H_2 SOLVED BY THE FINITE ELEMENT METHOD

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We report on the solution of the Hartree–Fock equations for the ground state of the H_2 molecule using the finite element method. Both the Hartree–Fock and the Poisson equations are solved with this method to an accuracy of 10^{-8} using only 26×11 grid points in two dimensions. A 41×16 grid gives a new Hartree–Fock benchmark to ten-figure accuracy.

Calculation of the ground-state energy of the H_2 molecule is the standard test to prove the quality of a new method for solving the Schrödinger equation of a many-electron molecule. A bibliography of publications on this system can be found in ref. [1].

Atomic physics has always preferred purely numerical [2,3] instead of basis-set methods to solve the many-electron Hartree–Fock equations. This is due to practical reasons as well as a certain arbitrariness always introduced by the choice of basis functions.

For molecules, basis set methods have been the only methods able to solve the problem in a reasonable time. However Laaksonen et al. [4] have recently devised a purely numerical finite difference method able to solve the many-electron Hartree–Fock–Slater problem for diatoms containing relatively heavy atoms [5]. Of course, this method is not expected to be an alternative to actual quantum chemical calculations but it can be regarded as a new development which might be interesting for the future. A review by the same authors can be found in ref. [6].

We would like to present another method which may also be of interest in time to come: The finite element method (FEM). This method is well known in engineering science, and recently it was shown that it might be useful for quantum mechanical problems as well [7].

We use this method to solve the Hartree–Fock equation for the ground state of H_2, which in this case can be written:

$$-\tfrac{1}{2}\nabla^2\varphi(\boldsymbol{r})+V^{\mathrm{nuc}}(\boldsymbol{r})\varphi(\boldsymbol{r})+\tfrac{1}{2}V^{\mathrm{c}}(\boldsymbol{r})\varphi(\boldsymbol{r})=\epsilon\varphi(\boldsymbol{r})\,, \tag{1}$$

with

$$V^{\mathrm{nuc}}(\boldsymbol{r})=-\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}|}-\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}|}\,.$$

The connection between the charge density and the potential V^{c} is given by the Poisson equation

$$\nabla^2 V^{\mathrm{c}}(\boldsymbol{r})=-4\pi\rho(\boldsymbol{r})\,, \tag{2}$$

with

$$\rho(\boldsymbol{r})=2|\varphi(\boldsymbol{r})|^2\,.$$

If eqs. (1) and (2) are both solved iteratively, a self-consistent solution can be reached.

In order to apply the finite element technique one has to start from the variational principle for the functional

$$\tfrac{1}{2}\int|\nabla\varphi|^2\mathrm{d}^3r+\int(V^{\mathrm{nuc}}+V^{\mathrm{c}})|\varphi|^2\mathrm{d}^3r-\epsilon\int|\varphi|^2\mathrm{d}^3r \tag{3}$$

to solve the Schrödinger-type Hartree–Fock equations, and from the functional

$$\tfrac{1}{2}\int(\nabla V^{\mathrm{c}})^2\mathrm{d}^3r-4\pi\int\rho V^{\mathrm{c}}\mathrm{d}^3r \tag{4}$$

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Table 1
Total energy and $1s_\sigma$ energy eigenvalue for H_2 for differing number of mesh points. The best values from ref. [4] are $E=-1.13362957$ and $\epsilon=-0.59465857$ au, respectively. The calculation with 41×16 points, i.e. 48 elements, leads to values with 2 more significant figures for E and ϵ

Number of points	Number of elements	E (au)	Relative error	ϵ (au)	Relative error
6×6	2	-1.12873769	-4.3×10^{-3}	-0.59583041	2.0×10^{-3}
11×11	8	-1.13362024	-8.2×10^{-6}	-0.59466119	4.4×10^{-6}
16×11	12	-1.13362884	-6.5×10^{-7}	-0.59465813	-7.4×10^{-7}
21×11	16	-1.13362949	-6.9×10^{-8}	-0.59465860	4.8×10^{-8}
26×11	20	-1.13362956	-5.3×10^{-9}	-0.59465856	-1.2×10^{-8}
41×16	48	$-1.1336295717(2)$		$-0.5946585694(3)$	

to solve the Hartree–Fock equations. This variational approach is analogous to the work by Becke [8]. The FEM method itself comprises the following: The whole space is divided into a finite number of elements (we use triangles for the two-dimensional H_2 problem). For each element the unknown function φ respectively V^c is described by a sum of polynomials with free coefficients. The order can be choosen freely but for this problem we use fifth order. The coefficients are determined by the solution of the matrix eigenvalue equation

$$\mathbf{H}x=\epsilon\mathbf{S}x \tag{5}$$

for eq. (1), and the matrix equation

$$\mathbf{D}y=d \tag{6}$$

for the Poisson equation (2).

The matrix **H** results from the insertion of the element trial functions into the first and second term of eq. (3) integrating the trial function over each element, and summing over all elements. The matrix **S** comes from the third term of eq. (3). Similarly the matrix **D** results from the first and the vector d from the second term of eq. (4). The vectors x and y contain the expansion coefficients. Details of finite element calculations as a general method can be found in ref. [9]. Full details of the method for this particular quantum mechanical application will be published elsewhere [10].

Here we present preliminary results for the ground state of the many-electron system H_2. Table 1 lists the total and orbital energies obtained as the number of elements used increases. No special care has been taken to partition the space in the most effective way in order to get the best results for this system. We simply divided the space equidistantly in intrinsic elliptic hyperbolic coordinates. For 26×11 points, i.e. 20 elements, the total energy obtained already has an accuracy better than 10^{-8}. For a comparison we used the definitive results of Laaksonen et al. [4]. With 41×16 points, i.e. 48 elements, we were able to add two more significant figures to the results (see table 1).

The high quality of the finite element calculation demonstrates the usefulness of this method. As is obvious from eqs. (5) and (6) this is, in principle, a matrix method using higher-order two-dimensional spline functions. These functions – which describe approximately the functions φ respectively V^c over each element – are the basis states. So, once one has chosen the order of the polynomials for the elements the basis is fixed. It should be noted that even for the relatively small number of 20 elements, the use of fifth-order polynomials over each element as in this case, leads to very accurate results.

We intend to extend this work to the solution of the Hartree–Fock–Slater equations for heavier systems.

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