

Finite Element Calculations for Molecules with multiple Coulomb Centers

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Abstract. A novel and efficient method to mitigate the challenges posed by the Coulomb potentials when solving three-dimensional effective Schrödinger equations for molecules or solids is presented. This approach assumes a product ansatz for the wave function, where the first factor satisfies the cusp condition, while the second factor is assumed to be smooth. This ansatz leads to a regularized non-singular potential and a transformed energy functional. Highly accurate finite element ground state energies obtained with this functional using two-and three dimensional calculations for the hydrogen molecular ion are also presented.

1. Introduction

Efficient and reliable methods to solve the effective three-dimensional Schrödinger equation are important for density functional or Hartree Fock methods to calculate the properties of molecules and solids. To judge the accuracy of methods using Gaussian basis functions, pseudo potentials[1] or linearized augmented plane waves(LAPW) [2], a method that promises to be less basis dependent, is desirable. The method of finite elements [3] can serve this purpose, since its convergence can be improved systematically.

Any method to solve an effective Schrödinger equation in three dimensions faces the following challenges due to the Coulomb singularities at the nuclei:

- (i) The cusp conditions at the nuclei[4]: $\lim_{r_i \rightarrow 0} \frac{df_C/dr_i}{f_C(r_i)} = -Z_i$ have to be satisfied.
- (ii) The wave functions will have many nodes close to the nuclei.

The competing methods mentioned also have some disadvantages: pseudopotentials have to be determined for each atomic species, the matching conditions for LAPW can become involved and Gaussian basis functions are in principle *unable* to satisfy the cusp conditions.

In this contribution a novel and efficient method to deal with the above mentioned challenges by regularization of the potential is outlined and results obtained for the ground state energy of the hydrogen molecular ions using the method of finite elements are shown. The remainder of the contribution is organized as follows: In section 2 the regularization approach is outlined , in section 3 the test case of H_2^+ is discussed, in section 4 the method of finite elements as used in this contribution is sketched, while in sections 5 and 6 results obtained via two-and three dimensional finite element calculations are given, followed by conclusions.

2. Regularization of the Potential

In the following we consider a system consisting of N electrons and A nuclei in the Born-Oppenheimer approximation with the Hamiltonian

$$H = - \sum_{i=1}^N \nabla_i^2 + \sum_{i>j=1}^N \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{j=1}^A \frac{2Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}, \quad (1)$$

where we use atomic units, i.e. measuring distances in a_{Bohr} and energies in $\text{Ryd} = 13.6 \text{ eV}$.

In order to mitigate the Coulomb singularities we use the following product ansatz for the wave function:

$$\Psi(\mathbf{r}) = f_C(\mathbf{r})\Phi(\mathbf{r}), \quad (2)$$

where f_C satisfies

$$\lim_{r_i \rightarrow 0} \frac{df_C/dr_i}{f_C(r_i)} = -Z_i, \quad r_i = |\mathbf{r} - \mathbf{R}_i| \quad (3)$$

and Φ is expected to be smooth.

Substituting the product ansatz into the standard energy functional for Ψ we obtain a transformed functional for Φ as

$$E(\Phi) = \frac{\langle f_C \nabla \Phi | f_C \nabla \Phi \rangle + \langle f_C \Phi | \tilde{V}(\mathbf{r}) | f_C \Phi \rangle}{\langle f_C \Phi | f_C \Phi \rangle}, \quad (4)$$

$$\tilde{V} = V - \frac{\nabla^2 f_C}{f_C}. \quad (5)$$

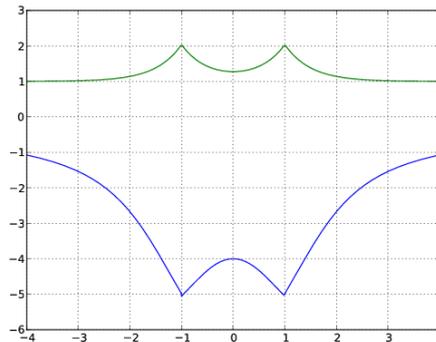
Choosing for f_C the form

$$f_C(\mathbf{r}) = 1 + \sum_{i=1}^A c_i \exp(-2Z_i r_i), \quad r_i = |\mathbf{r} - \mathbf{R}_i|, \quad (6)$$

the c_i can be determined from the following linear system of equations

$$\sum_{j=1}^N [\delta_{ij} - \nu_{ij} \exp(-2Z_i |\mathbf{R}_i - \mathbf{R}_j|)] c_j = 1, \quad \nu_{ij} = 1 - \delta_{ij}, \quad (7)$$

which results from eqn.(5) by requiring the Coulomb singularities to be removed from the potential. The resulting potential has singularities replaced by kinks as shown below by the lower curve for H_2^+ along the z -axis connecting the nuclei, while the upper curve shows f_C .



3. The test case H_2^+

Two protons and an electron constitute the simplest possible molecule. In the Born-Oppenheimer approximation the nuclei are considered as fixed. In this section we consider the system in those coordinates, that we will use for our calculations and in a third one, that has been used for highly accurate numerical benchmark calculations.

In Cartesian coordinates the Hamiltonian for an internuclear distance of $R = 2a_{\text{Bohr}}$, very close to the equilibrium value, reads

$$H = -\nabla^2 - \frac{2}{|\mathbf{r} - \mathbf{R}_1|} - \frac{2}{|\mathbf{r} - \mathbf{R}_2|} + 1, \quad (8)$$

while in cylindrical coordinates ρ, z and ϕ with nuclei on z -axis at $z = \pm 1$ and for $m = 0$, the Hamiltonian is two-dimensional, i.e.

$$H = -\frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} - \frac{2}{\sqrt{\rho^2 + (z+1)^2}} - \frac{2}{\sqrt{\rho^2 + (z-1)^2}} + 1. \quad (9)$$

Highly accurate benchmark numerical solutions for ground state energy and wave function were obtained by Peek in the 1960's using elliptic coordinates [5]

$$\lambda = \frac{1}{2}(r_1 + r_2) \quad , \quad 1 \leq \lambda \leq \infty \quad (10)$$

$$\mu = \frac{1}{2}(r_1 - r_2) \quad , \quad -1 \leq \mu \leq 1 \quad (11)$$

$$r_1 = |\mathbf{r} - \mathbf{R}_1| \quad , \quad r_2 = |\mathbf{r} - \mathbf{R}_2|. \quad (12)$$

leading to the Hamiltonian

$$H = -\frac{1}{\lambda^2 - \mu^2} \left[\sqrt{\lambda^2 - 1} \frac{\partial}{\partial \lambda} \left(\sqrt{\lambda^2 - 1} \frac{\partial}{\partial \lambda} \right) + \sqrt{1 - \mu^2} \frac{\partial}{\partial \mu} \left(\sqrt{1 - \mu^2} \frac{\partial}{\partial \mu} \right) \right] - 4 \frac{\lambda}{\lambda^2 - \mu^2} + 1, \quad (13)$$

which allows separation into two ordinary differential equations.

4. Method of Finite Elements

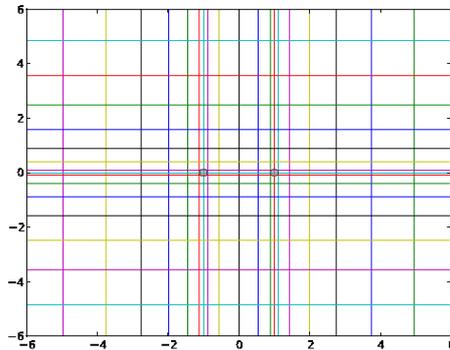
The variational problem obtained in section 2 will be solved using the method of finite elements [3]. We divide the region of interest into rectangular (for 2D) or box-shaped (for 3D) *elements* and expand Φ in terms of interpolating polynomials on each element. Applying the variational principle then leads to a symmetric generalized eigen value problem

$$H\mathbf{u} = \lambda U\mathbf{u} \quad (14)$$

with $N \approx 10^4 - 10^6$. Here \mathbf{u} is the coefficient vector of the expansion in the finite element basis set and the matrices H and U are sparse. The lowest eigenpair of the eigen value problem is obtained using the symmetric Jacobi Davidson method as provided by the **PySparse** package (<http://pysparse.sourceforge.net>). This method does not factorize matrices H and U and therefore needs less memory than traditional methods, that use factorization.

5. Calculations in Three Dimensions

We consider the problem in Cartesian coordinates as described by eqn.(8). Since higher derivatives of ϕ must be discontinuous at the nuclei they must be at the corners of elements. The grid for the finite element method is created on the volume $V = [-x_{\text{max}}, x_{\text{max}}]^3$ as the tensor product of separate x, y and z grids. The grids are compressed quadratically around the nuclei and the number of elements is chosen such, that elements at the nuclei have sides smaller than η . For H_2^+ with the nuclei positioned at $(-1, 0, 0)$ and $(1, 0, 0)$ a typical grid is shown below in its projection on the $x - y$ plane:



The drawback of the above tensor-grid is however that small elements are used in regions, where they are not really needed.

For the calculations interpolation polynomials up to order $p = 6$ order were used and the matrix elements were determined using Gauss-Legendre integration with up to $n_{GL} = 16$ points in each direction. The code was written in Python(www.python.org) with the numerical extension **numpy**(numpy.scipy.org) and some Fortran77 linked with **f2py**(www.scipy.org/F2py). The largest grid had $26 \times 22 \times 22 = 12\,584$ elements. leading to generalized eigen value problem of $N = 2659955$. The resulting sparse matrices were handled using the **Pysparse** Python extension and the lowest eigenpair was calculated using JDSYM in about 15000 CPU seconds on the high performance cluster of the University of South Africa, while the time to compute the matrix was approximately 85000 CPU seconds.

In Table 1 the results obtained for the ground state energy for different discretization and integration parameters are given. It is evident, that a reasonable accuracy of 10^{-5} can be

x_{\max}	p	η	n_{GL}	E_{gs}	ΔE	T_{CPU} [s]
8	4	0.50	6	-1.2052629814026	$5.448 \cdot 10^{-6}$	191
8	4	0.25	6	-1.2052675549928	$8.740 \cdot 10^{-7}$	435
8	4	0.25	12	-1.2052675476430	$8.813 \cdot 10^{-7}$	2024
12	6	0.15	12	-1.2052684289614	$2.845 \cdot 10^{-11}$	33665
12	6	0.12	16	-1.2052684289849	$4.92 \cdot 10^{-12}$	107152

Table 1. Ground state energies, their deviations from the value obtained by Peek[5] and run-time in CPU seconds for different grid and integration parameters

achieved using relatively modest resources. The best energy obtained in the last line of the table agrees with the the literature result of $E_{gs} = -1.2052684289898$ Ryd [5] to 11 digits.

6. Calculations in Two Dimensions

As mentioned in the previous section the tensor-grid employed for the three-dimensional calculation is computationally not very efficient. The open source project hermes for adaptive h-p-FEM (www.hpfem.org) provides libraries which allow for hexaedral grids with hanging nodes. Since H_2^+ has an axis of symmetry it can also be investigated using cylindrical coordinates and the Hamiltonian given in eqn.(9). As a first step towards improving the grid in three dimensions the calculation was done using the two dimensional version of hermes, namely the C++ library hermes2d.

The transformed potential is then given by

$$\tilde{V} = -\frac{2}{\sqrt{\rho^2 + (z+1)^2}} - \frac{2}{\sqrt{\rho^2 + (z-1)^2}} - \frac{\nabla^2 f_C(\rho, z)}{f_C(\rho, z)} + 1 \quad (15)$$

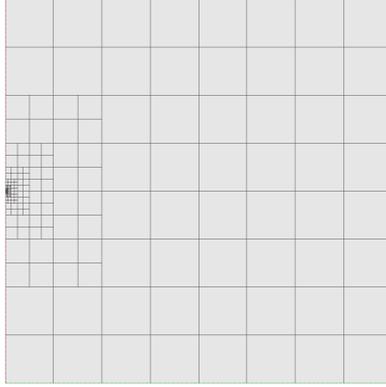


Figure 1. Grid used for region $[0, 2] \times [0, 2]$ in finite element calculation

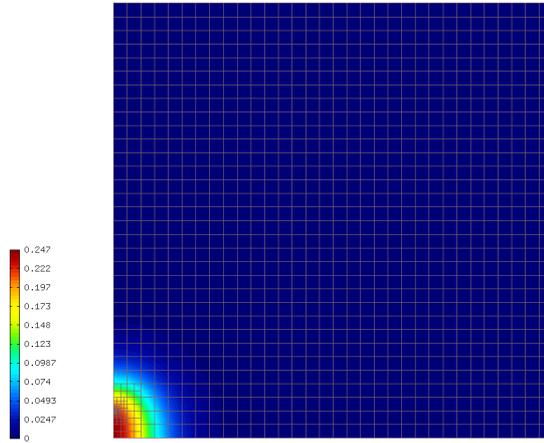


Figure 2. Function Φ for the hydrogen molecular ion

Using the C++ hermes2d library and also employing the JDSYM eigen-value solver the variational problem defined by eqn.(4) was numerically solved on the domain $(\rho, z) \in [0, 16] \times [0, 16]$ where symmetry with respect to $z = 0$ was used. The grid was refined towards the proton at $z = 1$ as shown in Fig. (1), where the hanging nodes [6], that allow for efficient subdivision also of rectangular grids, are evident. The Calculation was performed on an Dell centrino laptop with 4GB of RAM. The most accurate result obtained for $p = 6$ and $N = 45396$ was $E_{\text{gs}} = -2.2052684289897795$ Ryd, which agrees to 13 digits with the literature value by Peek[5] and T_{CPU} was 217 seconds. The function Φ obtained for these parameters is shown in Fig. (2) together with the grid.

The convergence of the discretization error for the finite element method of order p is expected to satisfy $\Delta E = h^{2p}$ [7, p. 232]. To investigate the convergence calculations were also done with $p = 3$ and $p = 4$ respectively resulting in the log-log plots shown in Figs. (3) and (4). The slopes are obtained as 5.87 ± 0.07 and 8.22 ± 0.12 respectively, compatible with the expected values of 6 and 8.

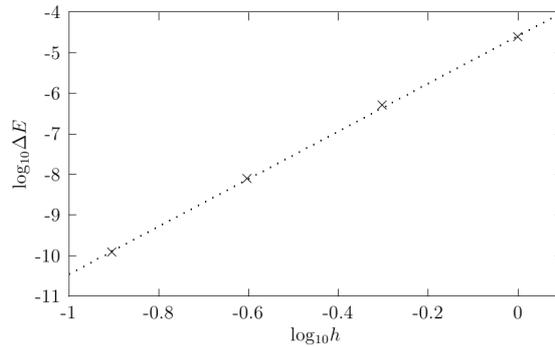


Figure 3. Log-log plot of ΔE versus h for $p = 3$

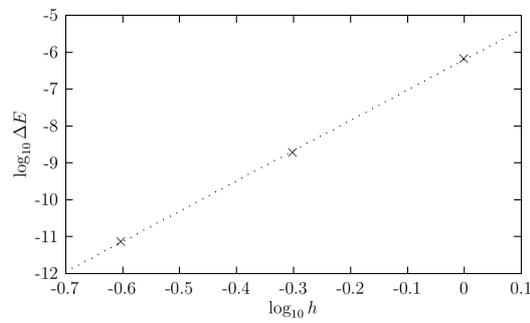


Figure 4. Log-log plot of ΔE versus h for $p = 4$

7. Conclusions

In this contribution it has been clearly demonstrated, that the singularities connected to the Coulomb potentials at the nuclei can be mitigated using the suggested product ansatz for the wave function. The resulting transformed variational problem for H_2+ has been solved both in Cartesian and cylindrical coordinates using the method of finite elements, yielding highly accurate energies.

Acknowledgments

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