H₂ 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 H₂ 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 H₂ 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 H₂, which in this case can be written:

\[-\frac{1}{2} \nabla^2 \varphi(r) + V_{\text{nuc}}(r) \varphi(r) + \frac{1}{2} V_{\text{c}}(r) \varphi(r) = \epsilon \varphi(r),\]

with

\[V_{\text{nuc}}(r) = -\frac{1}{|r_1 - r|} - \frac{1}{|r_2 - r|} \cdot\]

The connection between the charge density and the potential \(V_{\text{c}}\) is given by the Poisson equation

\[\nabla^2 V_{\text{c}}(r) = -4\pi \rho(r),\]

with

\[\rho(r) = 2|\varphi(r)|^2.\]

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

\[\frac{1}{2} \int |\nabla \varphi|^2 d^3 r + \int (V_{\text{nuc}} + V_{\text{c}})|\varphi|^2 d^3 r - \epsilon \int |\varphi|^2 d^3 r\]

\[= \frac{1}{2} \int (\nabla V_{\text{c}})^2 d^3 r - 4\pi \int \rho V_{\text{c}} d^3 r\]

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Table 1

Total energy and $1s\alpha$ 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 $41 \times 16$ points, i.e. 48 elements, leads to values with 2 more significant figures for $E$ and $\epsilon$.

| Number of | Number of | $E$ (au) | Relative | $\epsilon$ (au) | Relative |
| points | elements | | error | error |
| 6x6 | 2 | -1.12873769 | -4.3x$10^{-3}$ | -0.59583041 | 2.0x$10^{-3}$ |
| 11x11 | 8 | -1.13362024 | -8.2x$10^{-6}$ | -0.59466119 | 4.4x$10^{-6}$ |
| 16x11 | 12 | -1.13362884 | -6.5x$10^{-7}$ | -0.59465813 | -7.4x$10^{-7}$ |
| 21x11 | 16 | -1.13362949 | -6.9x$10^{-8}$ | -0.59465860 | 4.8x$10^{-8}$ |
| 26x11 | 20 | -1.13362956 | -5.3x$10^{-9}$ | -0.59465856 | -1.2x$10^{-8}$ |
| 41x16 | 48 | -1.1336295717(2) | -5.3x$10^{-9}$ | -0.5946585694(3) | -5.3x$10^{-9}$ |

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 $\varphi$ 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.

References


