Numerical solution of the Schrödinger equation for the hydrogen atom

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Introduction

The nonrelativistic Schrödinger equation for the hydrogen atom is solved numerically using the finite volume method.

Model equations

The three-dimensional Schrödinger equation is:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{k}{r}\psi \tag{1}$$

Where i is the imaginary number, $\hbar$ a constant, m the particle mass, k a constant depending on the charge of the electron, r the radial coordinate, ψ the dependent variable and t time. Expanding the Laplacian in (1) in spherical coordinates gives:

$$\begin{aligned} i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{r^2\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\phi)}\frac{\partial}{\partial\phi}\left(\sin(\phi)\frac{\partial\psi}{\partial\phi}\right)\right. \\ \left. + \frac{1}{r^2\sin^2(\phi)}\frac{\partial^2\psi}{\partial\theta^2}\right] - \frac{k}{r}\psi \end{aligned} \tag{2}$$

Where ϕ is the angle between the direction vector $\mathbf{r}$ and the z axis and θ the angle between the projection of $\mathbf{r}$ onto the xy plane and the x axis. The boundary conditions of the system are $\psi = 0$ at $r = 0$ and at $r = R$ with R the length of the domain in the r direction.

Discretization

The domain V of the system is partitioned into n_r nodes in the radial direction, n_θ nodes in the θ direction and n_ϕ nodes in the ϕ direction. Two additional linear grids consisting of n_r nodes represent the 'polar' regions. The nodes of these linear grids lie on the z axis, i.e.: at $\phi = 0, \pi$. Central differencing is applied to the diffusion terms. Time discretization is fully implicit. The resulting linear system is solved using the Gauss-Seidel method.

The discrete form of equation (1) for 'central' or non-polar nodes is:

$$\begin{aligned} i\hbar\frac{\psi^p_{i,j,k} - \psi^{p-1}_{i,j,k}}{\Delta t} = & -\frac{\hbar^2}{2m}\left(r^2_{i+1}\frac{\psi^p_{i+1,j,k} - \psi^p_{i,j,k}}{r^2_{i+\frac{1}{2}}\Delta r^2} - r^2_i\frac{\psi^p_{i,j,k} - \psi^p_{i-1,j,k}}{r^2_{i+\frac{1}{2}}\Delta r^2}\right) + \\ & -\frac{\hbar^2}{2m}\left(\frac{\psi^p_{i,j+1,k} - \psi^p_{i,j,k}}{r^2_{i+\frac{1}{2}}\sin^2(\phi_{j+\frac{1}{2}})\Delta\theta^2} - \frac{\psi^p_{i,j,k} - \psi^p_{i,j-1,k}}{r^2_{i+\frac{1}{2}}\sin^2(\phi_{j+\frac{1}{2}})\Delta\theta^2}\right) + \\ & -\frac{\hbar^2}{2m}\left(r^2_{i+1}\sin(\phi_{j+1})\frac{\psi^p_{i,j,k+1} - \psi^p_{i,j,k}}{r^2_{i+\frac{1}{2}}\sin(\phi_{j+\frac{1}{2}})\Delta\phi^2} - r^2_i\sin(\phi_j)\frac{\psi^p_{i,j,k} - \psi^p_{i,j,k-1}}{r^2_{i+\frac{1}{2}}\sin(\phi_{j+\frac{1}{2}})\Delta\phi^2}\right) - \frac{k}{r}\psi_{i,j,k} \end{aligned} \tag{3}$$

Where the indexes i, j and k denote node i in the radial r direction, node j in the θ direction and node k in the ϕ direction. The boundary conditions are $\psi = 0$ at $i = 0$ and at $i = n_r - 1$. The discrete form of (1) for the top polar nodes, i.e.: at $\phi = 0$ is:

$$\begin{aligned} i\hbar\Delta V \frac{\psi^p_{T,i} - \psi^{p-1}_{T,i}}{\Delta t} =& A_{r,i}\alpha\frac{\psi^p_{T,i} - \psi^p_{T,i-1}}{\Delta r} - A_{r,i+1}\alpha\frac{\psi^p_{T,i+1} - \psi^p_{T,i}}{\Delta r} + \\ & \sum_{j=0}^{n_{\theta-1}} A_{\phi,i}\frac{\alpha}{r_{i+\frac{1}{2}}}\frac{\psi^p_{T,i} - \psi^p_{i,j,0}}{\Delta\phi} - \frac{k}{r}\Delta V\psi^p_{T,i} \end{aligned} \tag{4}$$

Where $A_{r,i} = 2\pi r_i^2(1-\cos(\Delta\phi))$, $A_{\phi,i} = r_{i+\frac{1}{2}}\sin(\phi_0)\Delta\theta\Delta r$, $\alpha = \frac{\hbar}{2m}$ and $\Delta V = \frac{2\pi}{3}(r^3_{i+1} - r^3_i)(1-\cos(\Delta\phi))$. The subscript T indicates the top polar nodes. The discrete form of (1) for the bottom polar nodes, i.e.: at $\phi = \pi$ takes a similar form:

$$\begin{aligned} i\hbar\Delta V \frac{\psi^p_{B,i} - \psi^{p-1}_{B,i}}{\Delta t} =& A_{r,i}\alpha\frac{\psi^p_{B,i} - \psi^p_{B,i-1}}{\Delta r} - A_{r,i+1}\alpha\frac{\psi^p_{B,i+1} - \psi^p_{B,i}}{\Delta r} + \\ & \sum_{j=0}^{n_{\theta-1}} A_{\phi,i}\frac{\alpha}{r_{i+\frac{1}{2}}}\frac{\psi^p_{B,i} - \psi^p_{i,j,n_{\phi-1}}}{\Delta\phi} - \frac{k}{r}\Delta V\psi^p_{B,i} \end{aligned} \tag{5}$$

With $A_{\phi,i} = r_{i+\frac{1}{2}}\sin(\phi_{n_\phi - 1})\Delta\theta\Delta r$. The subscript B indicates the bottom polar nodes.

Normalization

The solution of ψ needs to be normalized:

$$\psi = \frac{\psi}{\sqrt{\int_V \psi\psi^* dV}} \tag{6}$$

Where ψ^* is the complex conjugate of ψ. Note that the statement (6) above is not an equality, but an assignment.

Verification

In order to verify that the computations proceed correctly it is verified that the linear system obtained from discretization of equation (1) is satisfied. Analysis of results show that the linear system is satisfied with an error in the order of 1e-12.