4.3 Schrödinger equation in three dimensions

4.3.1 Classification of Schrödinger equations

- Time-dependent Schrödinger equation

$$iu_t = -\Delta u + V(x,y,z)u,$$

where $u = u(x,y,z,t) \in \mathbb{C}$ is the wave function of a quantum particle and $V = V(x,y,z) \in \mathbb{R}$ is the quantum potential.

- Stationary Schrödinger equation

$$-\Delta\psi + V(x,y,z)\psi = E\psi,$$

such that $\psi \in L^2(\mathbb{R}^3)$ with the normalization condition:

$$\int_{\mathbb{R}^3} |\psi|^2 dxdydz = 1,$$

where $u(x,y,z,t) = \psi(x,y,z)e^{-iEt}$ and E is the energy level.

4.3.2 Spherically symmetric potentials $V = V(r)$

- Spherical coordinates:

$$\begin{aligned} x &= r\ \sin\theta\ \cos\phi, \\ y &= r\ \sin\theta\ \sin\phi, \\ z &= r\ \cos\theta \end{aligned}$$

where r is the radial variable, θ is the latitudinal angle, and ϕ is the azimuthal angle.

- The domain for the ball of radius a:

$$D = \{(r,\theta,\phi): \ \ 0 \le r \le a,\ 0 \le \theta \le \pi,\ 0 \le \phi \le 2\pi\}$$

- Laplace equation in spherical coordinates;

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

4.3.3 Sturm-Liouville problems after separation of variables

Consider the stationary Schrödinger equation with $V(r) = 0$ and

$$\psi(x, y, z) = R(r)\Theta(\theta)\Phi(\phi)$$

- Harmonic oscillator equation for $\Phi(\phi)$:

$$\Phi'' + \lambda\Phi = 0, \qquad 0 \le \phi \le 2\pi,$$

subject to the periodic boundary conditions:

$$\Phi(0) = \Phi(2\pi), \quad \Phi'(0) = \Phi'(2\pi)$$

- Legendre polynomial equation for $\Theta(\theta)$:

$$\Theta'' + \cot\theta\Theta' - \frac{n^2}{\sin^2\theta}\Theta + \mu\Theta = 0, \qquad 0 \le \theta \le \pi$$

subject to the bounded boundary conditions:

$$\Theta(0) \text{ and } \Theta(\pi) \text{ exist}$$

When $x = \cos\theta$ and $\Theta(\theta) = y(x)$, we have the associated Legendre equation:

$$(1 - x^2)y'' - 2xy' + \mu y - \frac{n^2}{1 - x^2}y = 0, \qquad -1 \le x \le 1$$

- Bessel function equation for $R(r)$:

$$r^2 R'' + 2rR' + \left(Er^2 - l(l+1)\right) R = 0, \qquad 0 \le r \le a,$$

subject to the Dirichlet boundary condition:

$$R(0) \text{ exists and } R(a) = 0$$

When $R(r) = y(r)/\sqrt{r}$ and $r = x$, we have the half-integer Bessel equation:

$$x^2 y'' + xy' + \left(Ex^2 - \left(l + \frac{1}{2}\right)^2\right) y = 0$$

4.3.4 Construction of spherical harmonics

- The set of 2π-periodic Fourier eigenfunctions:

$$\lambda = n^2, \qquad \Phi_n(\phi) = e^{in\phi}, \qquad n \in \mathbb{Z},$$

such that

$$(\Phi_n, \Phi_{n'}) = \int_0^{2\pi} \bar{\Phi}_n(\phi)\Phi_{n'}(\phi)d\phi = 2\pi\delta_{n,n'}$$

- The set of orthogonal (associated) Legendre polynomials:

$$\mu = l(l+1), \qquad \Theta_l(\theta) = P_l^{|n|}(\cos\theta), \qquad l \in \mathbb{N},$$

such that

$$(\Theta_l, \Theta_{l'}) = \int_0^{\pi} \sin\theta\ \Theta_l(\theta)\ \Theta_{l'}(\theta)\ d\theta = \frac{2}{2l+1}\frac{(l+|n|)!}{(l-|n|)!}\delta_{l,l'}$$

- The set of orthogonal half-integer Bessel functions:

$$E = \left(\frac{z_{l,m}}{a}\right)^2, \qquad R_m(r) = j_l\left(\frac{z_{m,l}r}{a}\right), \qquad m \in \mathbb{N}_+,$$

where $j_l(z)$ is a spherical Bessel's function:

$$j_l(z) = \sqrt{\frac{\pi}{2z}}J_{l+\frac{1}{2}}(z), \qquad j_l(z_{m,l}) = 0,$$

such that

$$(R_m, R_{m'}) = \int_0^{a} r^2\ R_m(r)\ R_{m'}(r)\ dr \sim \delta_{m,m'}$$

Eigenfunctions $Y_l^n(\theta,\phi) = P_l^{|n|}(\cos\theta)\ e^{in\phi}$, $n \in \mathbb{Z}$, $l \in \mathbb{N}$ are referred to as the spherical harmonics in $\mathbb{R}^3$.