Quantum Mechanics in Three Dimensions

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October 4, 2018

Schrödinger Equation in Three Dimensions

Schrödinger equation for the Hamiltonian operator $\hat{H}$ in three dimensions is still given by

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi,$$

where the Hamiltonian is

$$\hat{H} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V.$$

By the standard prescription

$$\hat{p} \to -i\hbar\nabla, \quad (\hat{p_i} \to -i\hbar\frac{\partial}{\partial i})$$

we finally obtain

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi. \tag{1}$$

General Solution to the Schrödinger Equation

When the potential V is independent of time, the general solution to the Schrödinger equation in three dimensions is

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar},$$

where ψ_n is the eigenfunctions with E_n of the time-independent Schrödinger equation:

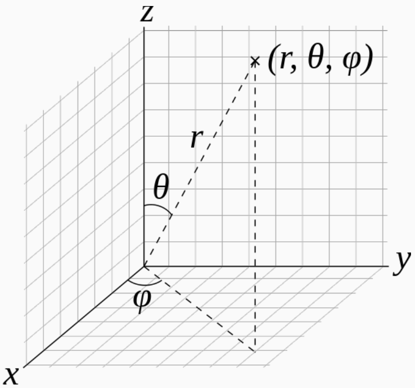
$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.$$

Note that the canonical commutation relations satisfy [see Problem (4.1) in Griffith]:

$$[r_i, p_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0.$$

Schrödinger Equation in Spherical Coordinates

$$x = r\sin\theta\cos\varphi, \quad y = r\sin\theta\sin\varphi, \quad z = r\cos\theta.$$



Spherical coordinate system (r, θ, ϕ)

Spherical Coordinate System

$$x = r\sin\theta\cos\varphi, \quad y = r\sin\theta\sin\varphi, \quad z = r\cos\theta.$$

Scale factor:

$$ds_i = h_i dq_i, \quad ds^2 = \sum_i (h_i dq_i)^2,$$

where

$$h_i^2 = \frac{\partial x}{\partial q_i}\frac{\partial x}{\partial q_i} + \frac{\partial y}{\partial q_i}\frac{\partial y}{\partial q_i} + \frac{\partial z}{\partial q_i}\frac{\partial z}{\partial q_i}.$$

In Spherical Coordinate System,

$$h_r = 1, \quad h_\theta = r, \quad h_\varphi = r\sin\theta.$$

Lapalcian operator in Spherical Coordinate System

$$h_r = 1, \quad h_\theta = r, \quad h_\varphi = r\sin\theta.$$

$$\begin{aligned}
\nabla\psi &= \frac{1}{h_1}\frac{\partial\psi}{\partial q_1}\hat{q}_1 + \frac{1}{h_2}\frac{\partial\psi}{\partial q_2}\hat{q}_2 + \frac{1}{h_3}\frac{\partial\psi}{\partial q_3}\hat{q}_3, \\
\nabla\cdot V &= \frac{1}{h_1h_2h_3}\left[\frac{\partial}{\partial q_1}(V_1h_2h_3) + \frac{\partial}{\partial q_2}(V_2h_3h_1) + \frac{\partial}{\partial q_3}(V_3h_1h_2)\right], \\
\nabla^2\psi &= \nabla\cdot\nabla\psi \\
&= \frac{1}{h_1h_2h_3}\left[\frac{\partial}{\partial q_1}\left(\frac{h_2h_3}{h_1}\frac{\partial\psi}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_3h_1}{h_2}\frac{\partial\psi}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_1h_2}{h_3}\frac{\partial\psi}{\partial q_3}\right)\right].
\end{aligned}$$

Thus, in spherical coordinates

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

Schrödinger Equation in Spherical Coordinates

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi.$$

Then, we attempt the method of separation of variables for $V = V(r)$,

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$$

Then, we have radial and angular equations:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E] = l(l+1),$$

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -l(l+1).$$

Radial Equation

The radial equation of Schrödinger equation:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1).$$

Introducing a variable $u = rR(r)$, we find

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu.$$

If we define the effective potential,

$$V_e = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2},$$

we find the equation that is identical to the one-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V_e u = Eu. \tag{2}$$

Angular Equation

The angular equation of Schrödinger equation:

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=-l(l+1).$$

The general solution of Y is called by spherical harmonics:

$$Y_l^m(\theta,\phi)=\epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi}P_l^m(\cos\theta), \quad (3)$$

where $\epsilon=(-1)^m$ for $m\geq 0$ and $\epsilon=1$ for $m\leq 0$ and P_l^m is the associated Legendre function.