

NON-BORN-OPPENHEIMER CALCULATIONS OF H₃*

MAURICIOCAFIERO^{1,2} AND LUDWIK ADAMOWICZ¹

¹*Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA*

²*Physical and Chemical Properties Division, Chemical Science and Technology Lab., National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

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Abstract. Molecular calculations without assuming the Born-Oppenheimer (BO) approximation present a level of complexity which is much higher than in calculations where the BO approximation is assumed and the nuclei are stationary. In this report we discuss how non-BO calculations can be carried out for a system with three nuclei and three electrons, i.e. H₃. In particular, the problem of basis set selection that is critical to achieving high accuracy in such calculations is discussed. As an illustration a small-scale non-BO calculations of H₃ are presented and discussed.

1. INTRODUCTION

The important works of Rychlewski and coworkers have demonstrated that very high accuracy can be achieved in molecular calculations if the wave function of the considered system is expanded in terms of functions explicitly dependent on the inter-electron distances [1-6]. The calculations of Rychlewski et al. have been carried out assuming the Born-Oppenheimer (BO) approximation, i.e. the nuclei forming the molecular system were placed in fixed spatial positions and only the electronic wave function was determined. In order to elevate the precision of molecular quantum-mechanical calculations of such properties as excitation energies, electron affinities, and ionization potentials, which are currently measured with the precision exceeding tenth or even hundredth of a wave number, an approach that departs from the BO approximation needs to be applied. Such an approach has been under development in our research group at Arizona. In the non-BO atomic and molecular calculations [7-15] we have carried out using that approach, we have employed the explicitly correlated gaussian functions which have been also used by Rychlewski and his coworkers.

Since we are not assuming the BO approximation regarding the separability of the electronic and nuclear motions, the problem we face in the calculations is considerably different from the standard BO problem. If the center-of-mass motion is separated from the "internal motion" in the Hamiltonian and, if the internal motions of the nuclei and the electrons forming the system are treated on equal footing, the task of determining stationary ground and excited states of the system, i.e. determinations of the total energies and the wave functions of the system, presents a level of difficulty and complication that is much higher than in the ordinary BO calculations. The additional difficulty arises from the fact that, when electrons and nuclei are equivalently treated, the wave function of the system has to properly describe not

* Dedicated to the memory of Professor Jacek Rychlewski

correlations. The latter two are more significant effects than the first one because the electrons, particularly the core electrons, very closely follow the nuclei, and the nuclei stay apart from each other in their very correlated motion. To describe these correlations in the non-BO wave function, one needs to employ basis functions that are capable of representing the reduced probability density of finding two electrons in the same point in space (the Coulomb hole), the further reduced probability of finding two nuclei together, and the increased probability of finding the electrons near the nuclei.

2. HAMILTONIAN

We begin with the full non-relativistic Hamiltonian for a molecular system with the total number of electrons and nuclei equal to $n + 1$ in the laboratory Cartesian coordinate system. It is written so that no distinction between electrons and nuclei is made by referring to $n + 1$ general particles with masses M_i , charges Q_i , and positions \mathbf{R}_i , where $i = 1, \dots, n + 1$:

$$\hat{H}_{\text{TOT}} = -\sum_{i=1}^{n+1} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^n \sum_{j>i}^{n+1} \frac{Q_i Q_j}{R_{ij}}, \quad (1)$$

where $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are inter-particle distances. This Hamiltonian describes a system in which the motions of electrons and nuclei are coupled. We then make a transformation to separate the Hamiltonian representing the motion of the center-of-mass in the laboratory coordinate system from the internal Hamiltonian, $\hat{H}_{\text{INT}} = \hat{H}$, thereby reducing the $(n + 1)$ -particle problem to an n -pseudoparticle problem. If we choose to place a heavy particle (particle 1 with mass M_1) at the center of the internal Cartesian coordinate system, the resulting internal Hamiltonian is:

$$\hat{H} = -\frac{1}{2} \left(\sum_i^n \frac{1}{m_i} \nabla_i^2 + \sum_{i \neq j} \frac{1}{M_1} \nabla_i \nabla_j \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i < j} \frac{q_i q_j}{r_{ij}}. \quad (2)$$

This Hamiltonian describes a system containing a heavy particle at the origin of the coordinates with charge $q_0 = Q_1$; also in the system there are n pseudoparticles, or internal particles, which are characterized by the reduced masses $m_i = (M_1 M_{i+1}) / (M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The second term in the parentheses is the mass polarization term, which arises from the transformation and couples the motion of all the particles. In the potential energy term, r_i and r_{ij} are defined as: $r_i = |\mathbf{R}_{i+1} - \mathbf{R}_1|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$. The eigenfunction of this Hamiltonian will be a function of the positions of all n pseudoparticles, meaning that all the particles forming the system, including the nuclei, are described by the wave function.

For H_3 , the internal Hamiltonian describes the motions of five pseudoparticles in the central field of a proton placed in the center of the coordinate system:

$$\hat{H} = -\frac{1}{2} \left(\sum_i^5 \frac{1}{m_i} \nabla_i^2 + \sum_{i \neq j} \frac{1}{M_1} \nabla_i \nabla_j \right) + \sum_{i=1}^5 \frac{q_0 q_i}{r_i} + \sum_{i < j} \frac{q_i q_j}{r_{ij}}. \quad (3)$$

where M_1 is the proton mass, $q_0 = q_1 = q_2 = 1$, and $q_3 = q_4 = q_5 = -1$.

3. WAVE FUNCTION

The model of the molecule described by Hamiltonian (2) is, in a way, similar to an atom, as has been noted by Monkhorst [16]. One can call the model a "molecular atom". In the "molecular atom", there is an analogue of the nucleus in the heavy particle that is placed at the center of the internal coordinate system, and there are analogues of electrons in the internal particles (pseudoparticles). However, while all particles in an atom, apart from the particle in the center, are electrons, in the "molecular atom", some of the internal particles are heavier than electrons and have positive charges. Formally, this difference is manifested in the effective masses of the pseudoparticles, in the interparticle interaction potential, and in the way the permutational symmetry is implemented in the wave function.

In order to enforce the required permutational symmetry of the wave function in the "atomic molecule", each set of identical particles must be symmetrized or antisymmetrized, depending on whether they are bosons or fermions. Thus, the operator enforcing the permutational symmetry has to be a direct product of "antisymmetrizers" (or "symmetrizers" in the case of bosons) representing the sets of identical particles. Formally, in our work, the permutational-symmetry operator is constructed as a product of Young operators, \hat{Y} . For H₃, the operator has the following form: $\hat{Y} = \hat{Y}_N(S_3) \otimes \hat{Y}_e(S_3)$, where $\hat{Y}_N(S_3)$ is a Young operator for the third-order symmetric group, which permutes the nuclear coordinates, and $\hat{Y}_e(S_3)$ is a Young operator for the third-order symmetric group which permutes the electronic coordinates. For H₃, both nuclear and electronic symmetry operators corresponded to a doublet representation. It should be noted that the permutations used in the internal particle basis functions are 'pseudo'-permutations induced by the permutations on real particles. For discussion of the construction of the operators, see, for example, the work of Pauncz [17].

The internal Hamiltonian of "atomic molecule" is "isotropic" and commutes with the square of the all-particle angular-momentum operator, \hat{N}^2 , which may be thought of as the sum of the electronic and nuclear angular momenta (or, more precisely, the total angular momenta of the pseudoparticles), $N = L + R$. Thus we have $[\hat{H}, \hat{N}^2] = 0$. Since the ground internal-angular-momentum state is spherically symmetric (by analogy with the atom), the wave function describing the ground state of the molecule is also spherically symmetric. Due to this symmetry one should use spherically symmetric basis functions in expanding the ground-state non-BO wave function in the analytical form. As we have proposed, such basis functions for H₃ should have the following form [7]:

$$\phi_k = r_1^{m_k} r_2^{l_k} r_{12}^{n_k} \exp \left[-\mathbf{r}' (\mathbf{A}_k \otimes \mathbf{I}_3) \mathbf{r} \right] \quad (4)$$

where r_1 , r_2 , and r_{12} are distances between nuclei 1-2, 1-3, and 2-3, respectively, \mathbf{A}_k is a symmetric 5 x 5 matrix of variational exponential parameters, \mathbf{I}_3 is the 3 x 3 identity matrix, (') denotes transposition, and \otimes is the Kronecker matrix product. The basis (4) properly

reflects the symmetry of the H_3 non-BO internal ground-state wave function and can effectively describe the electron-electron, nucleus-nucleus, and electron-nucleus correlation effects.

While the work on the implementation of the basis set (4) is being carried out in our research group, we have been recently exploring the possibility of using another basis set in molecular non-BO calculations [12-15, 18, 19]. It consists of n -particle explicitly correlated gaussians with shifted centers (or floating spherical explicitly correlated gaussians, FSECGs):

$$\phi_k = \exp[-(\mathbf{r}-\mathbf{s})'(\mathbf{A}_k \otimes \mathbf{I}_3)(\mathbf{r}-\mathbf{s})], \quad (5)$$

where \mathbf{s} is a $3n$ vector of cartesian coordinates of the gaussian centers. The basis has been employed in non-BO calculations of static electrical properties of small diatomic systems [12-15], as well as in non-BO calculations of H_3^+ isotopomers [18, 19]. By introducing the centers into the gaussian exponents and allowing the centers to move away from the coordinate center the flexibility of the functions is increased. However, it makes them not spherically symmetric. Thus if such functions are use in expanding the ground-state non-BO wave function, the function becomes "contaminated" by rotational states with the rotational quantum number higher than zero. If, however, the variational method is used in the calculations and both linear and non-linear parameters of the wave function are fully optimized, the contamination can be effectively reduced. So, if the focus of the calculation is the total ground-state energy, the use of FSECGs may be justified.

Another advantage of using FSECGs in non-BO calculations is their ability to describe molecular electronic configurations involving some electrons occupying higher angular-momentum states without explicitly introducing angular factors in the gaussian functions. Since FSECGs form a complete set, one should be able to use them to describe states with any symmetry. However, whether this would lead to an efficient and accurate approach remains unclear.

4. NON-BO CALCULATIONS OF H_3

The equilibrium structure of the H_3 complex has been studied with the use of BO approach by Truhlar and Horowitz [20], Wu et al. [21], Tang and Toennies, [22] as well as by our group [23]. The studies showed that in the lowest-energy structure H_3 is linear van der Waals complex ($H1-H2 \cdots H3$). Our calculations produced the distance between H1 and H2 equal to 1.4 Bohrs and the distance between H2 and H3 equal to 6.442 Bohrs. These distances are consistent with the results of the calculations performed by the others. With the approach we used in the BO calculations, we expanded the electronic wave function in terms of 64 explicitly correlated three-electron gaussians with floating centers and we optimized the geometrical parameters of the system simultaneously with the exponential parameters involved in the basis functions. Apart from the geometry of the H_3 complex, the calculations produced a well optimized BO wave function, which was used in the present work to generate the initial guess for the non-BO calculations as described below.

In our non-BO studies involving FSECGs, we found that an effective way to generate the initial guess for the wave function in the nonadiabatic calculation is to start with a BO wave function generated for equilibrium structure of the studied molecule with the heaviest nucleus placed in the center of the coordinate system and the other nuclei placed in their respective equilibrium positions. Expanding such a wave function by multiplying each basis function in the expansion of the BO wave function by a gaussian for each of the nuclei located away from the center of the coordinate system and approximately representing the vibration wave function of that nucleus generates a good starting guess for the nonadiabatic calculation. Once the calculation starts, the variational optimization of the energy functional, with respect to all gaussian exponential parameters (i.e. exponents and shifts) and the linear expansion coefficients, adjusts the basis functions to best describe the non-BO ground state of the system. One purpose of this adjustment is diffusing the distribution of the gaussian centers in the three-dimensional space to best describe the electronic and vibrational components of the wave function and the other is to minimize contributions of higher rotational states.

The transformation of the BO FSECG basis to non-BO basis can be easiest accomplished by realization that the χ_k of Eq. (5) can be alternatively expressed using the distance coordinates $\{r_{ij}\}$. The quadratic form, $\mathbf{r}'(A \otimes I_3)\mathbf{r}$, which is a part of the exponential of χ_k , may be converted to $\{r_{ij}\}$ variables as follows (we drop the subscript k for convenience):

$$\mathbf{r}'(A \otimes I_3)\mathbf{r} = \sum_{i,j} r_i' r_j A_{ij} = \text{tr} \left[(r_i' r_j) A \right] = \text{tr} \left[(r_{ij}^2) B \right] = \sum_{i,j} r_{ij}^2 B_{ij}, \quad (6)$$

where $\text{tr} [\]$ is the matrix trace operator, $(\mathbf{r}_i \mathbf{r}_j)$ is the $n \times n$ matrix of dot products of the component vectors of \mathbf{r} , (r_{ij}^2) is the $n \times n$ matrix of squared distance variables, and B is a matrix with elements given, in terms of the elements of an arbitrary matrix A , by the transformation:

$$B_{ij} = \begin{cases} \frac{1}{2} \sum_{k=1}^n (A_{ik} + A_{kj}), & i = j \\ -\frac{1}{4} (A_{ij} + A_{ji}), & i \neq j \end{cases}. \quad (7)$$

Hence, $\mathbf{r}'(A \otimes I_3)\mathbf{r}$ can be written using only distance coordinates. We should mention that, even though r_{ij} are not independent for more than four particles, there is no redundancy in writing the wave function in terms of them because the variables the wave function depends on are the internal cartesian coordinates which are all independent. If one has χ_k in terms of B_k i.e. a function of r_{ij} , and wishes to transform to A_k , a function of \mathbf{r} , the following relation can be used:

$$A_{ij} = \begin{cases} B_{ij} + \sum_{k \neq i,j}^n (B_{ik} + B_{kj}), & i = j \\ -(B_{ij} + B_{ji}), & i \neq j \end{cases}. \quad (8)$$

The square integrability of the basis can be assured by writing \mathbf{A}_k in Cholesky factored form as:

$$\mathbf{A}_k = \mathbf{L}_k \mathbf{L}_k', \quad (9)$$

where \mathbf{L}_k is a lower triangular matrix whose elements can vary in the range $[-\infty, \infty]$. The basis functions may then be written as:

$$g_k(\mathbf{r}) = \exp\left\{-\left(\mathbf{r} - \mathbf{s}_k\right)' \left[\left(\mathbf{L}_k \mathbf{L}_k'\right) \otimes \mathbf{I}_3\right] \left(\mathbf{r} - \mathbf{s}_k\right)\right\} \quad (10)$$

The H_3 ground-state energy and the wave function were obtained in variational optimization of the energy functional:

$$E[\Psi] = \min \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (11)$$

The wave function was optimized with respect to the parameters \mathbf{L}_k , \mathbf{s}_k , and c_k . This lead to $(1/2) n(n+1) + 3n + 1$ variational parameters per basis function (31 for the H_3 system). The optimization was based on the Newton-type algorithm involving analytical gradients of the energy with respect to both linear and non-linear parameters included in the basis functions [13]. The development of the analytical gradients has contributed to the breakthrough that has allowed us to achieve very high accuracy in BO and non-BO molecular calculations.

The calculations presented here have been carried out on a 64-node ATLON Beowulf cluster. Due to the shared user environment on this system, we have been only allowed to use up to 16-processors in a single job. This restrictions put a practical limit on the length of the basis set expansion of the wave function. Also, the results obtained with the 128 and 256-term basis sets shown here only represent preliminary data of a larger set of calculations involving more basis functions which we plan to publish in the near future [24].

Table 1. Values for the nonadiabatic energies, virial coefficients (η) and interparticle distances of H_3 . All values are in atomic units

m	$\langle H \rangle$	η	R_{HH}	r_{eH}	r_{ee}
128	-1.65641069	1.00016	6.67	5.03	7.05
256	-1.65671102	1.00026	6.23	4.74	6.61

In Table 1 we present the total energy and the average interparticle distances obtained in the calculations for each of the two basis sets. The non-BO energies are -1.65610833 and -1.65671102 hartrees for the 128-term and 256-term bases, respectively. These energies can be compared with our BO energy of -1.673468 hartree obtained for the equilibrium geometry of H_3 using a 64-term FSECG basis set [23]. The BO result is lower than the non-BO energy because it does not include the positive contribution from the kinetic energy of the nuclear motion. It also does not include the coupling effects of the electronic and nuclear motions.

Furthermore, even with the 256-term basis set, the non-BO energy is certainly not as well converged as the BO energy obtained with 64-term basis set. The present non-BO energy result can certainly be improved by further optimizations of the basis set parameters as well as by adding more functions to the basis set. One would probably need several thousand basis functions in this case to converge the energy below the micro-hartree accuracy. An assuring feature of the results are the very-close-to-one values of the virial coefficients for the two basis. Also, to this point the optimizations have shown steady progress in lowering the energy and no signs of ill-behaving (e.g. linear dependencies).

Since in the non-BO approach both electrons and nuclei are included in the wave function, the information on the molecular structure can be only obtained by calculating expectation values of the geometrical parameters (i.e. distances and angles). Since the operators representing the internuclear distances, r_i or r_{ij} do not commute with the Hamiltonian: $[\hat{H}, \hat{r}_i] \neq 0$, we cannot measure these distances exactly for stationary states of the system. Furthermore, the expectation values of the distances between any two particles in each subset of identical particles (including the distance to the particle at the origin, if that particle belongs to the subset) will be equal. This is a widely known fact for electrons, i.e. due to antisymmetry, or indistinguishability, all of the electrons are on average at the same distance from each other, as well as from each nucleus in the molecule. That this same fact applies to nuclei is, perhaps, less known. Thus for the H_3 system studied in the present work, there are only three distinct average interparticle distances, i.e., the electron-electron (e-e), e-H, and H-H distances, that we can obtain from the non-BO wave function (they are listed in Table 1). One should notice that the single internuclear H-H distance (we would also be only able to determine a single H-H-H angle being the average of the three H-H-H angles in H_3 . This average angle would be equal to 120°) does not permit determination of the molecular structure of the H_3 system. Other expectation values related to the structure need to be calculated to confirm that H_3 is a complex of an H_2 molecule with a distant third hydrogen colinear with H_2 , as differed from the BO calculations.

The average value of the H-H distance of 6.23 bohr obtained in the calculations with the 256-term basis set wave function can be compared with the average of the internuclear distances of 5.23 bohr obtained in our previous BO calculations ($r_{H_1-H_2} = 1.400$ bohr, $r_{H_2-H_3} = 6.442$ bohr, and $r_{H_1-H_3} = 7.842$ bohr) [23]. As expected, the non-BO average H-H distance is larger than the BO average distance because in the non-BO approach the calculation of the expectation values involves averaging over the wave function that includes the vibrational component. Since H_3 is a weakly bonded complex of H_2 with H, the potential surface along the $H_2 \cdots H$ coordinate is very shallow and anharmonic resulting in the equilibrium average H-H distance being considerably shorter than the vibrationally averaged distance. Also, the small sizes of the basis sets used in the present non-BO calculations contribute to the average H-H distance being longer than it should be. This effect is showing in going from

the 128-term to the 256-term wave function which results in shortening of the distance from 6.67 bohr to 6.23 bohr. Calculations with larger basis sets will show if this trend will continue.

5. CONCLUSION

In this work we showed our preliminary results of rigorous non-BO calculations concerning the H_3 system. These are the first such calculations performed for H_3 . The data obtained so far are encouraging and seem to indicate that the explicitly correlated n -particle floating gaussian functions provide an effective basis set for nonadiabatic calculations of this molecule. However, it is clear that many more basis functions are needed to achieve the accuracy that is desired and expected in non-BO calculations.

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