

ACCURATE HARTREE-FOCK-SLATER CALCULATIONS ON SMALL DIATOMIC MOLECULES WITH THE FINITE-ELEMENT METHOD

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We report on the self-consistent field solution of the Hartree-Fock-Slater equations using the finite-element method for the three small diatomic molecules N_2 , BH and CO as examples. The quality of the results is not only better by two orders of magnitude than the fully numerical finite difference method of Laaksonen et al. but the method also requires a smaller number of grid points.

Besides the standard basis set expansion methods [1] for solving the self-consistent Hartree-Fock equations for molecules, the fully numerical finite-difference method has recently been introduced by Laaksonen, Pyykkö and Sundholm. In a series of papers [2-4] they have shown that this method can be used with high accuracy to solve the same physical problem. Their examples were the solution of the Hartree-Fock-Slater equations for small diatomic molecules (a first step towards relativistic calculations has also been taken by the same authors [5]). The main disadvantage of this method is the need for a large number of points to achieve high accuracy.

The finite-element method represents an alternative approach to solve the same differential equations. In two preceding papers we have shown that the finite-element method can be adapted to quantum mechanical problems. The one-electron systems H_2^+ and HHe^{2+} [6] as well as the simplest two-electron system H_2 [7] have been solved with considerable success.

In the finite-element method the space is divided into a number of elements. On each of these elements basis functions are chosen. Hence from a practical point of view, the finite-element method is a basis set method, but no global basis functions are chosen as in standard basis set expansion methods. The local basis functions on each element are polynomials with free expansion coefficients. The size, the shape and the number of elements as well as the

order of the polynomials are the "parameters" which can be changed in this method. Once the final choice is made a matrix diagonalisation with respect to the free expansion coefficients leads to the solution of the differential equations.

In the case of the Hartree-Fock-Slater equations

$$\frac{1}{2}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) = \epsilon\Psi(\mathbf{r}), \quad (1)$$

with

$$V(\mathbf{r}) = V^{\text{nuc}}(\mathbf{r}) + V^{\text{c}}(\mathbf{r}) + V^{\text{x}}(\mathbf{r}),$$

$$V^{\text{nuc}}(\mathbf{r}) = -Z_1/|\mathbf{r}_1 - \mathbf{r}| - Z_2/|\mathbf{r}_2 - \mathbf{r}|,$$

$$V^{\text{c}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r',$$

$$V^{\text{x}}(\mathbf{r}) = -\frac{3}{2}\alpha[(3/\pi)\rho(\mathbf{r})]^{1/3},$$

the finite-element method can be applied if these equations are written as the functional

$$\begin{aligned} & \frac{1}{2} \int |\nabla\Psi|^2 d^3r + \int V(\mathbf{r})|\Psi|^2 d^3r \\ & - \epsilon \int |\Psi|^2 d^3r, \end{aligned} \quad (2)$$

which is minimised by the solution of the matrix equation

$$\mathbf{H}\mathbf{x} = \epsilon\mathbf{S}\mathbf{x}. \quad (3)$$

\mathbf{H} is the Hamiltonian matrix, \mathbf{S} the norm matrix and

x represents the values of the eigenfunctions at the grid points.

The solution of the Poisson equation which connects the electron charge density and the molecular potential is obtained by solving for the functional

$$\frac{1}{2} \int (\nabla V^c)^2 d^3r - 4\pi \int \rho V^c d^3r, \quad (4)$$

which leads to the matrix equation

$$Dy = d. \quad (5)$$

D , d and y are the analogs of H , S and x in eq. (3).

To actually calculate the matrix elements in eqs. (3) and (5) we choose prolate spheroidal coordinates and divide the space so as to be equidistant in these coordinates. The main problem, of course, is to have a sufficient number of elements in the vicinity of the nuclei where the large charge density of the inner electrons is concentrated. This shows up especially for large internuclear distances where the charge density is a strongly peaked function of the angular variable.

Using this finite-element method we have solved

Table 1

Total energy and energy eigenvalues for the systems N_2 , BH and CO. The Slater exchange parameter was 0.7 for all calculations. For the largest grids the last figure is uncertain. All values are given in au

N_2 , internuclear distance $R=2.07$ au					
	ref. [5]	this work, fifth-order polynomials			
points	5989	2601	3136	3721	4356
E_T	-108.346622	-108.346605	-108.3466076	-108.3466086	-108.3466090
$\epsilon(1\sigma_g)$	-13.981070	-13.9810680	-13.98106828	-13.98106837	-13.98106840
$\epsilon(1\sigma_u)$	-13.979661	-13.9796581	-13.97965838	-13.97965847	-13.97965850
$\epsilon(2\sigma_g)$	-1.007215	-1.00721471	-1.00721472	-1.00721471	-1.00721471
$\epsilon(2\sigma_u)$	-0.460725	-0.46072506	-0.46072505	-0.46072505	-0.46072505
$\epsilon(1\pi_u)$	-0.404235	-0.40423461	-0.40423462	-0.40423462	-0.40423462
$\epsilon(3\sigma_g)$	-0.350058	-0.35005851	-0.35005852	-0.35005852	-0.35005852
N_2 , internuclear distance $R=2.07$ au					
	ref. [5]	this work, sixth-order polynomials			
points	2401	3025	3721	4498	
E_T	-108.3466090	-108.34660925	-108.34660932	-108.34660934	
$\epsilon(1\sigma_g)$	-13.9810686	-13.98106844	-13.98106844	-13.98106844	
$\epsilon(1\sigma_u)$	-13.9796587	-13.97965854	-13.97965854	-13.97965854	
$\epsilon(2\sigma_g)$	-1.00721474	-1.00721471	-1.00721471	-1.00721471	
$\epsilon(2\sigma_u)$	-0.46072506	-0.46072505	-0.46072505	-0.46072505	
$\epsilon(1\pi_u)$	-0.40423461	-0.40423462	-0.40423462	-0.40423462	
$\epsilon(3\sigma_g)$	-0.35005852	-0.35005852	-0.35005853	-0.35005852	
	ref. [5]	this work, fifth-order polynomials			
	BH	CO	BH	CO	
points	15609	5989	4356	4356	
R	2.366	2.13	2.366	2.13	
E_T	-24.808852	-112.129925	-24.8088515	-112.129915	
$\epsilon(1\sigma)$	-6.5323604	-18.744146	-6.53236004	-18.7441431	
$\epsilon(2\sigma)$	-0.4078652	-9.911347	-0.40786519	-9.9113461	
$\epsilon(3\sigma)$	-0.1731323	-1.044171	-0.17313242	-1.0441708	
$\epsilon(4\sigma)$	-	-0.489071	-	-0.4890707	
$\epsilon(1\pi)$	-	-0.413613	-	-0.4126127	
$\epsilon(5\sigma)$	-	-0.303029	-	-0.3030299	

the three standard systems N_2 , BH and CO in order to ascertain whether or not this approach is a useful alternative to the finite-difference method.

Table 1 presents the energy eigenvalues as well as the total energies of N_2 for different grid sizes and fifth- and sixth-order two-dimensional polynomials as basis functions on the elements.

For 2401 points the accuracy of the sixth-order polynomial grid is comparable to that of the 4356-point fifth-order polynomial grid. This shows clearly the advantage of high-order polynomials as basis functions for the finite-element method in order to achieve results of high precision.

To compare the current results for N_2 with those of Laaksonen et al. [4,5] we emphasise that their number of points is the number of points in the half box, whereas our number of points refers to the whole box. Laaksonen et al. give an absolute error of 1×10^{-5} au for the total energy. This same accuracy is reached in our calculations with 2601 points and fifth-order polynomials. The error in the total energy attained with the 2401-point sixth-order grid is about 5×10^{-7} au. The results achieved with the 4489-point sixth-order grid are probably correct to 10^{-8} au. This value is two to three significant figures better than the values of Laaksonen et al., who used about a factor of two more points. Values for the systems BH

and CO are given at the end of table 1.

This comparison shows that the finite-element method is capable of solving the Hartree-Fock-Slater equations to an accuracy never reached before and thus is more than an alternative to all other methods. An attempt to achieve very accurate values for the Hartree-Fock equations as a bench mark for the quality of quantum chemical calculations is our next goal.

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