Solving the Hydrogen Atom in Quantum Mechanics

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Schrödinger's Equation

In quantum mechanics, we begin with the assumption that Schrödinger's Equation is true.

$$H\psi(\vec{x},t) = i\hbar\psi_t(\vec{x},t)$$

$$-\frac{\hbar^2}{2\mu}\Delta_x\psi(\vec{x},t) + V(\vec{x},t)\psi(\vec{x},t) = i\hbar\psi_t(\vec{x},t)$$

H is called the Hamiltonian Operator. It can be shown that H is self adjoint if $V(\vec{x},t)$ is real.

$$H = -\frac{\hbar^2}{2\mu}\Delta_x + V(\vec{x},t)$$

The Wave Function

The Schrödinger equation deals with solving something called the Wave Function $\psi(\vec{x},t)$.

$$P(\vec{x},t) = \bar{\psi}(\vec{x},t)\psi(\vec{x},t)$$

$P(\vec{x},t)$ is called the probability density of whatever particle that we are trying to model. Because of that

$$\int_{\mathbb{R}^N} P(\vec{x},t)\,\mathrm{d}V^N = 1$$

We define our inner product in this space to be

$$\langle \psi_1, \psi_2 \rangle = \int_{\mathbb{R}^N} \bar{\psi}_1 \psi_2 \,\mathrm{d}V^N$$

Time Independant Equation

In most realistic situations, the potential energy does not depend on time, but depends only on position. That means that the potential function is $V(\vec{x})$. We can then separate out time.

$$\psi(\vec{x},t) = \phi(\vec{x})T(t)$$

$$-\frac{\hbar^2}{2\mu}\frac{\Delta_x\phi(\vec{x})}{\phi(\vec{x})} + V(\vec{x}) = i\hbar\frac{T'(t)}{T(t)} = E$$

$$-\frac{\hbar^2}{2\mu}\Delta_x\phi(\vec{x}) + V(\vec{x})\phi(\vec{x}) = E\phi(\vec{x}) \qquad T(t) = e^{\frac{-iEt}{\hbar}}$$

This is called the Time Independant Schrödinger Equation

The Laplacian Operator

The Laplacian operator Δ_x in spherical coordinates in $\mathbb{R}^N$ can be written

$$\Delta_x = \frac{\partial^2}{\partial r^2} + \frac{(N-1)}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Delta_{S^{N-1}}$$

Where $\Delta_{S^{N-1}}$ is called the Spherical Laplacian which is the Laplacian on the coordinates of the unit sphere in $\mathbb{R}^N$.
If $Y_\ell(\omega)$ is an eigenfunction of $\Delta_{S^{N-1}}$ with $\omega \in S^{N-1}$, such that $\Delta_x\big(r^\ell Y_\ell(\omega)\big) = 0$, then

$$\ell(\ell-1)r^{\ell-2}Y_\ell(\omega) + \ell(N-1)r^{\ell-2}Y_\ell(\omega) + r^{\ell-2}\Delta_{S^{N-1}}Y_\ell(\omega) = 0$$

$$\Delta_{S^{N-1}}Y_\ell(\omega) = -\ell(\ell+N-2)Y_\ell(\omega)$$

Eigenfunctions and Eigenvalues (1)

For the time-independant Schrödinger equation, we have

$$H\phi_k(\vec{x}) = E_k\phi_k(\vec{x})$$

Where E_k is the eigenvalue of the eigenfunction $\phi_k(\vec{x})$. E_k turns out to be the energy associated with $\phi_k(\vec{x})$.
Since H is self-adjoint, there is an orthonormal collection of eigenfunctions $\{\phi_k(\vec{x})\}$ that span the space of all possible wave functions.

$$\Delta_{S^{N-1}}Y_\ell(\omega) = -\ell(\ell + N - 2)Y_\ell(\omega)$$

We have already observed this eigenfunction-eigenvalue pair for $\Delta_{S^{N-1}}$. It is also self adjoint so there is an orthonormal collection of $\{Y_\ell(\omega)\}$.

Eigenfunctions and Eigenvalues (2)

If $\phi(\vec{x}) = R(r)Y(\omega)$, then can the hamiltonian H and the spherical laplacian $\Delta_{S^{N-1}}$ share the same orthonormal eigenbasis?
Since H and $\Delta_{S^{N-1}}$ are both self adjoint operators, then they can share the same orthornormal basis if and only if

$$H\Delta_{S^{N-1}} - \Delta_{S^{N-1}}H = 0$$

If we do the math, we see that this condition is met if our potential V in the hamiltonian H is only a function of r. To continue, we will now use the potential $V(r)$ so that we can use a common eigenbasis for H and $\Delta_{S^{N-1}}$.

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{(N-1)}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Delta_{S^{N-1}}\right) + V(r)$$

Separate Radial Component

We have already made the assumption that

$$\phi_{k,\ell}(\vec{x}) = R_{k,\ell}(r)Y_\ell(\omega)$$

When we apply the Hamiltonian operator H on $\phi_{k,\ell}(\vec{x})$, we get two differential equations to solve for.

$$\begin{aligned} 0 = R''_{k,\ell}(r) + \frac{(N-1)}{r}R'_{k,\ell}(r) \\ + \left(\frac{2\mu E_{k,\ell}}{\hbar^2} - \frac{2\mu}{\hbar^2}V(r) - \frac{\ell(\ell+N-2)}{r^2}\right)R_{k,\ell}(r) \end{aligned}$$

$$\Delta_{S^{N-1}}Y_\ell(\omega) = -\ell(\ell+n-2)Y_\ell(\omega)$$

Possible Potentials

We have

$$0 = R''_{k,\ell}(r) + \frac{(N-1)}{r} R'_{k,\ell}(r) + \left(\frac{2\mu E_{k,\ell}}{\hbar^2} - \frac{2\mu}{\hbar^2} V(r) - \frac{\ell(\ell + N - 2)}{r^2} \right) R_{k,\ell}(r)$$

We notice that the solution of $R_{k,\ell}(r)$ depends heavily on $V(r)$. Some common potentials are:

$V(r) = \frac{\alpha}{r}$	Radial Electric Potential
$V(r) = \alpha r^2$	3D Harmonic Oscillator
$V(r) = 0$	Vacuum

We will look at $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ to solve for Hydrogen.

Simplifying The ODE (1)

Since we defined $V(r)$ in such a way that $V(r) \leq 0$ and $V(r) \to 0$ as $r \to \infty$, then if we want to study the bound states of the electron in orbit about a proton (i.e. Hydrogen), then the energy of the electron must be negative.

$$E_{k,l} \leq 0$$

First simplification is to say that we are working in three dimensions so $N = 3$. Other simplifications include defining $\Gamma^2_{k,\ell} = -\frac{2\mu E_{k,\ell}}{\hbar^2}$ and $\beta = \frac{2\mu e^2}{4\pi\epsilon_0\hbar^2}$. Substituting $V(r) = \frac{e^2}{4\mu\epsilon_0 r}$, we get

$$R''_{k,\ell}(r) + \frac{2}{r}R'_{k,\ell}(r) - \left(\Gamma^2_{k,\ell} - \frac{\beta}{r} + \frac{\ell(\ell+1)}{r^2}\right)R_{k,\ell}(r) = 0$$

Simplifying The ODE (2)

We will perform a change of variable $u_{k,\ell}(r) = rR_{k,\ell}(r)$

$$R'_{k,\ell}(r) = \frac{1}{r}u'_{k,\ell}(r) - \frac{1}{r^2}u_{k,\ell}(r)$$

$$R''_{k,\ell}(r) = \frac{1}{r}u''_{k,\ell}(r) - \frac{2}{r^2}u'_{k,\ell}(r) + \frac{2}{r^3}u_{k,\ell}(r)$$

$$= \frac{1}{r}u''_{k,\ell}(r) - \frac{2}{r}R'_{k,\ell}(r)$$

$$R''_{k,\ell}(r) + \frac{2}{r}R'_{k,\ell}(r) - \left(\Gamma^2_{k,\ell} - \frac{\beta}{r} + \frac{\ell(\ell+1)}{r^2}\right)R_{k,\ell}(r) = 0$$

$$\Rightarrow \quad u''_{k,\ell}(r) - \left(\Gamma^2_{k,\ell} - \frac{\beta}{r} + \frac{\ell(\ell+1)}{r^2}\right)u_{k,\ell}(r) = 0$$

Asymptotic Behavior (1)

$$u''_{k,\ell}(r) - \left(\Gamma^2_{k,\ell} - \frac{\beta}{r} + \frac{\ell(\ell+1)}{r^2}\right) u_{k,\ell}(r) = 0$$

We will now define $u_\infty(r)$ as the asymptotic behavior of $u_{k,\ell}(r)$ as $r \to \infty$. As $r \to \infty$, we get

$$u''_\infty(r) - \Gamma^2_{k,\ell} u_\infty(r) = 0$$

$$u_\infty(r) = Ae^{-r\Gamma_{k,\ell}} + Be^{r\Gamma_{k,\ell}}$$

We can set $B = 0$ because the $e^{r\Gamma_{k,\ell}}$ term is not normalizable. We can set $A = 1$ because we are only interested in the asymptotic behavior.

$$u_\infty(r) = e^{-r\Gamma_{k,\ell}}$$

Simplifying The ODE (3)

We will attempt to remove the asymptotic behavior by separating it out using another change of variable.

$$\begin{aligned} u_{k,\ell}(r) &= e^{-r\Gamma_{k,\ell}}\xi_{k,\ell}(r) \\ u'_{k,\ell}(r) &= e^{-r\Gamma_{k,\ell}}\left(\xi'_{k,\ell}(r) - \Gamma_{k,\ell}\xi_{k,\ell}(r)\right) \\ u''_{k,\ell}(r) &= e^{-r\Gamma_{k,\ell}}\left(\xi''_{k,\ell}(r) - 2\Gamma_{k,\ell}\xi'_{k,\ell}(r) + \Gamma^2_{k,\ell}\xi_{k,\ell}(r)\right) \end{aligned}$$

Plugging in this change of variable, we get

$$\xi''_{k,\ell}(r) - 2\Gamma_{k,\ell}\xi'_{k,\ell}(r) + \left(\frac{\beta}{r} - \frac{\ell(\ell+1)}{r^2}\right)\xi_{k,\ell}(r) = 0$$

Solving The ODE (1)

$$\xi''_{k,\ell}(r) - 2\Gamma_{k,\ell}\xi'_{k,\ell}(r) + \left(\frac{\beta}{r} - \frac{\ell(\ell+1)}{r^2}\right)\xi_{k,\ell}(r) = 0$$

To solve this equation, we will guess $\xi_{k,\ell}$ to be a power series

$$\xi_{k,\ell} = \sum_{q=0}^{\infty} c_q r^{q+s}$$

$$\xi'_{k,\ell} = \sum_{q=0}^{\infty} c_q (q+s) r^{q+s-1}$$

$$\xi''_{k,\ell} = \sum_{q=0}^{\infty} c_q (q+s)(q+s-1) r^{q+s-2}$$

Solving The ODE (2)

$$\sum_{q=0}^{\infty} c_q \left[(q+s)(q+s-1)r^{q+s-2} - 2\Gamma_{k,\ell}(q+s)r^{q+s-1} \right.$$
$$\left. + \beta r^{q+s-1} - \ell(\ell+1)r^{q+s-2} \right] = 0$$

$$\sum_{q=0}^{\infty} c_q r^{q+s-2} \Big((q+s)(q+s-1) - \ell(\ell+1) \Big)$$
$$+ \sum_{q=1}^{\infty} c_{q-1} r^{q+s-2} \Big(\beta - 2(q+s)\Gamma_{k,\ell} \Big) = 0$$

Solving The ODE (3)

$$\sum_{q=0}^{\infty} c_q r^{q+s-2}\Big((q+s)(q+s-1)-\ell(\ell+1)\Big) + \sum_{q=1}^{\infty} c_{q-1} r^{q+s-2}\Big(\beta - 2(q+s)\Gamma_{k,\ell}\Big) = 0$$

Consider $q = 0$, we get

$$c_0\,(s(s-1)-\ell(\ell+1)) = 0$$
$$\Rightarrow \quad s = \{\ell+1, -\ell\}$$

The only answer that works is $s = \ell + 1$.

Solving The ODE (4)

$$\sum_{q=0}^{\infty} c_q q(q+2\ell+1) r^{q+\ell-1} + \sum_{q=1}^{\infty} c_{q-1} r^{q+\ell-1} \big(\beta - 2(q+\ell+1)\Gamma_{k,\ell}\big) = 0$$

Consider $q > 0$

$$c_q q(q+2\ell+1) + c_{q-1}\big(\beta - 2(q+\ell+1)\Gamma_{k,\ell}\big) = 0$$

$$\Rightarrow \quad c_q = c_{q-1} \frac{2(q+\ell+1)\Gamma_{k,\ell} - \beta}{q(q+2\ell+1)}$$

Asymptotic Behavior (2)

Consider the asymptotic behavior of $\frac{c_q}{c_{q-1}}$ as $r \to \infty$.

$$\frac{c_q}{c_{q-1}} \to \frac{2\Gamma_{k,\ell}}{q}$$

$$\Rightarrow \xi_{k,\ell}(r) \to \sum_{q=0}^{\infty} \frac{(2\Gamma_{k,\ell})^q}{q!} r^q = e^{2r\Gamma_{k,\ell}}$$