

Calculations of the polycentric linear molecule H_3^{2+} with the finite element method

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A fully numerical two-dimensional solution of the Schrödinger equation is presented for the linear polyatomic molecule H_3^{2+} using the finite element method (FEM). The Coulomb singularities at the nuclei are rectified by using both a condensed element distribution around the singularities and special elements. The accuracy of the results for the 1σ and 2σ orbitals is of the order of 10^{-7} au.

The finite element method (FEM) is a well established technique for solving static and dynamical problems in engineering sciences [1]. During the last fifteen years it has been shown that this method can also provide accurate solutions for quantum mechanical problems [2–6].

Diatomic molecules have been treated fully numerically by the finite difference method (FDM) [7] and the FEM [8–10]. For a given number of points the results achieved with the FEM proved to be more accurate than those obtained with the FDM. Over the years the FEM has been extended successfully from the solutions of the Schrödinger equations for H_2^+ [8], to the Hartree–Fock–Slater [9], the Hartree–Fock [10], the two-center Dirac [11], and the Dirac–Fock–Slater equations [12] for small diatomic molecules.

As a next step we extended the method to the calculation of linear polycentric molecules. In this Letter we present results on the solution of the Schrödinger equation for the linear polyatomic molecule H_3^{2+} using the FEM.

Every one-electron quantum mechanical system like H_3^{2+} , which we are going to solve here, is described by the Schrödinger equation

$$-\frac{1}{2}\nabla^2\Psi_i + V\Psi_i = \epsilon_i\Psi_i, \quad (1)$$

with $\Psi_i(\mathbf{r})$ the electronic wavefunctions and $V(\mathbf{r})$ the nuclear three-center potential. The non-relativistic Hamiltonian in the cylindrical coordinates ρ , z and ϕ is given by

$$\begin{aligned} H = & -\frac{1}{2}\nabla_i^2 - \sum_{n=1}^M \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} \\ = & -\frac{1}{2}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}\right] \\ & - \sum_{n=1}^M Z_n[(\rho\cos\phi - \rho_n\cos\phi_n)^2 \\ & + (\rho\sin\phi - \rho_n\sin\phi_n)^2 + (z - z_n)^2]^{-1/2}, \quad (2) \end{aligned}$$

where M is the number of nuclear centers, Z_n is the charge of the n th center, ρ , ϕ and z are the coordinates of the electron and ρ_n , ϕ_n and z_n are the coordinates of the n th center. The equivalent variational problem is given by the requirement that the variation δJ of the functional

$$J = \frac{1}{2} \int |\nabla\Psi_i|^2 d^3r + \int (V - \epsilon_i) |\Psi_i|^2 d^3r \quad (3)$$

be zero.

Owing to the axial symmetry of linear molecules, in our case the problem is reduced to two dimensions using the Ansatz

$$\Psi_i(\rho, z, \phi) \rightarrow \Phi_i(\rho, z) e^{im\phi}$$

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for the electronic wavefunctions. Here m (the projection of the angular momentum onto the internuclear axis) is a good quantum number.

With the FEM approach the whole region of integration is subdivided into small regions, the *finite elements* [1,13]. We use triangles as finite elements because triangles of different size can be combined quite easily, thus enabling a problem-adapted element distribution (see fig. 1).

For the approximation of Φ we use the Ansatz

$$\Phi(\mathbf{r}) = \sum_{j=1}^P \Phi_j N_j(\mathbf{r}_k), \quad (4)$$

where P is the number of points.

The shapefunctions $N_j(\mathbf{r}_k)$ (polynomials of higher order) are defined such that the condition

$$N_j(\mathbf{r}_k) = 1, \quad j = k,$$

$$N_j(\mathbf{r}_k) = 0, \quad j \neq k,$$

holds for all grid points \mathbf{r}_k . Only for those elements to which these grid points belong do the shapefunctions $N_j(\mathbf{r}_k)$ possess values not equal to zero; this is localized to a very small area of the entire region. In this definition the coefficients (node variables) Φ_j are the approximate values of the unknown functions at the gridpoint j . In our calculations we use 5th-order polynomials as shapefunctions. With the Ansatz (4) the functional (3) becomes a function of the node variables Φ_j , the condition of the variation $\delta J = 0$ becomes equivalent to the condition

$$\frac{\partial J}{\partial \Phi_j} = 0.$$

All in all this leads to the matrix eigenvalue equation

$$\mathbf{H}\Phi = \epsilon \mathbf{S}\Phi. \quad (5)$$

The solution of this matrix equation leads to an approximate solution of the Schrödinger equation (1). The order of the matrices is equal to the total number of grid points used in the calculations.

The most appropriate coordinate system for polycentric linear molecules is the cylindrical coordinate system. In contrast to the one- or two-atomic problems it is not possible anymore to take care of the Coulomb singularities at the nuclei with suitable coordinates.

The two obvious ways of handling these singularities within the FEM approach [13] are:

- A condensed element distribution around the singularities
- *Special elements.*

A combination of both is possible and we have done so in our calculations. In order to construct a geometrically adapted element distribution we developed a pre-processing program. We start by constructing equi-curves in the physical space (see fig. 1) so that the sub-areas formed contribute almost equal amounts to the error of the system [14]. On these equi-curves we distribute points equidistantly, thus forming the edge points of triangles for the triangulation of the whole region. In order to avoid numerical problems it is assured that each element is a triangle with angles larger than $\approx 15^\circ$ and smaller than $\approx 130^\circ$. This approach leads to a condensed element distribution in the nuclear region (see ref. [14]); every triangle contributes about equal amounts to the error in energy.

The matrix elements arising from the functional (3) when using the Ansatz (4) were calculated by a conical product Gaussian integration rule [15] on each of the finite elements (triangles). This method is a product Gaussian integration rule where two edges of the normalized square are condensed to a single point to construct a normalized triangle (see fig. 2), which is then a special element.

Let

$$\int_0^1 \int_0^x f(x, y) dy dx \quad (6)$$

be the integral over a unit triangle. By a change of variables $x = u$ and $y = vu$ with

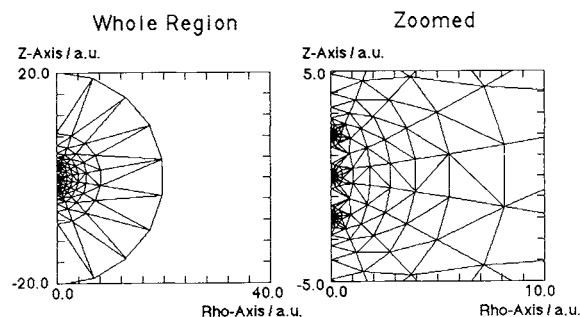


Fig. 1. Three-center mesh for H_3^+ as an example.

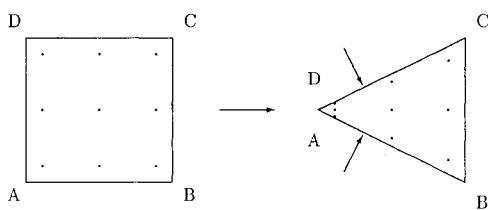


Fig. 2. Principle of the conical product Gaussian integration rule. The left square shows the integration point distribution for the product Gaussian integration rule with 3×3 integration points. By transforming the integration region into a triangle (right), edges A and D of the square become one point of the triangle and the integration points are concentrated at this edge.

$$\begin{aligned} x &= u, & 0 \leq u \leq 1, \\ y &= uv, & 0 \leq v \leq 1, \end{aligned} \quad (7)$$

this is transformed into the integral

$$\int_0^1 \int_0^1 f(u, v) dv u du. \quad (8)$$

From this it is inferred that the $1/r$ singularity in energy integrals is rectified by the factor u of the volume element provided the singularity is positioned in the conical edge of the triangle, because as a result of the conical transformation the integration points are properly condensed at one edge point. For accurate integration 8×8 integration points are just suitable.

We are able to show that just two correctly orientated triangles can handle the Coulomb singularities. Fig. 3 shows the principle of the correct orientation of the triangles at one center.

The current approach was tested by calculating H and H_2^+ in the grid constructed for the system He_3^{2+} (fig. 1). The results for H, H_2^+ and H_3^{2+} are given in table 1. To determine the accuracy of the energy eigenvalues for H_2^+ we use the results from ref. [16]. The calculations were performed with 5th-order polynomial shapefunctions. In the upper part of table 1 we use a mesh with 245 elements corresponding to 3125 points (see fig. 1) in order to calculate the H atom and the H_2^+ molecule in the three-center grid. As expected the accuracy of the results increases from H ($\Delta E_{1s} \approx 2.4 \times 10^{-6}$ au) over H_2^+ ($\Delta E_{1\sigma_g} \approx (1.4-6.3) \times 10^{-7}$ au) to H_3^{2+} because the

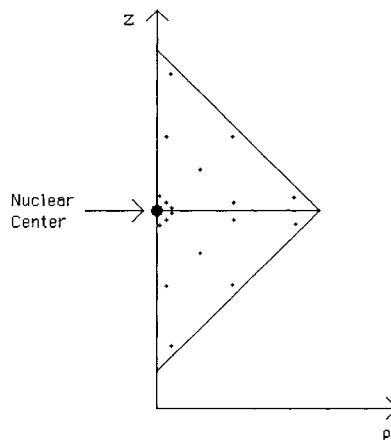


Fig. 3. Correct orientation of the triangles at a nuclear center. This figure shows the conical product Gaussian integration point distribution with 3×3 integration points at each triangle. The triangles are orientated such that the edge with the condensed integration points (point A=D in fig. 2) is congruent with the nuclear center.

mesh is optimized to the asymptotic behaviour of the low-lying electronic levels of the system H_3^{2+} . The differences in accuracy of the H calculations arise from the asymmetric grid for the outer-center calculations. In addition the mesh is better adapted for the middle-center calculation. The lower part of table 1 presents an additional calculation of H_2^+ in a mesh with 2665 points (209 elements). The number of mesh points differs according to the geometry changes of the mesh. In general the number of mesh points varies with R , roughly tripling for $R \rightarrow \infty$.

In fig. 4 we compare our results for the 1σ orbital (see table 2) with those found in the literature [17]. As reference line we use the mean values of upper and lower bounds given in ref. [17] but we should mention that we are several orders of magnitude more accurate. For distances greater than or equal to 2.0 au there is agreement within the accuracy given in ref. [17]. For small distances we find a significant discrepancy. We may infer our calculations to be accurate to the order of some units of 10^{-7} au by comparing our results on H and H_2^+ to precise values [16]. For the 2σ orbital (see table 2) the agreement with the values of ref. [18] (obtained from its fig. 12) is within drawing precision.

We were able to demonstrate the applicability of the FEM to the solution of those polycentric linear

Table 1

Results for H and H_2^+ (error ΔE from comparison with precise calculations [16]) and for H_3^{2+} in a mesh with 3125 points and a distance of 2.0 au between neighbouring centers (upper part of the table) and 2665 points and a distance of 1.0 au between neighbouring centers (lower part of the table), see also table 2. The full dots in the row Mesh symbolize the charged center(s) in the three-center grid (see fig. 1). All the calculations we performed by using 5th-order polynomial shapefunctions

Mesh	System	Orbital	E (au)	ΔE (au)
●○○	H	1s	-0.4999977	2.3×10^{-6}
		2s	-0.1249958	4.2×10^{-6}
○●○		1s	-0.4999995	5.3×10^{-7}
		2s	-0.1249980	2.0×10^{-6}
○○●		1s	-0.4999976	2.4×10^{-6}
		2s	-0.1249963	3.7×10^{-6}
●●○	H_2^+	$1\sigma_g$	-1.1026341	1.4×10^{-7}
	2.0 au	$1\sigma_u$	-0.6675337	6.9×10^{-7}
○●●		$1\sigma_g$	-1.1026341	1.4×10^{-7}
		$1\sigma_u$	-0.6675337	6.9×10^{-7}
...
●●○	H_2^+	$1\sigma_g$	-0.7960843	6.3×10^{-7}
	4.0 au	$1\sigma_u$	-0.6955490	1.6×10^{-7}
●●●	H_3^{2+}	1σ	-1.5241599	$\approx 10^{-7}$
	2.0/2.0 au	2σ	-1.1733743	$\approx 10^{-7}$
●○●	H_2^+	$1\sigma_g$	-1.1026340	2.0×10^{-7}
	2.0 au	$1\sigma_u$	-0.6675332	1.2×10^{-6}

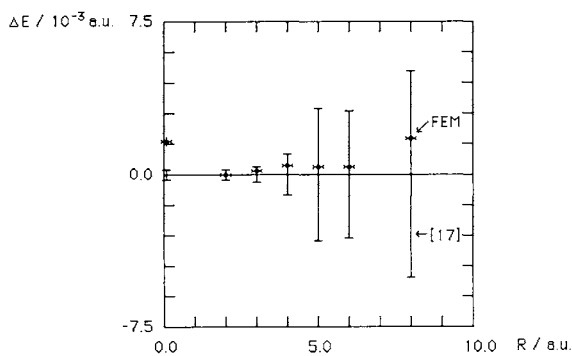


Fig. 4. Differences of the FEM calculations from the upper and lower bounds calculated mean values of ref. [17] for the 1σ orbital of H_3^{2+} . R is the distance between the outer centers and ΔE the energy deviation from the mean value.

Coulombic problems whose nuclei singularities are taken care of by the condensed element distribution and special elements. One also finds that the numerical accuracy increases strongly with the number

Table 2

Results for the linear symmetric H_3^{2+} molecule for the 1σ and 2σ orbital at different distances, R being the distance between the outer centers. In general the number of mesh points varies with R , roughly tripling for $R \rightarrow \infty$, however the ratio of R/r_i ought to be taken into account, too. The mesh with $R=4.0$ au belongs to the upper part of table 1 and the mesh with $R=2.0$ au to the lower part of table 1. We use 10 equi-curves ($r_1=0.24$ au, $r_2=0.61$ au, $r_3=1.90$ au, $r_4=1.66$ au, $r_5=2.35$ au, $r_6=3.20$ au, $r_7=4.31$ au, $r_8=5.86$ au, $r_9=8.39$ au, $r_{10}=20.00$ au). Only at $R=0.1$ au one additional radius ($r=0.03$ au) is necessary to construct at least one separate equi-line around the centers

R (au)	Orbital	E (au)	Points
0.1	1σ	-4.4300999	2435
	2σ	-1.1272460	
2.0	1σ	-2.2425227	2665
	2σ	-1.3509358	
3.0	1σ	-1.8015337	2205
	2σ	-1.2750837	
4.0	1σ	-1.5241599	3125
	2σ	-1.1733743	
5.0	1σ	-1.3343619	4045
	2σ	-1.0807938	
6.0	1σ	-1.1968609	3585
	2σ	-1.0011893	
8.0	1σ	-1.0155017	4045
	2σ	-0.8837918	

of grid points when using condensed element distribution and the special elements around the centers. As for a non-singular problem one recovers the full convergence order N^{-5} . Three-center Coulomb calculations do need quite a few more points for a given accuracy than for one- and two-center calculations with tailor-made coordinates where the Coulomb singularities are rectified [9] (spherical coordinates in one-center, elliptic-hyperbolic coordinates for two-center Coulombic problems); however, up to now they offer the only possibility to obtain the desired accuracies.

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