic and nuclear wave functions. Numerous techniques for solving the electronic Schrödinger equation have been developed over the last three to four decades, but there have been only a few that deal with solving the complete Schrödinger equation simultaneously describing the motion of the electron and the nuclei.^{1–7} Our contribution to the field has been the development of methods for performing atomic and molecular non-BO calculations employing explicitly correlated multiparticle Gaussian functions (see reviews^{8,9} and references therein).

Solving the complete nonrelativistic Schrödinger equation for an atomic or a molecular system that treats the nuclei on equal footing with the electrons and the determination of the wave function dependent on the electronic and nuclear degrees of freedom is a significantly more complicated task than solving the electronic Schrödinger equation, particularly, in the case of molecules. The complications result from

the strong correlation effects in the relative motion of the nuclei and in the coupling of the motions of the nuclei and the electrons. The nuclei correlate stronger than electrons because they are much heavier and the probability of finding two of them in a single point in space is virtually zero in contrast with the much lighter electrons whose wave functions usually significantly overlap. The strong nucleus–electron correlation is related to the strong attraction of these two classes of particles resulting in electrons following the nuclei in their motion within the system. To describe the above mentioned correlation effects in non-BO calculations, one needs to expand the wave functions in terms of basis functions that explicitly depend on the interparticle distances, i.e., the nucleus–nucleus, nucleus–electron, and electron–electron distances. Explicitly correlated Gaussians used in our non-BO calculations are such basis functions. Using expansions in terms of one-particle functions, i.e., employing the orbital approximation, is very inefficient in expanding the non-BO wave functions.

In this work we are presenting results of non-BO calculations of a diatomic molecule with six σ electrons. This eight particle problem (six electrons and two nuclei) is the largest ever attempted with a rigorous non-BO approach. The most challenging aspect of such calculations is the optimization of the nonlinear parameters contained in the wave function. One should note that, when fully explicitly correlated basis functions are used for systems containing identical particles, the calculation of the necessary matrix elements scales as $N! \times f(N)$, where N is the number of identical particles (electrons) in the system and $f(N)$ is some polynomial of N (the order of the polynomial depends on the system and the form of basis functions; usually it is around five). The $N!$ Factor comes from proper antisymmetrization, which needs to be applied to the wave function to make the electrons indistinguishable. For the BH molecule $N!=720$. Even

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though the algorithms used in our approach are very well parallelized and in the variational optimization of the wave function parameters, we use the analytical gradient of the energy determined with respect to the linear and nonlinear parameters contained in the wave function; the calculations take large amounts of central processing unit (CPU) time, because the energy and the gradient have to be computed very many times. The results shown in this work represent a year of continuous calculations with the use of 6 processors/24 cores (quadcore Intel Xeon 2.67 GHz or quad-core AMD Opteron 2.2 GHz).

There has been a number of theoretical calculations concerning the BH molecule (see, for example, Refs. 10–13) performed with *ab initio* quantum mechanical methods based on the BO approximation. Those works provided very sound estimations of the ground state dissociation energy (D_0), dipole moment, equilibrium internuclear distance, and some other measurable quantities. The most recent paper by Miliordos and Mavridis gives a value for D_0 of 81.43 kcal/mol (or 28 476 cm^{-1}) which probably is the best theoretical results calculated for BH. This value agrees very well with the best experimental estimate of 81.6 ± 0.6 kcal/mol (or $28\,535 \pm 210$ cm^{-1}) recommended by Bauschlicher *et al.*¹⁴

In addition to the BH calculations, we also calculated in this work the ground state energy of the boron atom. That energy and the energy of the hydrogen atom subtracted from the BH energy gives the dissociation energy, D_0 . Apart from D_0 , we also calculated some expectation values for BH and B, which provide additional information on the ground state non-BO wave functions of these systems.

II. THE METHOD USED IN THE CALCULATIONS

The calculations presented here have been performed using the standard variational method. The total energy of each N -particle system expressed as the expectation value of the internal nonrelativistic Hamiltonian, \hat{H}_{nonrel} , was minimized with respect to linear and nonlinear parameters. \hat{H}_{nonrel} is obtained by separating the kinetic energy of the center-of-mass motion from the “laboratory” Hamiltonian. The internal Hamiltonian expressed in terms of the internal Cartesian coordinates with the center at one of the particles in the system (called the reference particle; usually the heaviest nucleus) has the following form:

$$\hat{H}_{\text{nonrel}} = -\frac{1}{2} \left(\sum_{i=1}^n \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^n \sum_{j \neq i}^3 \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i < j}^n \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where $n=N-1$, q_0 is the charge of the reference particle, q_i , $i=1, \dots, n$ are the charges of the other particles, \mathbf{r}_i , $i=1, \dots, n$, are the position vectors of the other particles with respect to the reference particle, r_i are their lengths, $r_{ij}=|\mathbf{r}_j - \mathbf{r}_i|$, m_0 is the mass of the reference particle, m_i are the masses of other particles, and $\mu_i = m_0 m_i / (m_0 + m_i)$ is the reduced mass of particle $i+1$ ($i=1, \dots, n$). In the present calculations we used the mass of the B nucleus equal to

20 063.737 52 m_e and the mass of the H nucleus (proton) equal to 1836.152 672 47 m_e ,¹⁵ where m_e is the mass of the electron. The value of n is 5 for the B atom and 7 for the BH molecule. Thus the separation of the center-of-mass motion reduces the $(n+1)$ -particle problem to an n -particle problem. Also, it is important to note that the internal Hamiltonian (1) is spatially “isotropic” (rotationally invariant or “atom”-like) not only for the atomic case, but also for the molecular case. More information on the center-of-mass separation and the form of the internal Hamiltonian (1) can be found elsewhere.^{8,9}

In previous works^{16–21} we showed that the spatial part of the non-BO wave function describing the ground state of a diatomic system with σ electrons can be expanded in terms of one-center, spherically symmetric explicitly correlated Gaussian functions multiplied by even powers (m_k) of the distance between the nuclei, r_1 :

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

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$, the prime symbol means that a vector (matrix) is transposed, A_k is a 3×3 symmetric matrix of the Gaussian exponential parameters, I_3 is a 3×3 unit matrix, and \otimes denotes the Kronecker product. The addition of the $r_1^{m_k}$ factors to the Gaussians (2) provides a very effective description of the internuclear correlations in the wave function. These are the only correlation effects that require the presence of such factors in the basis functions. The electron-nucleus and electron-electron correlation can be very well represented by simple correlated Gaussians without the $r_1^{m_k}$ factors.

Basis functions (2) have to be square integrable. This imposes restrictions on the matrix elements of the A_k matrix, which has to be positive definite. In order to avoid dealing with these restrictions in the calculations, we use the Cholesky-factored form of A_k , $A_k \equiv L_k L_k'$, where L_k is a lower triangular matrix (all elements above the diagonal are zero). With the Cholesky-factored form of A_k , this matrix is automatically positive definite for any real values of the L_k matrix elements. The L_k matrix elements are the variables that are optimized in the calculations. The pre-exponential powers, m_k , in the present calculations ranged from 0 to 250. The power involved in each basis function is optimized when the function is first added to the basis set.

In the calculations of the 2P ground state of the boron atom, we used the basis functions,

$$\phi_k = z_{p_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (3)$$

which were previously considered in our works.^{22,23} Here we also use the Cholesky-factored form of the A_k matrix, $A_k = L_k L_k'$. Index p_k ranges from 1 to n and, similarly, to m_k in Eq. (2), can be considered as an integer variational parameter.

Spatial basis functions (2) and (3) multiplied by the corresponding spin wave functions must be properly antisymmetrized in order to be suitable for describing the states of systems containing fermions. In practical calculations, however, it is more convenient to use a spin-free formalism and apply Young operators to Eqs. (2) and (3) to implement the proper symmetry properties of the wave function.

TABLE I. Nonrelativistic and relativistic ($E^{\text{rel}}=E^{\text{nonrel}}+\alpha^2\langle H_{\text{MV}}\rangle+\alpha^2\langle H_{\text{D}}\rangle$) energies of B and BH in a.u. D_0 are the corresponding dissociation energies expressed in cm^{-1} .

Basis size	E^{nonrel} (B)	E^{rel} (B)	E^{nonrel} (BH)	E^{rel} (BH)	D_0^{nonrel}	D_0^{rel}
500	-24.652 069	-24.659 230	-25.270 646	-25.277 747	26 084	26 074
1000	-24.652 494	-24.659 659	-25.277 313	-25.284 438	27 454	27 449
1500	-24.652 573	-24.659 733	-25.279 332	-25.286 461	27 880	27 876
2000	-24.652 598	-24.659 758	-25.280 280	-25.287 408	28 083	28 079

The standard Rayleigh–Ritz variational method has been used in the calculations. It involves the solution of the secular equation:

$$(\mathbf{H} - \varepsilon \mathbf{S})\mathbf{c} = 0, \quad (4)$$

where \mathbf{H} and \mathbf{S} are the Hamiltonian and overlap matrices (with the size equal to the number of basis functions used), respectively, and \mathbf{c} is the vector of the linear expansion coefficients, \mathbf{c}_k . The elements of matrices \mathbf{H} and \mathbf{S} depend on L_k and m_k (or p_k). In order to obtain high accuracy results, the energy ε has to be minimized with respect to the Gaussians exponential parameters. Such a minimization is an extremely costly procedure. It can be greatly accelerated by using the analytic energy gradient determined with respect to the L_k exponential parameters. The use of the analytic gradient allowed us to extend the basis set size for both the BH molecule and the B atom to 2000 functions. In the 2000-function basis set there are 56 000 nonlinear L_k optimization parameters in the BH calculations and 30 000 parameters in the calculations on the B atom.

After the non-BO nonrelativistic wave functions were generated, they were used to calculate the following expectation values: $\langle 1/r_{\text{B-e}} \rangle$, $\langle 1/r_{\text{e-e}} \rangle$, $\langle r_{\text{B-e}} \rangle$, $\langle r_{\text{e-e}} \rangle$, $\langle r_{\text{B-e}}^2 \rangle$, $\langle r_{\text{e-e}}^2 \rangle$, $\langle \delta(\mathbf{r}_{\text{B-e}}) \rangle$, and $\langle \delta(\mathbf{r}_{\text{e-e}}) \rangle$, for the B atom, and $\langle 1/r_{\text{B-H}} \rangle$, $\langle 1/r_{\text{B-e}} \rangle$, $\langle 1/r_{\text{H-e}} \rangle$, $\langle 1/r_{\text{e-e}} \rangle$, $\langle r_{\text{B-H}} \rangle$, $\langle r_{\text{B-e}} \rangle$, $\langle r_{\text{H-e}} \rangle$, $\langle r_{\text{e-e}} \rangle$, $\langle r_{\text{B-H}}^2 \rangle$, $\langle r_{\text{B-e}}^2 \rangle$, $\langle r_{\text{H-e}}^2 \rangle$, $\langle r_{\text{e-e}}^2 \rangle$, $\langle \delta(\mathbf{r}_{\text{B-e}}) \rangle$, $\langle \delta(\mathbf{r}_{\text{H-e}}) \rangle$, and $\langle \delta(\mathbf{r}_{\text{e-e}}) \rangle$ for the BH molecule. Here $\delta(\mathbf{r})$ denotes a three-dimensional Dirac delta function, $\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z)$. We also calculated the two leading scalar relativistic corrections for each system, the mass-velocity and Darwin corrections, $\langle \hat{H}_{\text{MV}} \rangle$ and $\langle \hat{H}_{\text{D}} \rangle$. These two corrections should provide a reasonable approximation to the magnitude of relativistic effects in the systems considered in this work. The mass-velocity correction is represented by the following operator (in the internal coordinates):

$$\hat{H}_{\text{MV}} = -\frac{1}{8} \left[\frac{1}{m_0^3} \left(\sum_{i=1}^n \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^n \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right]. \quad (5)$$

The Darwin operators for the H and B atoms and the BH molecule are

$$\hat{H}_{\text{D}} = \frac{\pi}{2} \delta(\mathbf{r}_{\text{H-e}}), \quad (6)$$

$$\hat{H}_{\text{D}} = -\frac{\pi}{2} \left[\sum_{i=1}^5 \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) + \sum_{i=1}^5 \sum_{j>i}^5 \frac{q_i q_j}{m_i^2} \delta(\mathbf{r}_{ij}) \right], \quad (7)$$

and

$$\hat{H}_{\text{D}} = -\frac{\pi}{2} \left[\sum_{i=2}^7 \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) + \sum_{i=2}^7 \frac{q_1 q_i}{m_i^2} \delta(\mathbf{r}_{1i}) + \sum_{i=2}^7 \sum_{j>i}^7 \frac{q_i q_j}{m_i^2} \delta(\mathbf{r}_{ij}) \right], \quad (8)$$

respectively. Considering indistinguishability of the electrons, the average value of \hat{H}_{D} for B can be given as

$$\langle \hat{H}_{\text{D}} \rangle = \frac{25\pi}{2} \langle \delta(\mathbf{r}_{\text{B-e}}) \rangle - 5\pi \langle \delta(\mathbf{r}_{\text{e-e}}) \rangle, \quad (9)$$

and for BH as

$$\langle \hat{H}_{\text{D}} \rangle = 15\pi \langle \delta(\mathbf{r}_{\text{B-e}}) \rangle + 3\pi \langle \delta(\mathbf{r}_{\text{H-e}}) \rangle - \frac{15\pi}{2} \langle \delta(\mathbf{r}_{\text{e-e}}) \rangle. \quad (10)$$

The expectation values of \hat{H}_{D} and \hat{H}_{MV} multiplied by α^2 were added to the nonrelativistic energy. In the calculations, we used the following value of the fine structure constant $\alpha = 7.297\,352\,537\,6 \times 10^{-3}$.¹⁵ The conversion factor, used in this work to convert between hartrees and wavenumbers (cm^{-1}) is $1 \text{ hartree} = 2.194\,746\,313\,705 \times 10^5 \text{ cm}^{-1}$.¹⁵ The nonrelativistic energy of the hydrogen atom corresponding to the finite mass of the proton is $-0.499\,727\,8$ hartree.

We should add that the complete set of α^2 relativistic corrections should also contain orbit-orbit, spin-spin, and spin-orbit terms. However we expect them to have somewhat smaller magnitude than the mass-velocity and Darwin corrections.

III. RESULTS

The results of the calculations are summarized in Tables I and II. In the first table we show the convergence of the total non-BO ground state energies of the boron atom and the boron hydride molecule with and without including the relativistic corrections with the number of basis functions. We also show in the table the values of the dissociation energies obtained by subtracting the BH and (B+H) total energies. For each system the largest basis set used contained 2000 functions. For BH this was the practical limit of the number of basis functions we could handle with the computational resources allocated for this study. The calculation of the boron atom requires significantly smaller amount of CPU time due to the smaller size of this system. However, the accuracy of the calculation of the boron atom is much higher than the accuracy of the BH calculations with the same number of basis functions.

The calculations performed in this work involved growing the basis set for each system from a relatively small basis

TABLE II. Expectation values of various quantities computed with 500, 1000, 1500, and 2000 basis functions. All numbers are in a.u.

System	Quantity	500	1000	1500	2000	Exact
H	$\langle 1/r_{H-e} \rangle$					0.999 456
	$\langle r_{H-e} \rangle$					1.500 817
	$\langle r_{H-e}^2 \rangle$					3.003 269
	$\langle \delta(\mathbf{r}_{H-e}) \rangle$					0.563 729
	$\langle \hat{H}_{MV} \rangle$					-0.623 640
	$\langle \hat{H}_D \rangle$					0.885 503
B	$\langle 1/r_{B-e} \rangle$	2.278 881	2.278 887	2.278 882	2.278 882	
	$\langle 1/r_{e-e} \rangle$	0.766 792	0.766 714	0.766 691	0.766 686	
	$\langle r_{B-e} \rangle$	1.347 546	1.347 963	1.348 077	1.348 107	
	$\langle r_{e-e} \rangle$	2.243 881	2.244 798	2.245 043	2.245 109	
	$\langle r_{B-e}^2 \rangle$	3.095 843	3.100 081	3.101 178	3.101 474	
	$\langle r_{e-e}^2 \rangle$	6.695 128	6.703 626	6.705 867	6.706 467	
	$\langle \delta(\mathbf{r}_{B-e}) \rangle$	14.2900	14.3403	14.3442	14.3568	
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.356 61	0.354 97	0.354 79	0.354 48	
	$\langle \hat{H}_{MV} \rangle$	-690.04	-692.11	-692.17	-692.67	
	$\langle \hat{H}_D \rangle$	555.57	557.57	557.72	558.22	
BH	$\langle 1/r_{B-H} \rangle$	0.425 090	0.425 668	0.425 721	0.425 660	
	$\langle 1/r_{B-e} \rangle$	1.970 308	1.970 700	1.970 760	1.970 768	
	$\langle 1/r_{H-e} \rangle$	0.542 582	0.542 933	0.542 974	0.542 906	
	$\langle 1/r_{e-e} \rangle$	0.646 335	0.646 224	0.646 119	0.646 037	
	$\langle r_{B-H} \rangle$	2.371 939	2.364 371	2.362 582	2.362 239	
	$\langle r_{B-e} \rangle$	1.543 977	1.545 021	1.545 666	1.546 131	
	$\langle r_{H-e} \rangle$	2.556 048	2.553 226	2.552 623	2.552 808	
	$\langle r_{e-e} \rangle$	2.494 685	2.497 499	2.498 881	2.499 820	
	$\langle r_{B-H}^2 \rangle$	5.672 370	5.626 049	5.614 006	5.610 790	
	$\langle r_{B-e}^2 \rangle$	3.733 047	3.748 200	3.755 115	3.759 666	
	$\langle r_{H-e}^2 \rangle$	7.927 834	7.914 587	7.911 404	7.912 963	
	$\langle r_{e-e}^2 \rangle$	7.945 964	7.976 062	7.989 014	7.997 693	
	$\langle \delta(\mathbf{r}_{B-e}) \rangle$	11.6600	11.7799	11.8267	11.8363	
	$\langle \delta(\mathbf{r}_{H-e}) \rangle$	0.073 16	0.073 88	0.074 84	0.075 12	
	$\langle \delta(\mathbf{r}_{e-e}) \rangle$	0.240 89	0.239 02	0.238 49	0.237 77	
	$\langle \hat{H}_{MV} \rangle$	-677.82	-683.98	-686.28	-686.73	
$\langle \hat{H}_D \rangle$	544.48	550.18	552.40	552.88		

size to finally reaching the size of 2000 functions. At the initial stage of this process, when the basis is relatively small, we performed simultaneous optimization of all exponential parameters of the Gaussians. After that the optimization process involved an approach where only the nonlinear parameters of one function at a time were optimized using the analytic gradient. At this stage growing of the basis set was a multistep procedure with each step involving randomly selecting a set of ten new functions and, after optimizing the parameters of these new functions, cycling over all other basis functions in the basis set once (again, one function at a time) and reoptimizing their parameters as well. Such strategy has been used in most of our previous works concerning explicitly correlated Gaussians and it proved to be very efficient.

The nonrelativistic energy of the B atom in this work was computed using a finite mass of the nucleus. Since almost all previous works concerning the boron atom were performed with an infinitely heavy nucleus, in order to compare our energy with those works, we set the nuclear mass to infinity and recomputed the total nonrelativistic energy. The

nonlinear parameters of the basis functions were not reoptimized when the mass of the nucleus was changed. Our prior experience with atomic systems has shown that changing only the linear variational parameters by solving secular Eq. (4) is sufficient to recover adequately the energy shift due to the mass change. With the nuclear mass set to infinity, the nonrelativistic energy of the boron atom corresponding to 2000 function basis set was -24.653 840 a.u. This value agrees quite well with a nonrelativistic estimate (computed using experimental and theoretical data) of -24.653 91 a.u. from Ref. 24 and of -24.653 93 a.u. from a preceding work.²⁵ It also agrees with a recent accurate *ab initio* result of -24.653 57(3) a.u. obtained in diffusion Monte Carlo calculations.²⁶

As seen from the results shown in Table I, the energy convergence is different for B than for BH. As can be expected, the energy for the B atom converges significantly faster than for BH. With 2000 basis functions the nonrelativistic non-BO energy of B is essentially converged with the relative accuracy of 10^{-6} if not higher, while the relative convergence of the BH energy is only around 10^{-5} . The bet-

ter convergence for the B atom than for BH assures that the BH dissociation energy calculated as the difference between the total energy of BH and the sum of the energies of the B and H atoms is lower bound to the true dissociation energy of this system. We should add that, even with only 2000 basis functions, the non-BO energies of the B atom and the BH molecule obtained in the present calculations are the best variational upper bounds ever calculated for these systems. However, 2000 basis functions are only enough to assure convergence of two significant figures in the dissociation energy. Our best result for this energy is $D_0=28\,083\text{ cm}^{-1}$ ($28\,079\text{ cm}^{-1}$ after adding the relativistic corrections). Extrapolation to an infinite number of basis functions increases the dissociation energy to $D_0=28\,400\pm 150\text{ cm}^{-1}$. This result agrees with the experimental value recommended by Bauschlicher *et al.*¹⁴ of $28\,535\pm 210\text{ cm}^{-1}$. However, it is clear that, in order to better match the experimental value, the energies of B and, particularly, of BH will have to be computed with higher accuracy and much larger basis sets. At present, such calculations would be impractical, but when more computer resources become available to us, the calculations of the BH dissociation energy may be resumed. As for the B atom, in the near future, we are planning to present results concerning the ground and some lower lying excited states obtained with significantly larger basis sets than those shown in this work. The calculations of those states are currently in progress.

The non-BO wave functions obtained in the present calculations have been used to calculate some expectation values that provide characterization of the ground state non-BO wave functions of the B atom and the BH molecule. As the results shown in Table II indicate, 2000 basis functions seems to be quite enough to obtain reasonably good convergence of most of those values. For example, the expectation value for the B–H internuclear distance (which should be very close to the vibrationally averaged interatomic distance computed within the Born–Oppenheimer framework), $\langle r_{\text{B-H}} \rangle = 2.362\,239\text{ bohr}$, obtained with 2000 basis functions, is converged to four significant figures. In general the convergence of all expectation values (as it also was for the total energy) is much better for the B atom than for BH. Clearly a non-BO molecular wave function, even for the ground state, is a more difficult function to describe than an atomic wave function. In the case of BH the wave function has to not only represent one more electron compared to the case of B atom, but it also needs to describe the motion of the second nucleus and the correlation of this motion with the motions of the first nucleus and the electrons.

IV. SUMMARY

In this work we performed accurate non-BO calculations of the ground states of the boron atom and the boron monohydrate molecule using up to 2000 explicitly correlated Gaussian functions for each system. These are the largest systems ever calculated with an approach that treats the nuclei (the nucleus in the atomic calculations) and the electrons on equal footing. The calculated energies were used to deter-

mine the BH dissociation energy, which agrees with the best experimental estimate. In order to improve the quality of the present calculations, a larger number of basis functions needs to be used (at least two to three times larger than the number used in the present study). To achieve this, not only should a larger number of processors be employed in the calculations, but a new strategy for the optimization of the Gaussian exponential parameters should also be implemented. The work on such developments is currently being thought out in our laboratory. Our ultimate goal here is to develop an approach that would allow for studying few electron molecules, such as BH and even larger systems, without the Born–Oppenheimer approximation and to reach the spectroscopic (subwavenumber) accuracy in the calculations. Such an accuracy is almost impossible to achieve using conventional quantum chemical methods.

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