Schrödinger equation for hydrogen: The form of the potential

- The Coulomb potential between the electron and the proton is

$$V = -Ze^2/4\pi\varepsilon_0 r$$

- The hamiltonian for both the proton and electron is:

$$-\frac{\hbar^2}{2m_e}\nabla^2{}_{\mathrm{elec}}\Psi - \frac{\hbar^2}{2m_N}\nabla^2{}_{\mathrm{nuc}}\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = \mathbf{E}\Psi$$

- Separation of nuclear and electronic variables results in an electronic equation in the center-of-mass coordinates:

$$-\frac{\hbar^2}{2\mu}\nabla^2{}_{\mathrm{elec}}\psi_{\mathrm{elec}} - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi_{\mathrm{elec}} = \mathbf{E}_{\mathbf{elec}}\psi_{\mathrm{elec}}$$

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

Separation of variables

The del-squared operator in spherical polar coordinates is:

$$\nabla^2\Psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\Psi + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)\Psi$$

It is not possible to solve the equation with all three variables simultaneously. Instead a procedure known as separation of variables is used.

The steps are:

1. Multiply both sides by $2\mu r^2$
2. Substitute in $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$
3. Divide both sides by $R(r)Y(\theta,\phi)$

Using a separation constant called β we can write the Schrodinger equation as two separate equations.

$$-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi - \mathbf{E}\psi = -\beta\psi$$

$$\frac{-\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi + \frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Psi = \beta\psi$$

We write the total wave function as a product of two wave functions. $\psi(r,\theta,\phi) = R(r)Y_m^{\ell}(\theta,\phi)$

Then we divide the radial equation by Y_m^l and the angular equation by R to get two separate equations.

$$-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\mathrm{R} - \frac{Ze^2}{4\pi\varepsilon_0 r}\mathrm{R} - \mathbf{E}\mathrm{R} = -\beta\mathrm{R}$$

$$-\hbar^2\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y\right)\right) = \beta Y$$