

The time dependent Schrödinger equation for the hydrogen-like atom is [1]

$$\frac{i\hbar}{2\pi} \frac{\partial}{\partial t} \Psi(\vec{r}_n, \vec{r}_e, t) = H\Psi(\vec{r}_n, \vec{r}_e, t)$$

Where the classical Hamiltonian for a single electron atom is given by:

$$H = \frac{p_n^2}{2m_n} + \frac{p_e^2}{2m_e} - \frac{Ze^2}{\|\vec{r}_n - \vec{r}_e\|^{1/2}}$$

$$p_n^2 = p_{nx}^2 + p_{ny}^2 + p_{nz}^2$$

$$p_e^2 = p_{ex}^2 + p_{ey}^2 + p_{ez}^2$$

$$\|\vec{r}_n - \vec{r}_e\|^{1/2} = \sqrt{(x_n - x_e)^2 + (y_n - y_e)^2 + (z_n - z_e)^2}$$

We transform from classical momenta to quantum mechanics as follows:

$$p_n^2 = -\frac{\hbar^2}{4\pi^2} \nabla_n^2 = -\frac{\hbar^2}{4\pi^2} \left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2} \right)$$

Next, we transform from laboratory frame of reference to the center of mass frame of reference.

$$x = x_n - x_e$$

$$y = y_n - y_e$$

$$z = z_n - z_e$$

$$r = \|\vec{r}_n - \vec{r}_e\|^{1/2} = \sqrt{x^2 + y^2 + z^2}$$

$$X_n = x_n - X$$

$$X_e = x_e - X$$

$$m_n X_n + m_e X_e = m_n x_n + m_e x_e - m_n X - m_e X = 0$$

$$(m_n + m_e)X = MX = m_n x_n + m_e x_e$$

$$(m_n + m_e)Y = MY = m_n y_n + m_e y_e$$

$$(m_n + m_e)Z = MZ = m_n z_n + m_e z_e$$

Eliminate the electron position from the x and X equations by addition of the following two equations:

$$m_e x = m_e x_n - m_e x_e$$

$$MX = m_n x_n + m_e x_e$$

$$m_e x + MX = m_e x_n + m_n x_n = (m_e + m_n)x_n = Mx_n$$

$$x_n = \frac{m_e x}{M} + X$$

$$x_e = x_n + x = \frac{m_e x}{M} + X + x$$

$$dx_n = \frac{m_e dx}{M} + dX$$

$$dx_e = \frac{m_e dx}{M} + dX + dx$$

$$\frac{\partial x_n}{\partial x} = \frac{m_e}{M}$$

$$\frac{\partial x_n}{\partial X} = 1$$

$$\frac{\partial x_e}{\partial x} = \frac{m_e}{M} + 1 = \frac{m_n + 2m_e}{M}$$

$$\frac{\partial x_e}{\partial X} = 1$$

$$\frac{\partial}{\partial x_n} = \frac{\partial x}{\partial x_n} \frac{\partial}{\partial x} + \frac{\partial X}{\partial x_n} \frac{\partial}{\partial X}$$

$$\frac{\partial^2}{\partial x_n^2} = \frac{\partial x}{\partial x_n} \frac{\partial^2}{\partial x^2} + \frac{\partial X}{\partial x_n} \frac{\partial^2}{\partial X^2} = \frac{M}{m_e} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial X^2}$$

$$\frac{\partial^2}{\partial x_e^2} = \frac{\partial x}{\partial x_e} \frac{\partial^2}{\partial x^2} + \frac{\partial X}{\partial x_e} \frac{\partial^2}{\partial X^2} = \frac{M}{m_n + 2m_e} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial X^2}$$

$$p_n^2 = -\frac{\hbar^2}{4\pi^2} \nabla_n^2 = -\frac{\hbar^2}{4\pi^2} \frac{M}{m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{4\pi^2} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right)$$

$$p_e^2 = -\frac{\hbar^2}{4\pi^2} \nabla_e^2 = -\frac{\hbar^2}{4\pi^2} \frac{M}{m_n + 2m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{4\pi^2} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right)$$

$$H = -\frac{\hbar^2}{8\pi^2} \frac{M}{m_n m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{8\pi^2 m_n} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) \\ - \frac{\hbar^2}{8\pi^2} \frac{M}{m_e (m_n + 2m_e)} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{8\pi^2 m_e} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right)$$

$$H = -\frac{\hbar^2}{8\pi^2 \mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{8\pi^2 M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right)$$

$$\Psi(\vec{r}_n, \vec{r}_e, t) = \Psi(\vec{r}, \vec{R}, t) = \psi(\vec{r})U(\vec{R})T(t)$$

$$\frac{i\hbar}{2\pi T} \frac{dT}{dt} = -\frac{\hbar^2}{8\pi^2 \mu \psi} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) - \frac{\hbar^2}{8\pi^2 M U} \left(\frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} + \frac{\partial^2 U}{\partial Z^2} \right) - \frac{Ze^2}{r} = E + E'$$

$$\frac{dT}{T} = -\frac{2\pi i}{\hbar} (E + E') dt$$

$$-\frac{\hbar^2}{8\pi^2 \mu} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) - \frac{Ze^2}{r} \psi = E\psi$$

$$-\frac{h^2}{8\pi^2 M} \left(\frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} + \frac{\partial^2 U}{\partial Z^2} \right) = E' U$$

$$T(t) = e^{-2\pi i(E+E')t/h}$$

$$U(X, Y, Z) = u(X)v(Y)w(Z)$$

$$\frac{1}{u} \frac{d^2 u}{dX^2} + \frac{1}{v} \frac{d^2 v}{dY^2} + \frac{1}{w} \frac{d^2 w}{dZ^2} = -\frac{8\pi^2 M E'}{h^2}$$

$$E' = E_X + E_Y + E_Z$$

$$\frac{1}{u} \frac{d^2 u}{dX^2} = -\frac{8\pi^2 M E_X}{h^2}$$

$$\frac{1}{v} \frac{d^2 v}{dY^2} = -\frac{8\pi^2 M E_Y}{h^2}$$

$$\frac{1}{w} \frac{d^2 w}{dZ^2} = -\frac{8\pi^2 M E_Z}{h^2}$$

$$\frac{d^2 u}{dX^2} + \frac{8\pi^2 M E_X}{h^2} u = 0$$

$$\frac{d^2 v}{dY^2} + \frac{8\pi^2 M E_Y}{h^2} v = 0$$

$$\frac{d^2 w}{dZ^2} + \frac{8\pi^2 M E_Z}{h^2} w = 0$$

$$\frac{d^2 u}{dX^2} + \alpha^2 u = 0$$

$$\frac{d^2 v}{dY^2} + \beta^2 v = 0$$

$$\frac{d^2 w}{dZ^2} + \gamma^2 w = 0$$

$$\alpha^2 = \frac{8\pi^2 M E_X}{h^2}$$

$$\beta^2 = \frac{8\pi^2 M E_Y}{h^2}$$

$$\gamma^2 = \frac{8\pi^2 M E_Z}{h^2}$$

$$u(X) = A_X \sin(\alpha X) + B_X \cos(\alpha X)$$

$$v(Y) = A_Y \sin(\beta Y) + B_Y \cos(\beta Y)$$

$$w(Z) = A_Z \sin(\gamma Z) + B_Z \cos(\gamma Z)$$

References

- [1] L. I. Schiff, "Chapter 4 Discrete Eigenvalues: Bound States Section 16 The Hydrogen Atom," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill Inc., 1968, pp. 88-90.