A Finite B-Spline Basis Set for Accurate Diatomic Molecule Calculations

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Abstract: A finite basis set particularly adapted for solving the Hartree–Fock equation for diatomic molecules in prolate spheroidal coordinates has been constructed. These basis functions have been devised as products of B-splines times associated Legendre polynomials. Due to the large number of B-splines, the resulting set of eigenfunctions is amply distributed over excited states. This gives the possibility of using these basis sets to calculate sums over excited states, appearing in various orders of perturbation theory. As an illustration, the second-order corrections to the ground-state energy of some atoms and diatomic molecules with closed electron shells have been calculated.


Key words: B-spline basis set; diatomic molecule calculations

Introduction

In recent years, methods based on B-splines1 for solving the Schrödinger or the Dirac equations using various external potentials have become very popular (for a review, see ref. 2, and references therein). The main advantage of these methods is that the resulting set of eigenfunctions and eigenvalues allows us to evaluate, with very good accuracy, sums over excited states, appearing in various orders of the perturbation theory. In this article we describe the use of a finite basis set based on B-splines to solve the Hartree–Fock equation for diatomic molecules.

There are two main approaches for the study of the electronic structure of diatomic molecules at the Hartree–Fock level. The first one is the traditional quantum chemistry approach based on Hartree–Fock–Roothaan calculations. In this method, molecular orbitals are constructed as linear combination of atomic orbitals (LCAO). See, for example, the works of Cade et al.3,4 describing the optimization of atom-centered Slater-type basis for various diatomic molecules.

A second approach, developed essentially in recent years, involves the numerical solution of the Hartree–Fock equation in prolate spheroidal coordinates (for diatomic molecules, coordinates with two poles such as prolate spheroidal ones are a very natural and suitable choice). The numerical treatment can be cast in terms of two-dimensional equation as is done in the works of Kobus et al.5,6 in terms of a set of one-dimensional equations arising from the expansion of orbitals over spherical harmonics as in the works of McCullough et al. (see ref. 7, and references therein), or in terms of the finite-elements as in the works of Heinemann et al.8,9

Of course, due to the limitations of the Hartree–Fock approximation, it becomes necessary to resort to beyond Hartree–Fock methods if one wishes to calculate properties of diatomic molecules with sufficient accuracy. To include electronic correlation effects not accounted for in the Hartree–Fock approximation, one may employ variational-based methods such as those involving configuration interaction (CI) expansions, multiconfigurational self-consistent field methods (MCSCF), coupled-cluster and related methods, or one may take advantage of the different schemes available in the context of many-body perturbation theory (MBPT), etc. For reviews on correlation methods on atoms and molecules, see, for example, the works of Jankowski et al.10 and of Urban et al.,11 and the more recent one of Kutzelnigg.12

In the present article we combine the B-spline basis set and partial wave expansion approaches for the purpose of obtaining a quasi-complete set of solutions to the Hartree–Fock equations for diatomic molecules with closed electron shells. Obviously, the emphasis in constructing this quasi-complete set stems from the

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fact that, in principle, such a set coupled to MBPT opens a very realistic possibility of calculating with high accuracy correlation-dependent properties of diatomic molecules.

Other types of splines, such as Hermite splines, have been used previously, in conjunction with the collocation method, to solve numerically the Hartree–Fock equations for diatomic molecules. In the present work, the B-splines are used to approximate the molecular orbitals, so that, in fact, we can inscribe the present work within the traditional orbital approaches to the determination of the electronic structure of diatomic molecules. Atomic units are used throughout this article.

Variational Formulation

As is well known, the Hartree–Fock equations for a system of \( N \) particles can be derived from the extremum (minimum) condition

\[ \delta E = 0 \]  \hspace{1cm} (1)

of the energy functional:

\[ E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \]  \hspace{1cm} (2)

where

\[ \Psi = \frac{1}{\sqrt{N!}} \det[\phi_i(x)], \]  \hspace{1cm} (3)

In eq. (3), the variable \( x \) has three space and one spin components, and \( \hat{H} \) is the diatomic molecule Hamiltonian in the Born–Oppenheimer approximation:

\[ \hat{H} = \sum_{i=1}^{N} \left( -\frac{1}{2} \Delta_i - \frac{Z_a}{|r_i - R_a|} - \frac{Z_b}{|r_i - R_b|} \right) \]

\[ + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|r_i - r_j|} + \sum_{i=1}^{N} \frac{Z_a Z_b}{|R_a - R_b|}. \]  \hspace{1cm} (4)

In eq. (4) \( R_{a,b} \) and \( Z_{a,b} \) denote the positions and charges of the first and second nuclei, respectively. The last term in this equation describes the internuclear repulsion. Of course, this term for fixed internuclear distance gives just a fixed shift to the energy levels. This term will be omitted in subsequent formulas but will be included in the final result. The minimum is taken over all the space of one-electron spin-orbitals \( \psi(x) \) with \( \psi \in \mathcal{L} \), where \( \mathcal{L} \) is the Hilbert space of functions and where we assume that the integral \( \int |\psi|^2 dV < \infty \) exists.

The main idea of the finite basis set approach is to make a projection of \( \mathcal{L} \) onto another subspace \( \mathcal{P} \) where the basis of \( \mathcal{P} \) is given by a finite set of functions \( \{ \psi_i \}_{i=1}^{M} \). If such a projection is feasible, then we can represent each spin-orbital \( \psi_i(x) \) in the form:

\[ \psi_i(x) = \Phi_i(r) \chi_i(s), \]  \hspace{1cm} (5)

\[ \Phi_i(r) = \sum_{a=1}^{M} C_{a,i} \zeta_a(r), \]  \hspace{1cm} (6)

where \( \chi \) is a single-particle spin function and where the basis functions \( \tau \) can, in general, differ for each orbital of a given spin and symmetry.

In the case of diatomic molecules the three-dimensional problem can be reduced to a two-dimensional one if we take into account the symmetry of the molecule. This means that all orbitals are eigenfunctions of the operator that projects the momentum onto the molecular axis. Thus, all orbitals have the following factorized form:

\[ \Phi(r) = T_{\alpha\beta}(\tau_{\alpha\beta} - \frac{1}{2} \Delta |\tau_{\alpha\beta}|), \]  \hspace{1cm} (7)

where \( m \) is a value of momentum projection and \( \Phi \) does not depend on the polar angle \( \phi \).

Using eqs. (3)–(7) and assuming that the orbitals \( \psi \) are orthonormalized (this can always be done for molecules with closed electron shells), we get for the energy expression:

\[ E = \sum_{a=1}^{N} \sum_{\alpha=1}^{m} \sum_{\beta=1}^{M} C_{a1}^{\alpha} C_{b1}^{\beta} T_{a\beta}^{\alpha} + V_{a\beta}^{\alpha} + J_{a\beta}^{\alpha} + K_{a\beta}^{\alpha} - E_a S_{a\beta}^{\alpha}, \]  \hspace{1cm} (8)

where we have introduced the matrices

\[ T_{a\beta}^{\alpha} = \langle \tau_{\alpha\beta} | - \frac{1}{2} \Delta | \tau_{\alpha\beta} \rangle, \]  \hspace{1cm} (9)

\[ V_{a\beta}^{\alpha} = \langle \tau_{\alpha\beta} | - \frac{Z_a}{|r_{a} - R_a|} - \frac{Z_b}{|r_{b} - R_b|} | \tau_{\alpha\beta} \rangle, \]  \hspace{1cm} (10)

\[ J_{a\beta}^{\alpha} = \langle \tau_{\alpha\beta} | K | \tau_{\alpha\beta} \rangle, \]  \hspace{1cm} (11)

\[ K_{a\beta}^{\alpha} = \langle \tau_{\alpha\beta} | K | \tau_{\alpha\beta} \rangle, \]  \hspace{1cm} (12)

\[ S_{a\beta}^{\alpha} = \langle \tau_{\alpha\beta} | \tau_{\alpha\beta} \rangle, \]  \hspace{1cm} (13)

and where the Coulomb and exchange interaction operators \( J \) and \( K \), respectively, are determined by

\[ \langle \psi | J | \psi \rangle = 2 \int dV \int dV \int dV \int dV \frac{f_{\alpha}(\mathbf{r}_1) f_{\beta}(\mathbf{r}_2) \sum_{\gamma \gamma'} \Phi_{\alpha}(\mathbf{r}_1) \Phi_{\beta}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \]  \hspace{1cm} (14)

\[ \langle \psi | K | \psi \rangle = - \int dV \int dV \int dV \int dV \frac{f_{\alpha}(\mathbf{r}_1) f_{\beta}(\mathbf{r}_2) \sum_{\gamma \gamma'} \Phi_{\alpha}(\mathbf{r}_1) \Phi_{\beta}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \]  \hspace{1cm} (15)

In eq. (15) \( N_o \) is number of occupied orbitals.

The parameters \( e_i \) in eq. (8) are Lagrange multipliers introduced to ensure that the normalization condition is satisfied while searching for the extremum of the variational principle. The quantity \( S_{a\beta}^{\alpha} \) are the usual overlap integrals.
Now, the condition for the minimum of the energy functional (8) can be written as

\[ \nabla C E = 0 \] (16)
or, in a more detailed way, as:

\[ \frac{\partial E}{\partial C^i} = 0 \] (17)
for each \( i \) and \( \alpha \). Calculation of the gradient in eq. (16) leads to the system of equations:

\[ (T + V + J + K) C' = e_\alpha S^\alpha, \] (18)
which can be solved using standard methods of linear algebra. It should be noted that the closer the subspace \( \mathcal{P} \) is to the complete space \( \mathcal{L} \), the more accurate the results yielded by the calculations will be.

**Basis Set**

As it was noted above, in the case of diatomic molecules one of the most natural choices for a coordinate system is that of prolate spheroidal coordinates. Denoting the internuclear distance as \( R \), the prolate spheroidal coordinates of a point are given by

\[ \xi = \frac{r_a + r_b}{R}, \quad 1 \leq \xi < \infty, \]
\[ \eta = \frac{r_a - r_b}{R}, \quad -1 \leq \eta \leq 1, \]
\[ \phi, \quad 0 \leq \phi \leq 2\pi, \] (19)
where \( r_a \) and \( r_b \) are the scalar distances from the corresponding nucleus to the point, and \( \phi \) is the angle of rotation about the molecular axis.

The transformation of these coordinates into Cartesian ones, with \( z \) coinciding with the molecular axis and with the zero point located at the middle of internuclear interval, is given by the expressions:

\[ x = \frac{R}{2} \sqrt{\xi^2 - 1} \sqrt{1 - \eta^2} \cos \phi, \]
\[ y = \frac{R}{2} \sqrt{\xi^2 - 1} \sqrt{1 - \eta^2} \sin \phi, \]
\[ z = \frac{R}{2} \eta. \] (20)

In our calculations we have used transformed prolate spheroidal coordinates given by the following equations:

\[ \eta = \cos \nu, \quad 0 \leq \nu \leq \pi. \] (21)

Having chosen the coordinates as indicated above, we now define the basis set \( \{ \tau_{\alpha} \}_{\alpha=1}^M \). In our calculations we used the basis functions for orbital with momentum projection \( m \) in the form

\[ \tau_{\alpha m} = B_{\alpha m}(u) P_{\alpha m}(\cos \nu), \] (22)
where \( B_{\alpha m}(u) \) is the \( \alpha \)th B-spline of the order \( k \) (see the following subsection) and \( P_{\alpha m}(\cos \nu) \) is the associated Legendre polynomial. Of course, we can easily renumber the basis functions so that \( \tau \), as in eq. (6) is labeled by the single index \( \alpha \).

### B-Splines

Following the notation of deBoor,\(^1\) let us define the interval \([0, U_{\text{max}}]\) on the axis \( u \). Then we need to choose an arbitrary number of subintervals \([t_i, t_{i+1}]\) with knots \( t_i \) spaced also arbitrarily. (Our choice of coordinates and exponential damping of the wave function depending on the distance from the nuclei allows us to use an equidistant grid of knots \( t \) in our calculations.) It follows that the B-spline of the order \( k \) on this knot sequence is defined as

\[ B_{i,j}(u) = \begin{cases} 1, & t_i \leq u < t_{i+1} \\ 0, & \text{otherwise} \end{cases} \] (23)

\[ B_{i,j}(u) = \frac{u - t_i}{t_{i+k} - t_i} B_{i,k}(-u) + \frac{t_{i+k} - u}{t_{i+k} - t_i} B_{i+1,k}(-u). \] (24)

Let us note some important properties of B-splines:

1. A B-spline of the order \( k \) is a piecewise polynomial of degree \( k - 1 \).
2. \( B_{i,j}(u) \) is different from zero only if \( t_i \leq u < t_{i+k} \). Hence, on each interval we have just \( k \) nonzero splines.
3. B-splines of the order \( k \) and their derivatives up to the order \( k - 2 \) are continuous.
4. The sum of all B-splines in every point is equal to 1.

Because of these properties, B-splines can be used quite advantageously in different types of calculations.

Let us comment, finally, on the choice of the knots \( t_i \). The end points 0 and \( U_{\text{max}} \) correspond to “multiple knots.” This means that for a given order \( k \) we need to make the first \( k \) knots equal 0 and the last \( k \) knots equal to \( U_{\text{max}} \). Thus, for example, for five B-splines of the order 3 on the interval \([0, 3]\) we need eight knots: \( t_1 = t_2 = t_3 = 0, t_4 = 1, t_5 = 2, t_6 = t_7 = t_8 = 3 \). An example of graphical representation of B-splines of order 4 is shown in Fig. 1.

### Calculations

The volume element and the Laplacian in the transformed prolate spheroidal coordinates are given by
Calculations by a Finite B-Spline Basis Set

\[ d^3r = \frac{R^3}{8} (\cosh^2 u - \cos^2 v) \sinh u \sin v \, du \, dv \, d\phi, \]
\[ \Delta = \frac{4}{R^4 (\cosh^2 u - \cos^2 v)} \times \left[ \frac{1}{\sinh u} \frac{\partial}{\partial u} \sinh u \frac{\partial}{\partial u} \right. \]
\[ + \left. \frac{1}{\sin v} \frac{\partial}{\partial v} \sin v \frac{\partial}{\partial v} + \left( \frac{1}{\sinh^2 u} + \frac{1}{\sin^2 v} \right) \frac{\partial^2}{\partial \phi^2} \right]. \]

Using these formulas and the expressions
\[ \left[ \frac{1}{\sin v} \frac{\partial}{\partial v} \sin v \frac{\partial}{\partial v} + \frac{1}{\sinh u} \frac{\partial}{\partial u} \frac{\partial}{\partial u} \right] \times (P_{lm}(\cos v) \exp(imp)) \]
\[ = -(l+1)(P_{lm}(\cos v) \exp(imp)), \]
\[ \frac{\partial^2}{\partial \phi^2} (P_{lm}(\cos v) \exp(imp)) = -m^2 (P_{lm}(\cos v) \exp(imp)) \]

it is easy to calculate the matrices \( T, V, \) and \( B \) [eqs. (9), (10), and (13)] containing one-electron integrals.

To calculate matrices \( J \) and \( K \) [eqs. (11) and (12)] containing two-electron integrals we used the Neumann expansion of \( 1/R^2 \) in spherical coordinates:
\[ \frac{1}{r_{12}} = \frac{8 \pi}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m (l+|m|)! \]
\[ \times \left( \frac{l-|m|}{(l+|m|)} \right) P_{l|m}(\cos u_c) Y_{l|m}^m(\cos v_1, \phi_1) Y_{l|m}^m(\cos v_2, \phi_2), \]
\[ P_{l|m} \]
where \( P \) and \( Q \) are the Legendre functions of the first and second kind and \( u_c, v_1, v_2, \) and \( \phi_1, \phi_2 \) are the greatest and smallest of \( u, v, \) and \( \phi, \) respectively.

The integrals over variables \( v \) and \( \phi \) can be easily calculated using the formula for the integral of the product of three spherical harmonics
\[ \int d^3v \int d\phi Y_{l|m}(\cos v, \phi) Y_{l|m}(\cos v, \phi) Y_{l|m}(\cos v, \phi) \]
\[ = \frac{(2l+1)(2l+1)(2l+1)}{4\pi} \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} m_1 & m_2 & m_3 \end{array} \right). \]

All the integrals over variables \( u \) in eqs. (9)–(13) were calculated numerically using a Gauss–Legendre quadrature.

Because, in our calculations, we used the finite number of the Legendre polynomials, the infinite sum over \( l \) in eq. (29) is cut by the angular integration condition (30). So, after performing the angular integration, only the finite number of the terms in eq. (29) remains to be different from zero.

It is clear from the determination of the matrices described by eqs. (9)–(13) that the one-electron integrals need to be calculated only once during the procedure. However, for the two-electron case, because the operators \( K \) and \( J \) depend on orbitals, the matrices \( J \) and \( K \) must be recalculated at every iteration step.

Although it is theoretically possible to calculate and store at the outset the basic two-electron integrals over the basis functions \( \{ \tau_n \} \).
\[ \int_{u,v,h} \tau_n^{m_1,m_2,m_3} \tau_n^{m_1,m_2,m_3} \frac{d^3r_1 d^3r_2}{|r_1 - r_2|} \]
\[ = \int d^3r_1 d^3r_2 \tau_n^{m_1,m_2,m_3} \tau_n^{m_1,m_2,m_3} \frac{d^3r_1 d^3r_2}{|r_1 - r_2|} \]

for even a small number of basis functions, the number of such integrals becomes too large to be stored in the RAM of a usual PC. Letting \( N \) denote the number of splines, \( k \) their order, and \( N_L \) the number of associated Legendre polynomials, we have, for example, that for a given set \( \{ m_1, m_2, m_3 \} \) there are \( N^2 \times k^2 \times N_L^2 \) different nonzero integrals. Hence, for \( N = 20, k = 5, \) and \( N_L = 10, \) we already have \( 10^6 \) different integrals \( j_{u,v,h}^{m_1,m_2,m_3,m_4} \) whose storage would require \( 8 \times 10^8 \) bytes of RAM. As this number should be multiplied by all different combinations of \( \{ m_1, m_2, m_3, m_4 \}, \) it is clearly realized that even for such small basis set, the required RAM is of the order of gigabytes. However, taking advantage of the expansion given by eq. (29) we can take as the basic two-electron integrals the following quantities:
\[ C_{l_1,m_1,l_2,m_2,l_3,m_3} = \int du_1 \int du_2 P_{l_1,m_1}(\cosh u_c) \times \]
\[ \times P_{l_2,m_2}(\cosh u_c) P_{l_3,m_3}(\cosh u_c) \]

Clearly, for any \( M \), the number of these basic integrals is just \( N^2 \times k^2 \times 2 N_L \times 2 N_L \times 2 N_L \). This number is \( N^2 / 2 \) times less than the previous one and can be easily stored in the RAM of most currently available PCs.

In terms of these basic integrals, the evaluation of matrices \( J \) and \( K \) involves sums over \( l \) and \( m \) as is given by eq. (29), as well as sums over the orbital coefficients \( \{ C_{l,m} \} \) determining the expansion of each \( \Phi_l(r) \) in eq. (6). Although the handling of matrices \( J \) and \( K \) in terms of basic integrals reduces the calculation time, the evaluation of these two matrices remains, however, as the main problem in these calculations.

Typically, one iteration takes from some seconds to 30 min in the Pentium III CPU with 512 Mb of RAM. The time of the iteration depends very much on the dimension of the basis. The number of the iterations, of course, depends on the initial approximation. To reduce the number of iterations with a large basis in our calculations we used the following algorithm. First, we performed Hartree–Fock calculations with some basis of small dimension. The output of this calculation was then used as the input for the calculation with a larger basis. So we could start the calculation with a large basis with a very good initial approximation.

From the definition of the basis set (22) it follows that we need to calculate matrices for each momentum projection \( m \) but not for each orbital. Moreover, as a result of solving eq. (16) we obtain an orbital subset for each \( m \) comprising both occupied and excited states.

Also, when we solve the orbital Hartree–Fock equations and obtain the eigenfunctions and eigenvalues of Fock’s operator we generate a quasi-complete system of excited eigenfunctions and
eigenvalues. Using this system of functions we can approximate (in terms of this finite but large basis set) the infinite sums over excited states, appearing in perturbation theory expressions. In this respect, to investigate the adequacy of the present approach, we have evaluated the second-order perturbation theory correction to the energy levels of some atoms and diatomic molecules:

$$
\Delta E^{(2)} = \sum_{\epsilon_i \epsilon_j} \frac{(\Psi_i V - V_i \Psi_j)(\Psi_j V - V_j \Psi_i)}{E_i - E_j},
$$

(33)

where \( V_0 \) is the approximate zeroth order potential and \( V \) is the exact potential. The calculations for atoms have been carried out by simply setting one of the nuclear charges equal to zero. The results of these calculations are discussed in the following section.

In the present calculations (depending on the system) we have used the following parameters:

1. Order of B-splines \( k = 7 \).
2. Maximal value of \( u \), \( U_{\text{max}} = \ln(4z_{\text{max}}/R) \), with \( z_{\text{max}} \) varying from 20 to 25.
3. Number of B-splines: from 20 to 30.
4. Number of Legendre polynomials: from 7 to 15.

### Results and Discussion

To assess the accuracy of the present method we have first considered the simple and well-known example of the He atom in the zeroth-order approximation, namely, without electron–electron interaction. We have solved the Schrödinger equation for this atom in prolate spheroidal coordinates, and have subsequently calculated the first- and second-order corrections with respect to the perturbation term \( 1/r_{12} \). It is well known, that for this atom the exact value of the zero-order energy is \( E_0^{(0)} = -4 \) hartrees; the first-order correction, which can be easily calculated analytically with \( 1s \) wave functions, yields the value \( \Delta E^{(1)} = 1.25 \) hartrees. In Table 1, we present the results of our calculations for different initial basis sets and compare them to the exact values. For the second-order correction we have taken as the “exact” value that of Middel:\[15] \( \Delta E^{(2)} = -0.15766643 \) hartrees.

The method has been further tested by performing Hartree–Fock calculations on the He, Be, and Ne atoms. In Table 2, we present the results of these calculations and compare them to the accurate Hartree–Fock values, to other second-order corrections calculations, and to available total energy values. In the first, third, and fifth line of this table we present results of our calculations of the Hartree–Fock energy, second-order correction, and the sum of these two values, respectively. Because in the present case, the corrections are taken with respect to the Hartree–Fock results, the second-order correction is, in fact, the well-known MP2 correction.\[16] In the second line, for comparison, we give results of the Hartree–Fock calculations taken from the book of C. Froese Fisher.\[17] In the fourth line of the table we give the second-order corrections, recently calculated by Flores et al.\[18]

As one can see from the table, our results for atoms are in very good agreement with results obtained by other methods. The biggest difference can be seen in the second-order energy calculations for Ne: \(-0.3874(1)\) a.u. and \(-0.38811\) a.u. in the present article and in ref. 18, respectively. Here we would like to note, that the prolate spheroidal coordinates are not the most natural ones in case of atoms. In the case of atoms, the calculations can be reduced to one dimension in spherical coordinates, and the infinite summation over the momentum of the excited orbitals can be easily extrapolated, while the summation over momentum projection can be performed analytically for each value of momentum. In the case of two-dimensional calculations we have to restrict from the very beginning the number of used Legendre polynomials, so it is quite difficult to perform some extrapolation of the results to the infinite number of the Legendre polynomials. Taking this into account the difference \((7 \pm 1) \times 10^{-4}\) a.u. in calculations of the second-order energy can be considered as a very good agreement between two methods.

In the last line of this table we include total ground states energy values derived by combining experimental data and improved \textit{ab initio} calculations, taken from ref. 19. As one can see from this table, the second-order correction to Hartree–Fock energy yields accounts for a sizable portion of the correlation energy so that the sum of the Hartree–Fock plus second-order correction approximates rather closely the listed total ground-state energies of the atoms considered.

### Table 1. Perturbation Theory Calculations for the Atom of He in Prolate Spheroidal Coordinates with Various Numbers of Basis Functions with Zero Approximation without Interaction.

<table>
<thead>
<tr>
<th>Number of splines</th>
<th>× order of splines</th>
<th>× number of Legendre polynomials</th>
<th>( E^{(0)} ) – ( E^{(0)}_{\text{exact}} )</th>
<th>( \Delta E^{(1)} – \Delta E^{(1)}_{\text{exact}} )</th>
<th>( \Delta E^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 15 \times 5 \times 4 )</td>
<td>( 3 \times 10^{-4} )</td>
<td>( -2 \times 10^{-4} )</td>
<td>( -0.15738 )</td>
<td>( 3 \times 10^{-10} )</td>
<td>( -0.15764 )</td>
</tr>
<tr>
<td>( 20 \times 5 \times 5 )</td>
<td>( 2 \times 10^{-6} )</td>
<td>( -2 \times 10^{-6} )</td>
<td>( -0.15734 )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15763 )</td>
</tr>
<tr>
<td>( 20 \times 5 \times 10 )</td>
<td>( 2 \times 10^{-8} )</td>
<td>( -2 \times 10^{-8} )</td>
<td>( -0.15756 )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15763 )</td>
</tr>
<tr>
<td>( 30 \times 5 \times 10 )</td>
<td>( 2 \times 10^{-8} )</td>
<td>( -2 \times 10^{-8} )</td>
<td>( -0.15763 )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15763 )</td>
</tr>
<tr>
<td>( 30 \times 7 \times 10 )</td>
<td>( 2 \times 10^{-10} )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15764 )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15764 )</td>
</tr>
<tr>
<td>( 30 \times 7 \times 15 )</td>
<td>( 2 \times 10^{-10} )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15764 )</td>
<td>( -2 \times 10^{-10} )</td>
<td>( -0.15764 )</td>
</tr>
</tbody>
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### Table 2. Results of Hartree–Fock and Second-Order Correction Calculations for Atoms.

<table>
<thead>
<tr>
<th>Property</th>
<th>He</th>
<th>Be</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{HF}} )</td>
<td>(-2.861680)</td>
<td>(-14.573023)</td>
<td>(-128.547098)</td>
</tr>
<tr>
<td>( E_{\text{HF}} ) from ref. 17</td>
<td>(-2.861680)</td>
<td>(-14.573023)</td>
<td>(-128.547098)</td>
</tr>
<tr>
<td>( \Delta E^{(2)} )</td>
<td>(-0.03735)</td>
<td>(-0.07628)</td>
<td>(-0.3874(1))</td>
</tr>
<tr>
<td>( \Delta E^{(2)} ) from ref. 18</td>
<td>(-0.03734)</td>
<td>(-0.07629)</td>
<td>(-0.38811)</td>
</tr>
<tr>
<td>( E_{\text{HF}} + \Delta E^{(2)} )</td>
<td>(-2.89903)</td>
<td>(-14.64930)</td>
<td>(-128.9345(1))</td>
</tr>
<tr>
<td>Semiempirical energy*</td>
<td>(-2.9037)</td>
<td>(-14.6674)</td>
<td>(-128.939)</td>
</tr>
</tbody>
</table>

*Ref. 19.
In the present applications of this method to atoms we have fixed the parameter $R$ at the value 0.1 bohrs. This allows us to use in our calculations just a small number of Legendre polynomials. As it was noted in ref. 7, for large nuclear charge $Z$, the low-lying orbitals become strongly localized in the region close to the nucleus. This means that to describe accurately such orbitals in prolate spheroidal coordinates, when the parameter $R \approx 1$ or is greater than 1 we need to use a large enough number of Legendre polynomials. Of course, this is avoided by choosing $R = 0.1$ bohrs.

Our next example is a diatomic molecule, for which we have selected a small but already sufficiently complex system: the molecule CO. In the Table 3 we show that the results of Hartree–Fock calculations and second-order correction to the energy converge with increasing number and order both of B-splines and Legendre polynomials. For the sake of comparison we have calculated for this molecule the Hartree–Fock energy with the numerical program of Kobus. For internuclear distance $R = 2.1316$, this program yields the Hartree–Fock energy value $E_{HF} = -112.790935$ hartrees. This value is in perfect agreement with $E_{HF} = -112.790934$ hartrees obtained with our program for a basis containing 30 B-splines up to the seventh order and 15 Legendre polynomials. However, as one can see from Table 3, even for a smaller number of Legendre polynomials and B-splines we can obtain a result that lies quite close to the exact one.

For completeness, we have also calculated the Hartree–Fock and their corresponding second-order, MP2, correction energies for some selected first-row hydrides and homonuclear diatomic molecules. The results of these calculations are shown in Tables 4 and 5, respectively. As in the case of CO, for these molecules we have repeated all the Hartree–Fock energy calculations using the numerical diatomic molecule program. In all cases, the absolute value of the difference between the results obtained with the two programs was found to be less than $10^{-6}$ hartrees. Our results of Hartree–Fock calculations can also be compared to the results, obtained using the finite-elements method by Heinemann et al. Because the total Hartree–Fock energy is sensible to the internuclear distance, and in refs. 8 and 9 for all the molecules except BH were used slightly different distances then in the present article, we can perform accurate comparison of our results with those of Heinemann only for the molecule of BH. These results are also in very good agreement: $-25.1315987$ hartrees in ref. 9 and $-25.131599$ hartrees in the present article. Nevertheless, the results of Heinemann et al. for the molecules of $H_2$ and LiH, although there were used different radii, differs from ours only by 1 in the seventh digit. In Tables 4 and 5 “experimental” correlation energies for diatomic molecules are also given for the comparison.

It should be noted, that in the case of homonuclear diatomic molecules, the orbitals can be symmetric or antisymmetric with respect to the plane perpendicular to the molecular axis, which passes through the middle point of the distance between nuclei. For the basis used in the present work, this orbital symmetry can be incorporated in the following way. For symmetric orbitals use only Legendre polynomials with even $l$ and for antisymmetric ones, with odd $l$. Hence, there is no need to construct special matrices for symmetric or antisymmetric orbitals. The above method yields them with the necessary symmetry without having to resort to any additional restrictions.

As it was noted above, in the case of two-dimensional calculations it is very difficult to make the exact extrapolation of the

### Table 3. Convergence of Hartree–Fock and Second-Order Correction Calculations for Molecule CO in Configuration $1\sigma_2^22\sigma_3^23\pi_4^24\pi_5^25\pi_7^2$ for Internuclear Distance $R = 2.1316$ a.u.

<table>
<thead>
<tr>
<th>Number of splines $\times$ order of splines $\times$ number of Legendre polynomials</th>
<th>$E_{HF}$</th>
<th>$\Delta E^{(2)}$</th>
<th>$E_{HF} + \Delta E^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 $\times$ 5 $\times$ 5</td>
<td>$-105.711438$</td>
<td>$-0.4397$</td>
<td>$-106.1511$</td>
</tr>
<tr>
<td>20 $\times$ 5 $\times$ 10</td>
<td>$-112.782215$</td>
<td>$-0.5115$</td>
<td>$-113.2937$</td>
</tr>
<tr>
<td>20 $\times$ 5 $\times$ 15</td>
<td>$-112.790891$</td>
<td>$-0.5162$</td>
<td>$-113.3068$</td>
</tr>
<tr>
<td>30 $\times$ 5 $\times$ 15</td>
<td>$-112.790931$</td>
<td>$-0.5175$</td>
<td>$-113.3085$</td>
</tr>
<tr>
<td>30 $\times$ 7 $\times$ 15</td>
<td>$-112.790934$</td>
<td>$-0.5175(2)$</td>
<td>$-113.3085(2)$</td>
</tr>
</tbody>
</table>

### Table 4. Results of Hartree–Fock and Second-Order Correction Calculations for Some Hydrides.

<table>
<thead>
<tr>
<th>Property</th>
<th>LiH</th>
<th>BH</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>3.0141</td>
<td>2.336</td>
<td>1.7329</td>
</tr>
<tr>
<td>Configuration</td>
<td>$1\sigma_2^22\sigma_3^23\pi_4^24\pi_5^25\pi_7^2$</td>
<td>$1\sigma_2^22\sigma_3^23\pi_4^24\pi_5^25\pi_7^2$</td>
<td>$1\sigma_2^22\sigma_3^23\pi_4^24\pi_5^25\pi_7^2$</td>
</tr>
<tr>
<td>$E_{HF}$</td>
<td>$-7.978351$</td>
<td>$-25.131599$</td>
<td>$-100.070800$</td>
</tr>
<tr>
<td>$\Delta E^{(2)}$</td>
<td>$-0.07268$</td>
<td>$-0.1313$</td>
<td>$-0.3832$</td>
</tr>
<tr>
<td>Others calculations of correlation energy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Experimental” correlation energy</td>
<td>$-0.08183^a$</td>
<td>$-0.1307^b$</td>
<td>$-0.37978^c$</td>
</tr>
<tr>
<td>$E_{HF} + \Delta E^{(2)}$</td>
<td>$-8.06003$</td>
<td>$-25.2629$</td>
<td>$-100.4540$</td>
</tr>
</tbody>
</table>

$^a$Ref. 20.  
$^b$Ref. 21.  
$^c$Ref. 22.  
$^d$Ref. 23.

### Table 5. Results of Hartree–Fock and Second-Order Correction Calculations for Some Homonuclear Molecules.

<table>
<thead>
<tr>
<th>Property</th>
<th>$H_2$</th>
<th>Li$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>1.4003</td>
<td>5.0456</td>
<td>2.0749</td>
</tr>
<tr>
<td>Configuration</td>
<td>$1\sigma_2^2$</td>
<td>$1\sigma_2^22\sigma_3^1\sigma_4^1$</td>
<td>$1\sigma_2^22\sigma_3^23\pi_4^2\pi_5^2\pi_7^21\pi_8^1$</td>
</tr>
<tr>
<td>$E_{HF}$</td>
<td>$-1.133628$</td>
<td>$-14.871543$</td>
<td>$-108.993110$</td>
</tr>
<tr>
<td>$\Delta E^{(2)}$</td>
<td>$-0.03423$</td>
<td>$-0.1064$</td>
<td>$-0.5350$</td>
</tr>
<tr>
<td>“Experimental” correlation energy</td>
<td>0.04085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{HF} + \Delta E^{(2)}$</td>
<td>$-1.16786$</td>
<td>$-14.9780$</td>
<td>$-109.5281$</td>
</tr>
</tbody>
</table>

$^a$Ref. 24.
second-order energy calculations to the infinite number of the Legendre polynomials. So in our calculations we did not perform this extrapolation. To estimate the numerical uncertainty, arising from the truncation of the infinite sum over momentum projections of the excited states, the present method has been used for evaluation of the second-order energy corrections. We have calculated this quantity using excited orbitals up to an absolute value of 10 for the momentum projection \( m \). The rest of the sum was estimated by the polynomial fitting in \( 1/\sqrt{m} \). As a result, we estimate, that the absolute value of total numerical error of our calculations due to a truncation of the sum over excited states to the above maximum value of momentum projection, is less than \( 10^{-5} \) hartrees. Thus, we may conclude that the main contribution to the numerical error of calculations arise from the use of a finite number of Legendre polynomials for description of the occupied orbitals.

**Conclusion**

In the present article we have advanced a new method for the generation of a quasi-complete set of eigenfunctions arising from the solution of Hartree–Fock equation for diatomic molecules. This method is based on the B-splines approach and partial wave expansion in transformed prolate spheroidal coordinates. Using the quasi-complete set of eigenfunctions of the Fockian operator, one can calculate to good accuracy sums over excited states appearing in various orders of perturbation theory. The Hartree–Fock energies as well as of the second-order energy correction to the energy obtained in this work are in a good agreement with those obtained by other methods.

It is clear that this method allows us to perform calculations of higher order terms in perturbation theory. We may certainly infer from the second-order results obtained in the present work, that implementation of these calculations using the excited functions generated by this method will, very likely, yield highly accurate values for the correlation energies as well as for other properties of diatomic molecules.

**Acknowledgments**

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**References**