FINITE ELEMENT METHOD FOR THE ACCURATE SOLUTION OF DIATOMIC MOLECULES

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ABSTRACT. We present the Finite-Element-Method (FEM) in its application to quantum mechanical problems solving for diatomic molecules. Results for Hartree-Fock calculations of H_2 and Hartree-Fock-Slater calculations of molecules like N_2 and CO have been obtained. The accuracy achieved with less then 5000 grid points for the total energies of these systems is 10^{-8} a.u. , which is demonstrated for N_2.

1. INTRODUCTION

The Finite Element Method (FEM) is a well known technique for solving static and dynamical problems in engineering science. Examples can be found in the textbooks of Ref. 1-3. The idea of this method is to divide the space into a number of 2 or 3 dimensional domains and describe the properties of interest on each of these elements separately connected via boundary conditions. In engineering science one uses low order polynomials to specify the interesting quantities on each element.
We applied the FEM to quantum mechanical problems where the accuracy required is very high. To achieve this accuracy we were forced to use high order polynomials on each element and, in order to minimize the total number of points, to use a small number of elements.

2. THE HARTREE-FOCK-SLATER EQUATIONS

The Hartree-Fock equations for a diatomic molecule read :

$$H_{HF}(\underline{r})\ \varphi_i(\underline{r}) = \varepsilon_i\ \varphi_i(\underline{r}) \qquad ; \ i = 1,2,\ldots,N \qquad . \qquad (1)$$

With

$$H_{HF}(\underline{r}) = h(\underline{r}) + V^C(\underline{r}) + V^X(\underline{r}) \tag{2}$$

$$h(\underline{r}) = -\frac{1}{2}\nabla^2 - \frac{Z_1}{|\underline{r}_1 - \underline{r}|} - \frac{Z_2}{|\underline{r}_1 - \underline{r}|} \tag{3}$$

$$V^C(\underline{r}) = \sum_{i=1}^{N} \int \varphi_i^*(\underline{r}') \frac{1}{\underline{r} - \underline{r}'} \varphi_j(\underline{r}') \, d\underline{r}'$$

and

$$V^X(\underline{r}) \; \varphi_j(\underline{r}) = \sum_{i=1}^{N} \int \varphi_i^*(\underline{r}') \frac{1}{|\underline{r} - \underline{r}'|} \varphi_j(\underline{r}') \, d\underline{r}' \; \varphi_i(\underline{r}) \; .$$

The interelectronic Coulomb potential $V^C(\underline{r})$ satisfies the Poisson equation

$$\nabla^2 V^C(\underline{r}) = -4\pi \, \rho(\underline{r}) \tag{4}$$

where $\rho(\underline{r})$ is the total electronic density.
In the Hartree-Fock-Slater equations the nonlocal exchange potential $V^X(\underline{r})$ of the Hartree-Fock equations is replaced by the local exchange potential

$$V^X(\underline{r}) = -3/2 \; \alpha \; (3/\pi \, \rho(\underline{r}))^{1/3} \tag{5}$$

where α is a constant. We use this simplified form of a local exchange with $\alpha = 0.7$.
The total molecular energy then is

$$E_{tot} = \sum_{i=1}^{N} \varepsilon_i - 1/2 \int \rho(\underline{r}) \, V^C(\underline{r}) \, d\underline{r} - $$
$$- 1/4 \int \rho(\underline{r}) \, V^X(\underline{r}) \, d\underline{r} \qquad . \tag{6}$$

The differential equations to be solved are the Schrödinger type equation derived from Equ. (1) with potentials kept fixed, and the Poisson equation (4) relating the potential V^C to the electronic density

3. THE COORDINATE SYSTEM

To solve the Hartree-Fock-Slater differential equations for a diatomic molecule numerically we chose the prolate spheroidal coordinates

$$x_1 = R/2 \ \sinh(s) \ \sin(t) \ \cos(\varphi)$$

$$x_2 = R/2 \ \sinh(s) \ \sin(t) \ \sin(\varphi) \qquad\qquad (7)$$

$$x_3 = R/2 \ \cosh(s) \ \cos(t)$$

which where also used by Laaksonen et al.[4] and Becke[5] for their num erical approach. Within these coordinates the unknown one electron wave functions are:

$$\varphi_i(s,t,\ ) = \varphi_i(s,t) \ \exp(i \ m \ \varphi) \qquad ; \qquad (8)$$

m denotes the projection of the angular momentum onto the internuclear axis.
Using this ansatz the Schrödinger type equation (1) can be rewritten as a two dimensional differential equation

$$- \frac{1}{2} \frac{\partial}{\partial s} \left(K_1(s,t) \ \frac{\partial \varphi_i}{\partial s} \right) \ - \ \frac{1}{2} \frac{\partial}{\partial t} \left(K_2(s,t) \ \frac{\partial \varphi_i}{\partial t} \right) -$$

$$- \ 1/2 \ m^2 \ K_3(s,t) \ \varphi_i(s,t) \ + \ K_4(s,t) \ V(s,t) \ \varphi_i(s,t) \qquad (9)$$

$$= \varepsilon_i \ K_4(s,t) \ \varphi_i(s,t)$$

Similary we get for the Poisson equation (4)

$$- \frac{1}{2} \frac{\partial}{\partial s} \left(K_1(s,t) \ \frac{\partial V^c}{\partial s} \right) \ - \ \frac{1}{2} \frac{\partial}{\partial t} \left(K_2(s,t) \ \frac{\partial V^c}{\partial t} \right)$$

$$= -4\pi \ K_4(s,t) \ \rho(s,t) \qquad (10)$$

with

$$K_1(s,t) = K_2(s,t) = R/2 \ \sinh(s) \ \sin(t)$$

$$K_3(s,t) = R/2 \ (\sinh^2(s) + \sin^2(t))/(\sinh(s) \ \sin(t)) \qquad (11)$$

$$K_4(s,t) = R^3/2 \ (\sinh^2(s) + \sin^2(t)) \ \sinh(s) \ \sin(t) \qquad .$$

4. THE FINITE ELEMENT METHOD[1-3]

The FEM orginally was developed in engineering science in order to calculate static and dynamic stresses of compli-cated constructions. In order to apply the FEM to the solu-tion of the Hartree-Fock-Slater equations, one best starts from the equivalent variational principle

$$I_1 = \iint \{ -\frac{1}{4} K_1 \left(\frac{\partial \varphi_i}{\partial s} \right)^2 - \frac{1}{4} K_2 \left(\frac{\partial \varphi_i}{\partial t} \right)^2 -$$

$$-\frac{1}{4} m^2 K_3 (\varphi_i)^2 - \frac{1}{2} (V - \varepsilon_i) K_4 (\varphi_i)^2 \} \; ds \; dt \qquad (12)$$

for the Schrödinger type equation (9) and

$$I_2 = \iint \{ -\frac{1}{2} K_1 \left(\frac{\partial V^c}{\partial s} \right)^2 - \frac{1}{4} K_2 \left(\frac{\partial V^c}{\partial t} \right)^2$$

$$+ 4\pi K_4(s,t) \, \rho(s,t) \, V^c \} \; ds \; dt \qquad (13)$$

for the Poisson equation (10).

We subdivide the two dimensional space by the use of tri-
angles. On each element a number of points, the nodal
points, are chosen. If $u^e(s,t)$ is the approximation of the
unknown function on the element with the number e, this
function is written as a linear combination of the nodal
values

$$u^e(s,t) = \sum_{i=1}^{p} u_i^e \, N_i^e(s,t) \qquad (14)$$

were u_i^e is the i-th nodal value of the e-th element. The
function $N_i^e(s,t)$ is the i-th shape function. The sum runs
over all p nodal values of the element.

Because of the subdivision of the region into N_s elements
the functionals I_1 equ. (12) and I_2 equ. (13) can be written
as a sum of element integrals

$$I_1 = \sum_{e=1}^{N_s} I_1^e \qquad \text{and} \qquad I_2 = \sum_{e=1}^{N_s} I_2^e \qquad (15)$$

The substitution of the trial function (14) into the element
integrals (15) leads to

$$I_1^e = (\underline{u}^e)^t \cdot \underline{\underline{H}}^e \cdot \underline{u}^e - (\underline{u}^e)^t \cdot \underline{\underline{S}}^e \cdot \underline{u}^e \qquad (16)$$

with the matrix elements

$$H_{ij} = -\frac{1}{4} \iint \{ K_1 \frac{\partial N_i^e}{\partial s} \frac{\partial N_j^e}{\partial s} + K_2 \frac{\partial N_i^e}{\partial t} \frac{\partial N_j^e}{\partial t} + \qquad (17)$$

$$+ (K_3 \, m^2 + 2 K_4 \, V) \, N_i^e \, N_j^e \} \; ds \; dt$$

and

$$S_{ij} = \iint \frac{1}{2} K_4 N_i^e N_j^e \quad ds\ dt \tag{18}$$

and for the Poisson equation similary

$$I_2^e = (\underline{u}^e)^t \cdot \underline{\underline{D}}^e \cdot \underline{u}^e - (\underline{u}^e)^t \cdot \underline{d}^e \tag{19}$$

with the matrix elements

$$D_{ij} = \frac{1}{2} \iint \{ K_1 \frac{\partial N_i^e}{\partial s} \frac{\partial N_j^e}{\partial s} + K_2 \frac{\partial N_i^e}{\partial t} \frac{\partial N_j^e}{\partial t} \}\ ds\ dt \tag{20}$$

and the vector elements

$$d_i = 4\pi \iint K_4 \rho(s,t) N_i^e \quad ds\ dt \quad . \tag{21}$$

The vector $\underline{u}^e$ is the element nodal vector of the e-th element.
Adding the contributions of all elements leads to the expressions :

$$I_1 = \underline{u}^t \cdot \underline{\underline{H}} \cdot \underline{u} - \underline{u}^t \cdot \underline{\underline{S}} \cdot \underline{u} \tag{22}$$

and

$$I_2 = \underline{u}^t \cdot \underline{\underline{D}} \cdot \underline{u} - \underline{u}^t \cdot \underline{d} \tag{23}$$

where $\underline{u}^t$ denotes the global nodal vector. Minimizing I_1 and I_2 with respect to the nodal values leads to the matrix eigenvalue problem

$$\underline{\underline{H}} \cdot \underline{u} = \varepsilon \cdot \underline{\underline{S}} \cdot \underline{u} \tag{24}$$

for the Schrödinger type equation and to the matrix equation

$$\underline{\underline{D}} \cdot \underline{u} = \underline{d} \tag{25}$$

for the Poisson equation.
The calculation of the matrix elements (17, 18, 20, 21) is done numerically with a conical product Gauss integration rule[6].
To account for the asymptotic decrease of the potential V^c we introduce a function $g(s,t)$

$$V^c = g(s,t) \cdot f^V(s,t) \tag{26}$$

and solve for the function $f^V(s,t)$ by the FEM.

5. RESULTS

For the calculations the points were distributed equidistant in both coordinates for simplicity. Such an equidistant point distribution is not at all optimal and it will be shown that point distributions which are physically more adequate will increase the accuracy.

In Tab. I we compare the convergence of the results with increasing grid size for both 5-th and for 6-th order polynomials for the system N_2. These results are expected to be accurate within 10^{-8} a.u. .

Table I:

N_2, internuclear distance R = 2.07 a.u.
Laaksonen⁴this work, 5-th order polynomials

Points	5989	3136	4356
E_T	-108.346622	-108.3466076	-108.3466090
$(1\sigma_g)$	-13.981070	-13.98106828	-13.98106840
$(1\sigma_u)$	-13.979661	-13.97965838	-13.97965850
$(2\sigma_g)$	-1.007215	-1.00721472	-1.00721471
$(2\sigma_u)$	-0.460725	-0.46072505	-0.46072505
$(1\pi_u)$	-0.404235	-0.40423462	-0.40423462
$(3\sigma_g)$	-0.350058	0.35005852	-0.35005852

this work, 6-th order polynomials

Points	2401	3025	4489
E_T	-108.3466090	-108.34660925	-108.34660934
$(1\sigma_g)$	-13.9810686	-13.98106844	-13.98106844
$(1\sigma_u)$	-13.9796587	-13.97965854	-13.97965854
$(2\sigma_g)$	-1.00721474	-1.00721471	-1.00721471
$(2\sigma_u)$	-0.46072506	-0.46072505	-0.46072505
$(1\pi_u)$	-0.40423461	-0.40423462	-0.40423462
$(3\sigma_g)$	-0.35005852	0.35005852	-0.35005852

Total energy and energy eigenvalues of the system N_2 for different grid sizes and different order of the polynomials on the elements. For the largest grids the last figure is uncertain. All values are given in a.u. .

In Tab. II a step towards an optimized point distribution is documented. In this table we compare the results for the system N_2 for a 31*31 points grid of 6-th order. In mesh A we use an equidistant distribution of the points whereas in mesh B the s-coordinates (Equ. 7) of the vertices of the triangles are distributed logarithmically improving the accuracy by about a factor of 15.

Table II:

N_2, internuclear distance R = 2.07 a.u.
6-th order polynomials

	Mesh A	Mesh B
Points	961	961
E_T	-108.34645	-108.34659
$(1\,\sigma_g)$	-13.98104	-13.981066
$(1\,\sigma_u)$	-13.97963	-13.979656
$(2\,\sigma_g)$	-1.0072143	-1.0072150
$(2\,\sigma_u)$	-0.4607255	-0.4607253
$(1\,\pi_u)$	-0.4042346	-0.4042347
$(3\,\sigma_g)$	-0.3500577	0.3500587

Total energy and energy eigenvalues of the system N_2 for two different point distributions. Mesh A refers to a equidistant grid with all elements of equal size whereas mesh B refers to a logarithmically point distribution in the s-coordinate. All values are given in a.u. .

The results presented are by 2 orders of magnitude more accurate then the results achieved by Laaksonen et al.[4] with the finite difference method, although we used a much smaller number of points.
A Hartree-Fock approach to diatomic molecules will be one of our next goals. The first attempt towards an optimized element distribution shows a very nice increase in accuracy. With better adapted element distributions one may tackle the 3-dimensional problems within reasonable computer times.

Acknowledgement

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