Notes

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Contents

Chapter 1

Formalism

1.1 Hilbert Space

Contructs:

- state: wave function
- observables: operators
- vectors: defining conditions
- linear transformation: the operators act on vectors
- linear algebra: the natural language of Quantum Mechanics

Properties:

1. wave function live in
2. complete inner product space
3. squre-integrable

Definition 1 *Inner product of two function*

$$\langle f|g\rangle \equiv \int_a^b f(x)^* g(x)\mathrm{d}x$$

Discussion:

- Schwarz inequality:

$$\left|\int_a^b f(x)^* g(x)\mathrm{d}x\right| \leqslant \sqrt{\int_a^b |f(x)|^2\mathrm{d}x \int_a^b |g(x)|^2\mathrm{d}x}$$

- $\langle g|f\rangle = \langle f|g\rangle^*$
- normalized $\langle f|f\rangle = 1$
- orthonormal $\langle f_m|f_n = \delta_{mn}\rangle$
- complete and orthonormal $f(x) = \sum_{n=1}^{\infty} c_n f_n(x), c_n = \langle f_n|f\rangle$

1.2 Observables

1.2.1 Hermitian Operators

Definition 2 *Hermitian Operators*

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle \qquad \textit{for all f(x) and g(x)}$$

Discussion:

- Observables are represented by hermitian operators
- hermitian conjugate $\hat{Q}^\dagger = \hat{Q}$
- momentum operator is hermitian

$$\langle f|\hat{p}g\rangle = \int_{-\infty}^{\infty} f^*(-i\hbar)\frac{\mathrm{d}g}{\mathrm{d}x}\mathrm{d}x = -i\hbar f^* g\Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\left(-i\hbar\frac{\mathrm{d}f}{\mathrm{d}x}\right)^* g\mathrm{d}x = \langle \hat{p}f|g\rangle$$

1.2.2 Determinate State

$$\sigma^2 = \left\langle (Q - \langle Q\rangle)^2\right\rangle = \left\langle (\Psi|(\hat{Q}-q)^2\Psi\right\rangle = \left\langle ((\hat{Q}-q)\Psi|(\hat{Q}-q)\Psi\right\rangle = 0$$

$$\Downarrow$$

$$\hat{Q}\Psi = q\Psi$$

Discussion:

- This is eigenvalue equation for $\hat{Q}$
- Ψ if an eigenfuction of $\hat{Q}$, and q is the corresponding eigenvalue
- Determinate state of Q are eigenfuction of $\hat{Q}$
- spectrum: the collection of all the eigenvalues of an operator
- degenerate: linearly independent eigenfuctions share the same eigenvalue

1.3 Eigenfuctions of a Hermitain Operator

1.3.1 Discrete Spectra

- the eigenvalues are separated from another
- the eigenfuctions lie in Hilbert space and constitute physically realizable states

Properties of normalizable eigenfuctions of a hermitian operator:

1. Their eigenvalues are *real*
2. Eigenfuctions belonging to distinct eigenvalues are *orthognal*

1.3.2 Continuous Spectra

- the eigenvalues fill out an entire range
- the eigenfuctions are not normalizable and do not represent possible wave functions

The eigenfuctions and eigenvalues of the momentum operator (on the interval $(-\infty < x < \infty)$:

$$-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}f_p(x) = pf_p(x) \quad \Rightarrow \quad f_p(x) = Ae^{ipx/\hbar}$$

$$\downarrow$$

$$\int_{-\infty}^{\infty} f_{p'}^*(x)f_p(x)\mathrm{d}x = |A|^2\int_{-\infty}^{\infty} e^{i(p-p')x/\hbar}\mathrm{d}x = |A|^2 2\pi\hbar\delta(p-p')$$

$$\Downarrow$$

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}$$

- Dirac orthonormality: $\langle f_{p'}|f_p\rangle = \delta(p-p')$
- Complete:

$$f(x) = \int_{-\infty}^{\infty} c(p)f_p(x)dp = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} c(p)e^{ipx/\hbar}\mathrm{d}p$$

$$\langle f_{p'}|f\rangle = \int_{-\infty}^{\infty} c(p)\langle f_{p'}|f\rangle\,\mathrm{d}p = \int_{-\infty}^{\infty} c(p)\delta(p-p')\mathrm{d}p = c(p')$$

The eigenfuctions and eigenvalues of the positoin operator:

$$\hat{x}g_y(x) = g_y x \quad \Rightarrow \quad g_y(x) = A\delta(x-y)$$

$$\downarrow$$

$$\int_{-\infty}^{\infty} g_{y'}^* g_y(x)\mathrm{d}x = |A|^2\int_{-\infty}^{\infty} \delta(x-y')\delta(x-y)\mathrm{d}x = |A|^2\delta(y-y')$$

$$\Downarrow$$

$$g_y(x) = \delta(x-y)$$

1.4 Generalized Statistical Interpretation

Observable: $Q(x,p)$
State: $\Psi(x,t)$
One of eigenvalues: $\hat{Q}(x - i\hbar d/dx)$
The probablility of getting eigenvalues(orthonormal):

1. Discrete spectrum
    - probablility of getting q_n

$$|c_n|^2, \qquad \text{where} \quad c_n = \langle f_n|\Psi\rangle$$

- Complete:

$$\Psi(x,t) = \sum_n c_n(t) f_n(x)$$
$$c_n(t) = \langle f_n | \Psi \rangle = \int f_n(x)^* \Psi(x,t) \mathrm{d}x$$
$$\sum_n |c_n|^2 = 1$$

- The expectation value of Q:

$$\langle Q \rangle = \left\langle \Psi | \hat{Q} \Psi \right\rangle = \sum_n q_n |c_n|^2$$

2. Continuous spectrum

- probablility of getting a result in the range $\mathrm{d}z$

$$|c(z)|^2 \mathrm{d}z, \qquad \text{where} \quad c(z) = \langle f_z | \Psi \rangle$$

- For positoin measurements:

$$c(y) = \langle g_y | \Psi \rangle = \int_{-\infty}^{\infty} \delta(x-y) \Psi(x,t) \mathrm{d}x = \Psi(y,t)$$

- For momentum measurements:

$$c(p) = \langle f_p | \Psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x,t) \mathrm{d}x$$

- Fourier transformation:

$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x,t) \mathrm{d}x$$
$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p,t) \mathrm{d}p$$

- Expectation:

$$\langle Q(x,p,t) \rangle = \begin{cases} \int \Psi^* \hat{Q}\left(x, -i\hbar\frac{\partial}{\partial x}, t\right) \Psi \,\mathrm{d}x, & \text{in position space} \\ \int \Phi^* \hat{Q}\left(i\hbar\frac{\partial}{\partial p}, p, t\right) \Phi \,\mathrm{d}p, & \text{in momentum space} \end{cases}$$

1.5 The Uncertainty Principle

1.5.1 Proof of the Generalized Uncertainty Principle

$$f \equiv \left(\hat{A} - \langle A \rangle\right) \Psi \quad \rightarrow \quad \sigma_A^2 \sigma_B^2 = \langle f|f \rangle \langle g|g \rangle \geqslant |\langle f|g \rangle|^2$$
$$|z|^2 \geqslant [\mathrm{Im}(z)]^2 = \left[\frac{1}{2i}(z - z^*)\right]^2 \quad \Rightarrow \quad \sigma_A^2 \sigma_B^2 \geqslant \left(\frac{1}{2i}\left[\langle f|g \rangle - \langle g|f \rangle\right]\right)^2$$
$$\langle f|g \rangle - \langle g|f \rangle = \left\langle \hat{A}\hat{B} \right\rangle - \langle A \rangle \langle B \rangle - \left(\left\langle \hat{B}\hat{A} \right\rangle - \langle A \rangle \langle B \rangle\right) = \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle$$
$$\Downarrow$$
$$\boxed{\sigma_A^2 \sigma_B^2 \geqslant \left(\frac{1}{2i}\left\langle \left[\hat{A}, \hat{B}\right] \right\rangle\right)^2}$$

1.5.2 The Minimum-Uncertainty Wave Packet

$$g(x) = iaf(x), \qquad \text{where } a \text{ is real}$$
$$\Rightarrow \left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi$$
$$\Rightarrow \Psi(x) = Ae^{-a(x-\langle x\rangle)^2/2\hbar}e^{i\langle p\rangle/\hbar}$$

1.5.3 The Energy-Time Uncertainty Principle

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\left\langle \Psi|\hat{Q}\Psi\right\rangle \\ i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi, \quad \text{where} \quad H = \frac{p^2}{2m} + V \\ \left\langle \hat{H}\Phi\middle|\hat{Q}\Phi\right\rangle = \left\langle \Phi\middle|\hat{H}\hat{Q}\Phi\right\rangle \end{cases} \Rightarrow$$

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle = \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle}$$

Assume that Q does not depend explicity on t:

$$\sigma_H^2\sigma_Q^2 \geqslant \left(\frac{1}{2i}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle\right)^2 = \left(\frac{\hbar}{2}\right)^2\left(\frac{d\langle Q\rangle}{dt}\right)^2$$

$$\begin{aligned} \Delta E &\equiv \sigma_H \\ \Delta t &\equiv \frac{\sigma_Q}{|d\langle Q\rangle/dt|} \end{aligned} \qquad \Rightarrow \qquad \Delta t\Delta E \geqslant \frac{\hbar}{2}$$

1.6 Vectors and Operators

1.6.1 Bases in Hillbert Space

$$\begin{aligned} \Psi(x,t) &= \langle x|\mathcal{S}(t)\rangle \\ \Phi(p,t) &= \langle p|\mathcal{S}(t)\rangle \\ c_n(t) &= \langle n|\mathcal{S}(t)\rangle \end{aligned}$$
$$|\mathcal{S}(t)\rangle \to \int \Psi(y,t)\delta(x-y)\,\mathrm{d}y = \int \Phi(p,t)\frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\,\mathrm{d}p$$
$$= \sum c_n e^{-iE_nt/\hbar}\psi_n(x)$$

Operator "Trandform"

$$|\beta\rangle = \hat{Q}\,|\alpha\rangle, \quad \text{components} \begin{cases} |\alpha\rangle = \sum_n a_n\,|e_n\rangle & a_n = \langle e_n|\alpha\rangle \\ |\beta\rangle = \sum_n b_n\,|e_n\rangle & b_n = \langle e_n|\beta\rangle \end{cases}$$

➥ $$\langle e_m|\hat{Q}|e_n\rangle \equiv Q_{mn} \qquad \to \sum_n b_n\,\langle e_m|e_n\rangle = \sum_n \langle e_m|\hat{Q}|e_n\rangle$$

$$\Rightarrow \qquad b_m = \sum_n Q_{mn}a_n$$

Schrodinger equation:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\mathcal{S}(t)\rangle = \hat{H}|\mathcal{S}(t)\rangle, \qquad \text{Time-dependent}$$

$$\hat{H}|s\rangle = E|s\rangle, \qquad \text{Time-independent}$$

Particular example of vectors:

$$\hat{x}\,(\text{the position operator}) \rightarrow \begin{cases} x & \text{(in positoin space)} \\ i\hbar\partial/\partial p & \text{(in momentum space)} \end{cases}$$

$$\hat{p}\,(\text{the momentum operator}) \rightarrow \begin{cases} -i\hbar\partial/\partial x & \text{(in positoin space)} \\ p & \text{(in momentum space)} \end{cases}$$

1.6.2 Dirac Notation

bra: $\langle\alpha|$
ket: $|\beta\rangle$
Orthonormal basis (complete):

- Discrete

$$\langle e_m|e_n\rangle = \delta_{mn} \qquad \rightarrow \qquad \sum_n |e_n\rangle\langle e_n| = 1$$

- Continuous

$$\langle e_z|e_{z'}\rangle = \delta(z - z') \qquad \rightarrow \qquad \int |e_z\rangle\langle e_{z'}|\,\mathrm{d}z = 1$$

Baker-Campbell-Hausdrff formula:

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\hat{C}/2}, \qquad \text{where} \qquad \hat{C} = \left[\hat{A}, \hat{B}\right]$$

1.6.3 Changing Bases in Dirac Notation

$$\text{the positoin eigenstats : } |x\rangle \qquad 1 = \int dx\,|x\rangle\langle x|$$

$$\rightarrow \quad |\mathcal{S}(t)\rangle = \int dx\,|x\rangle\langle x|\mathcal{S}(t)\rangle \equiv \int \Psi(x,t)\,|x\rangle\,\mathrm{d}x$$

$$\text{the momentum eigenstats : } |p\rangle \qquad 1 = \int dp\,|p\rangle\langle p|$$

$$\rightarrow \quad |\mathcal{S}(t)\rangle = \int dp\,|p\rangle\langle p|\mathcal{S}(t)\rangle \equiv \int \Phi(p,t)\,|p\rangle\,\mathrm{d}p$$

$$\text{the energy eigenstats : } |n\rangle \qquad 1 = \sum |n\rangle\langle n|$$

$$\rightarrow \quad |\mathcal{S}(t)\rangle = \sum_n |n\rangle\langle n|\mathcal{S}(t)\rangle \equiv \sum c_n(t)\,|n\rangle$$

Operators act on kets

$$\langle x|\hat{x}|\mathcal{S}(t)\rangle = \text{action of position operator in } x \text{ basis} = x\Psi(x,t)$$

$$\langle p|\hat{x}|\mathcal{S}(t)\rangle = \text{action of position operator in } p \text{ basis} = i\hbar\frac{\partial\Phi}{\partial p}$$

Proof:

$$\langle p|\hat{x}|\mathcal{S}(t)\rangle = \left\langle p\left|\hat{x}\int dx|x\rangle\langle x|\right|\mathcal{S}(t)\right\rangle = \int\langle p|x|x\rangle\langle x|\mathcal{S}(t)\rangle dx = i\hbar\frac{\partial}{\partial p}\langle p|\mathcal{S}(t)\rangle$$

1.7 Wave Functions in Position and Momentum Space(Additio

NOTE: x,$f(x)$,p are operators, different form all above

1.7.1 Position-Space Wave Function

The base ket used are the position kets satisfying

$$x|x'\rangle = x'|x'\rangle \qquad \langle x''|x'\rangle = \delta(x'' - x')$$

A physical state can be expanded in terms of x'

$$\begin{aligned} |\alpha\rangle = \int dx' |x'\rangle\langle x'|\alpha\rangle \\ |\langle x'|\alpha\rangle|^2 dx' \qquad \text{probablility} \\ \langle x'|\alpha\rangle \equiv \psi_\alpha(x') \qquad \text{wave function} \end{aligned}$$

Using the completness of $|x'\rangle$, we have

$$\langle\beta|\alpha\rangle = \int dx' \, \langle\beta|x'\rangle\langle x'|\alpha\rangle = \int dx' \psi_\beta^*(x')\psi_\alpha^*(x')$$

the probablility amplitude for state $|\alpha\rangle$ to be found in state $|\beta\rangle$

$f(x)$ is a function of x

$$\begin{aligned} \langle x'|f(x)|x''\rangle &= (\langle x'|) \cdot (f(x'')|x'') = f(x')\delta(x' - x'') \\ \langle\beta|f(x)|\alpha\rangle &= \int dx' \int dx'' \, \langle\beta|x'\rangle\langle x'|f(x)|x''\rangle\langle x''|\alpha\rangle \\ &= \int dx' \, \psi_\beta^*(x')f(x')\psi_\alpha(x') \end{aligned}$$

1.7.2 Momentum Operator in the Position Basis

$$\begin{aligned} p|\alpha\rangle = \int dx'|x'\rangle \left(-i\hbar\frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right) \\ \Rightarrow \langle x'|p|\alpha\rangle = -i\hbar\frac{\partial}{\partial x'}\langle x'|\alpha\rangle \end{aligned}$$

Properties:

$$\begin{aligned} \langle x'|p^n|x''\rangle = (-i\hbar)^n \frac{\partial^n}{\partial x'^n}\delta(x' - x'') \\ \langle\beta|p^n|\alpha\rangle = \int dx' \, \psi_\beta^*(x') \left((-i\hbar)^n \frac{\partial^n}{\partial x'^n}\right) \psi_\alpha(x') \end{aligned}$$

1.7.3 Momentum-Space Wave Function

The base eigenkets in the p-basis specify

$$p|p'\rangle = p'|p'\rangle \qquad \langle p'|p''\rangle = \delta(p' - p'')$$

Same way as $|x'\rangle$

$$
\begin{aligned}
&|\alpha\rangle = \int dp' |p'\rangle\langle p'|\alpha\rangle \\
&|\langle p'|\alpha\rangle|^2 dp' \qquad \text{probablility} \\
&\langle p'|\alpha\rangle \equiv \phi_\alpha(p') \qquad \text{momentum-space wave function}
\end{aligned}
$$

Transformation function from x to p: $\langle x'|p'\rangle$

$$
\begin{aligned}
\langle x'|p|p'\rangle &= -i\hbar\frac{\partial}{\partial x'}\langle x'|p'\rangle = p'\langle x'|p'\rangle \\
&\Rightarrow \langle x'|p'\rangle = N\exp\left(\frac{ip'x'}{\hbar}\right)
\end{aligned}
$$

Discussion:

- the probablility amplitude for $|p'\rangle$ specified by p' to be found at positoin x'
- the wave function for $|p'\rangle$, referred to as the momentum eigenfuction (still in the x-space)
- Nomalization: $N = \frac{1}{\sqrt{2\pi\hbar}}$

Rewrite:

$$
\begin{cases}
\langle x'|\alpha\rangle = \int dp' \langle x'|p'\rangle\langle p'|\alpha\rangle \\
\langle p'|\alpha\rangle = \int dx' \langle p'|x'\rangle\langle x'|\alpha\rangle
\end{cases}
\qquad \Leftrightarrow \qquad
\begin{aligned}
\psi_\alpha(x') &= \left[\frac{1}{\sqrt{2\pi\hbar}}\right]\int dp' \exp\left(\frac{ip'x'}{\hbar}\right)\phi_\alpha(p') \\
\phi_\alpha(p') &= \left[\frac{1}{\sqrt{2\pi\hbar}}\right]\int dx' \exp\left(\frac{-ip'x'}{\hbar}\right)\psi_\alpha(x')
\end{aligned}
$$

Chapter 2

Quantum Mechanics in Three Dimensionss

2.1 The Schroding Equation

2.1.1 Cartesian Coordinates

Laplacian

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schroding's Equation

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

Canonical commutation relations

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

Three-Dimensional of Ehrenfest's theorem

$$\frac{\mathrm{d}}{\mathrm{d}r}\langle \mathbf{r} \rangle = \frac{1}{m}\langle \mathbf{p} \rangle, \qquad \text{and} \quad \frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{p} \rangle = \langle -\nabla V \rangle$$

Heisenberg's uncertainty principle

$$\sigma_{x,y,z}\sigma_{p_x,p_y,p_z} \geqslant \hbar/2$$

2.1.2 Spherical Coordinates

Time-independent Schrodinger equation

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

$$\Downarrow$$

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad \Rightarrow \qquad \begin{array}{l} \dfrac{1}{R}\dfrac{\mathrm{d}}{\mathrm{d}r}\left(r^2\dfrac{\mathrm{d}R}{\mathrm{d}r}\right) - \dfrac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell+1) \\ \dfrac{1}{Y}\left\{\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial Y}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2 Y}{\partial\phi^2}\right\} = -\ell(\ell+1) \end{array}$$

2.1.3 The Angular Equation

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \qquad \Rightarrow \qquad \begin{aligned} &\frac{1}{\Theta}\left[\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right]+\ell(\ell+1)\sin^2\theta=m^2 \\ &\frac{1}{\Phi}\frac{\mathrm{d}^2\Theta}{\mathrm{d}\theta^2}=-m^2 \end{aligned}$$

Associated Legendre function

$$P_\ell^m(x)\equiv(-1)^m\left(1-x^2\right)^{m/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^m P_\ell(x)$$

Legendre polynomial

$$P_\ell(x)\equiv\frac{1}{2^\ell\ell!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^\ell\left(x^2-1\right)^\ell$$

Spherical harmonics

$$\boxed{Y_\ell^m(\theta,\phi)=\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}e^{im\phi}P_\ell^m(\cos\theta)}$$

- $\ell=0,1,2\cdots$
- $m=-\ell,-\ell+1,\cdots,-1,0,1,\cdots,\ell-1,\ell$

Nomalization

$$\int_0^\infty |R|^2r^2\mathrm{d}r=1 \qquad \int_0^\pi\int_0^{2\pi}|Y|^2\sin\theta\mathrm{d}\theta\mathrm{d}\phi=1$$

orthognal

$$\int_0^\pi\int_0^{2\pi}\left[Y_\ell^m(\theta,\phi)\right]^*\left[Y_{\ell'}^{m'}(\theta,\phi)\right]\sin\theta\mathrm{d}\theta\mathrm{d}\phi=\delta_{\ell\ell'}\delta_{mm'}$$

2.1.4 The Radial Equation

$$u(r)\equiv rR(r)$$

$$\Rightarrow \qquad -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2}+\left[V+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u=Eu$$

Effective potential

$$V_{\text{eff}}=V+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

Nomalization

$$\int_0^\infty|u|^2\mathrm{d}r=1$$

2.2 The Hydrogen Atom

$$V(r)=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

2.2.1 The Radial Wave Function

Let

$$\kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar} \qquad \rho \equiv \kappa r \qquad \rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 \kappa}$$

$$\Rightarrow \qquad \frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

Asymptitic behavior

- As $\rho \to \infty$

$$u(\rho) \sim A e^{-\rho}$$

- As $\rho \to 0$

$$u(\rho) = C \rho^{\ell+1}$$

Peel off Asymptitic behavior

$$u(\rho) = \rho^{\ell+1} e^{\rho} v(\rho) \quad \rightarrow \quad v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad \rightarrow \quad c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j$$

For large j

$$c_j \approx \frac{2^j}{j!} c_0$$

Then

$$v(\rho) = c_0 e^{2\rho} \quad \rightarrow \quad u(\rho) = c_0 \rho^{\ell+1} e^{\rho}$$

The series must terminate

$$c_{N-1} \neq 0 \quad \text{but} \quad c_N = 0$$

$$\begin{cases} 2(N+\ell) - \rho_0 = 0 \\ n \equiv N + \ell \end{cases} \quad \Rightarrow \quad \rho_0 = 2n \qquad \Rightarrow$$

Bohr formula

$$\boxed{E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1, 2, 3, \cdots}$$

Summary

- n: principal quantum number
- ℓ: azimuthal quantum number
- m: magnetic quantum number

Ground State

The polynomial $v(\rho)$

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$$

- Associated Laguerre polynomial
- qth Laguerre polynomial

$$\boxed{\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na} \left(\frac{2r}{na}\right)^{\ell} \left[L_{n-\ell-1}^{2\ell+1}(2r/na)\right] Y_\ell^m(\theta, \phi)}$$

2.2.2 The Spectrum of Hydrogen

$$E_\gamma = E_i - E_f = -13.6\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\frac{1}{\lambda} = \mathcal{R}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

2.3 Angular Momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x$$

2.3.1 Eigenvalues

Fundamental commutation relations for angular momentum

$$[L_x, L_y] = i\hbar L_z \qquad [L^2, \mathbf{L}] = 0 \qquad \sigma_{L_x}\sigma_{L_y} \geqslant \frac{\hbar}{2}|\langle L_z\rangle|$$

Find simultaneous eigenstates

$$L^2 f = \lambda f \qquad \text{and} \qquad L_z f = \mu f$$

Let

$$L_\pm \equiv L_x \pm iL_y \qquad \to \qquad \begin{cases} [L_z, L_\pm] = \pm\hbar L_\pm \\ [L^2, L_\pm] = 0 \end{cases} \qquad \Rightarrow$$

f is an eigenfuction of L^2 and L_z

$$\begin{aligned} L^2(L_\pm f) &= L_\pm(L^2 f) = L_\pm(\lambda f) \\ &= \lambda(L_\pm f) \end{aligned}$$

$$\begin{aligned} L_z(L_\pm f) &= (L_z L_\pm - L_\pm L_z)f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm(\mu f) \\ &= (\mu \pm \hbar)(L_\pm f) \end{aligned}$$

- top rung

$$L_+ f_t = 0$$

- bottom rung

$$L_- f_b = 0$$

- compare them

$$\boxed{L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m \qquad L_z f_\ell^m = \hbar m f_\ell^m}$$

  where

$$\ell = 0, 1/2, 1, 3/2, \cdots; \quad m = -\ell, -\ell+1, \cdots, \ell-1, \ell$$

2.3.2 Eigenfunctions

$$\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla) \quad \rightarrow \quad \nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

$$\mathbf{L} = -i\hbar\left(\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right)$$

$$\Rightarrow \quad \boxed{L_z = -i\hbar\frac{\partial}{\partial \phi}}$$

$$\boxed{L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]}$$

Conclusion: Spherical harmonics are the eigenfuctions pf L^2 and L_z

2.4 Spin

$$\begin{aligned}
S^2\left|s\,m\right\rangle &= \hbar^2 s(s+1)\left|s\,m\right\rangle \\
S_z\left|s\,m\right\rangle &= \hbar m\left|s\,m\right\rangle \\
S_\pm\left|s\,m\right\rangle &= \hbar\sqrt{s(s+1) - m(m+1)}\left|s\,(m\pm 1)\right\rangle
\end{aligned}$$

where

$$s = 0, \frac{1}{2}, 2, \frac{3}{2}, \cdots \qquad m = -s, -s+1, \cdots, s-1, s$$

2.4.1 Spin 1/2

for $s = 1/2$, there are two eigenstates

- spin up ($\uparrow$): $\left|\frac{1}{2}\,\frac{1}{2}\right\rangle$
- spin down ($\downarrow$): $\left|\frac{1}{2}\left(-\frac{1}{2}\right)\right\rangle$

spinor

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-$$

- spin up ($\uparrow$): $X_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$
- spin down ($\downarrow$): $X_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

in Matrix

$$\begin{cases} \mathsf{S}^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \\ \mathsf{S}^2\chi_- = \frac{3}{4}\hbar^2\chi_- \end{cases} \quad \Rightarrow \quad \mathsf{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{cases} \mathsf{S}_z\chi_+ = \frac{\hbar}{2}\chi_+ \\ \mathsf{S}_z\chi_- = -\frac{\hbar}{2}\chi_- \end{cases} \quad \Rightarrow \quad \mathsf{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\begin{cases} \mathsf{S}_+\chi_- = \hbar\chi_+ \\ \mathsf{S}_-\chi_+ = \hbar\chi_- \\ \mathsf{S}_+\chi_+ = \mathsf{S}_-\chi_- = 0 \end{cases} \Rightarrow \begin{matrix} \mathsf{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ \mathsf{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{matrix} \Rightarrow \begin{matrix} \mathsf{S}_x = \hbar/2\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \mathsf{S}_y = \hbar/2\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \end{matrix}$$

Pauli spin Matrix

$$\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma} \qquad \Rightarrow \qquad \boxed{\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

2.4.2 Electron in a Magnetic Field

Hamiltonian matrix for a spinning charged particle, at rest in **B**

$$\begin{cases} \boldsymbol{\mu} = \gamma\mathbf{S} \\ H = -\boldsymbol{\mu}\cdot\mathbf{B} \end{cases} \Rightarrow \quad \mathsf{H} = -\gamma\mathbf{B}\cdot\mathsf{S}$$

- $\boldsymbol{\mu}$: magnetic dipole momentum
- γ: gyromagnetic ratio

1. Larmor precession:

$$\mathbf{B} = B_0\hat{k} \quad \Rightarrow \quad \mathsf{H} = -\gamma B_0 \mathsf{S}_z = -\frac{\gamma B_0\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\Rightarrow \quad \text{eigenstates} \begin{cases} \chi_+, \text{ with } E_= - (\gamma B_0\hbar)/2 \\ \chi_-, \text{with } E_= + (\gamma B_0\hbar)/2 \end{cases}$$

$$i\hbar\frac{\partial\chi}{\partial t} = \mathsf{H}\chi \qquad \Rightarrow$$

$$\chi(t) = a\chi_+e^{-iE_+t/\hbar} + b\chi_-e^{-iE_-t/\hbar} = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix}$$

$$|a|^2 + |b|^2 = 1 \quad \Rightarrow \quad \chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}$$

$$\Downarrow$$

$$\langle S_x\rangle = \chi(t)^\dagger \mathsf{S}_x\chi(t) = \frac{\hbar}{2}\sin\alpha\cos(\gamma B_0 t)$$
$$\langle S_y\rangle = \chi(t)^\dagger \mathsf{S}_y\chi(t) = -\frac{\hbar}{2}\sin\alpha\sin(\gamma B_0 t)$$
$$\langle S_z\rangle = \chi(t)^\dagger \mathsf{S}_z\chi(t) = \frac{\hbar}{2}\cos\alpha$$

Larmor frequency:

$$\omega = \gamma B_0$$

2. The Stern-Gerlach experiment

2.4.3 Addition of Angular Momenta

Two Particles

$$\begin{aligned} S^{(1)^2}|s_1s_2m_1m_2\rangle &= s_1(s_1+1)\hbar^2|s_1s_2m_1m_2\rangle \\ S^{(2)^2}|s_1s_2m_1m_2\rangle &= s_2(s_2+1)\hbar^2|s_1s_2m_1m_2\rangle \\ S_z^{(1)}|s_1s_2m_1m_2\rangle &= m_1\hbar|s_1s_2m_1m_2\rangle \\ S_z^{(2)}|s_1s_2m_1m_2\rangle &= m_2\hbar|s_1s_2m_1m_2\rangle \end{aligned}$$

totol angular momentum

$$\mathbf{S} = \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$$

z component

$$\left.\begin{aligned} S_z|s_1s_2m_1m_2\rangle &= S_z^{(1)}|s_1s_2m_1m_2\rangle + S_z^{(2)}|s_1s_2m_1m_2\rangle \\ &= \hbar(m_1+m_2)|s_1s_2m_1m_2\rangle = \hbar m|s_1s_2m_1m_2\rangle \end{aligned}\right. \quad \Rightarrow \quad m = m_1 + m_2$$

Consider the spin-1/2 Particles

$$\boxed{\left\{\begin{array}{ccc} |1\,1\rangle & = & |\uparrow\uparrow\rangle \\ |1\,0\rangle & = & \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1\;-1\rangle & = & |\downarrow\downarrow\rangle \end{array}\right\} \quad s = 1\,(\text{triplet})}$$

- triplet states are eigenvectors of S^2 with eigenvalue $2\hbar^2$

$$\boxed{\left\{|0\,0\rangle \;=\; \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\right\} \quad s = 0\,(\text{singlet})}$$

- singlet state is an eigenvector of S^2 with eigenvalue 0

Clebsch-Gordan coefficients

$$|s\,m\rangle = \sum_{m_1+m_2=m} C^{s_1s_2s}_{m_1m_2m}|s_1\,s_2\,m_1\,m_2\rangle$$

2.5 Electromagnetic Interactions

2.5.1 Minimal Coupling

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = \left[\frac{1}{2m}(-i\hbar\nabla - q\mathbf{A})^2 + q\varphi\right]\Psi}$$

- quantum implementation of the Lorentz force law
- minimal coupling rule

2.5.2 The Aharonov-Bohm Effect

Chapter 3

Identical Particles

3.1 Two-Particle System

- $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$
- $i\hbar \dfrac{\partial \Psi}{\partial t} = \hat{H}\Psi, \qquad \text{where} \quad \hat{H} = -\dfrac{\hbar^2}{2m_1}\nabla_1^2 - \dfrac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$
- $\displaystyle\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 = 1$
- $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) e^{-iEt/\hbar}$
- $-\dfrac{\hbar^2}{2m_1}\nabla_1^2\psi - \dfrac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi$

1. Nointeracting Particles

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_a(\mathbf{r}_1, t) + \Psi_a(\mathbf{r}_2, t)$$

2. Central potential (helium atom)

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\epsilon_0}\left(-\frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

3.1.1 Bosons and Fermions

1. Bosons state

$$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] \qquad A = \frac{1}{\sqrt{2}}$$

   - symmetric under interchange: $\psi_+(\mathbf{r}_1, \mathbf{r}_2) = \psi_+(\mathbf{r}_2, \mathbf{r}_1)$
   - all particles with integer spin are bosons

2. Fermions state

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] \qquad A = \frac{1}{\sqrt{2}}$$

   - symmetric under interchange: $\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1)$

- all particles with half integer spin are fermions
- Pauli exclusion principle: two identical fermions cannot occupy the same state
$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0$$

3.1.2 Exchange Forces

Suppose $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$
calculate $\langle(x_1 - x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle$

1. Distinguishable particles
$$\left\langle(x_1 - x_2)^2\right\rangle_d = \left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b + 2\langle x\rangle_a \langle x\rangle_b$$

2. Identical particles
$$\langle x_1^2\rangle = \langle x_2^2\rangle = \frac{1}{2}\left(\left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b\right)$$
$$\langle x_1 x_2\rangle = \langle x\rangle_a \langle x\rangle_b \pm |\langle x\rangle_{ab}|^2$$
where
$$\langle x\rangle_{ab} \equiv \int x\psi_a(x)^*\psi_b(x)\mathrm{d}x$$
thus
$$\left\langle(x_1 - x_2)^2\right\rangle_\pm = \left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b + 2\langle x\rangle_a \langle x\rangle_b \mp 2|\langle x\rangle_{ab}|^2$$
$$\Rightarrow \qquad \left\langle(\Delta x)^2\right\rangle_\pm = \left\langle(\Delta)^2\right\rangle_d \mp 2|\langle x\rangle_{ab}|^2$$

Exchange force: (if $\langle x\rangle_{ab} \neq 0$)

- force of attraction between identical bosons
- force of repulsion between identical fermions

3.1.3 Spin

Pauli principle: two electrons in a given position state as long as their spins are in the singlet configuration
$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)\chi(2, 1)$$

3.1.4 Generlized Symmetrization Principle

general statement, if you have n identical particles
$$|(1, 2, \cdots, i, \cdots, j, \cdots, n)\rangle = \pm\,|(1, 2, \cdots, j, \cdots, i, \cdots, n)\rangle$$

3.2 Atoms

$$\hat{H} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_j|}$$

- Z: atomic number
- Ze: electric charge
- in curly brackets: kinetic plus potential energy of the jth electron
- the second sum: the potential energy associated with the mutual repulsion of the electrons

3.2.1 Helium

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

ignore the last term

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n\ell m}(\mathbf{r}_1)\psi_{n'\ell' m'}(\mathbf{r}_2) \qquad \text{with} \quad E = 4(E_n + E_{n'})$$

ground state

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}\mathrm{e}^{-2(r_1+r_2)/a} \qquad \text{with} \quad E = 8(-13.6\,\mathrm{eV}) = -109\,\mathrm{eV}$$

- symmetric function
- singlet

3.2.2 The Periodic Table

Hund's rules

$$^{2S+1}L_J$$

3.3 Solids

3.3.1 The Free Elctron Gas

Suppose

$$V(x, y, z) = \begin{cases} 0, & 0 < x < l_x, 0 < y < l_y, 0 < z < l_z \\ \infty & \textit{otherwise} \end{cases}$$

Wave functions are

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x\pi}{l_x}x\right) \sin\left(\frac{n_y\pi}{l_y}y\right) \sin\left(\frac{n_z\pi}{l_z}z\right)$$

energies are

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2 k^2}{2m} \qquad \mathbf{k} \equiv (k_x, k_y, k_z)$$

3.3.2 Band Structure

Bloch's therem

$$V(x+a) = V(x) \qquad \to \qquad \psi(x+a) = \mathrm{e}^{iqa}\psi(x)$$

Dirac comb

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$

Chapter 4

Symmeties and Conservation Laws

4.1 Introduction

what a symmetry is: that the Hamiltonian is unchanged by some transformation, such as a rotation or a translation

4.1.1 Transformations in Space

Translation Operator

$$\hat{T}(a)\psi(x) = \psi'(x) = \psi(x-a)$$

Parity Operator

$$\hat{\Pi}\psi(x) = \psi'(x) = \psi(-x)$$

$$\hat{\Pi}\psi(x,y,z) = \psi'(x,y,z) = \psi(-x,-y,-z)$$

$$\hat{\Pi}\psi(r,\theta,\varphi) = \psi'(x,y,z) = \psi(r,\pi-\theta,\phi+\pi)$$

Rotation Operator (about z axis through an φ)

$$\hat{R}_z(\varphi)\psi(r,\theta,\phi) = \psi'(r,\theta,\phi) = \psi(r,\theta,\phi-\varphi)$$

4.2 The Translation Operator

by Taylor series

$$\begin{aligned} \hat{T}(a)\psi(x) = \psi(x-a) &= \sum_{n=0}^{\infty} \frac{1}{n!}(-a)^n \frac{\mathrm{d}^n}{\mathrm{d}x^n}\psi(x) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{-ia}{\hbar}\hat{p}\right)^n \psi(x) \end{aligned} \quad \Rightarrow$$

"generator" of translations

$$\boxed{\hat{T}(a) = \exp\left[-\frac{ia}{\hbar}\hat{p}\right]}$$

- $\hat{T}(a)$ is a unitary operator

$$\hat{T}(a)^{-1} = \hat{T}(-a) = \hat{T}(a)^\dagger$$

4.2.1 How Operators Transform

$$\begin{aligned} \langle\psi'|\hat{Q}|\psi'\rangle &= \langle\psi|\hat{Q}'|\psi\rangle \\ &= \langle\psi|\hat{T}^\dagger\hat{Q}\hat{T}|\psi\rangle \end{aligned} \quad \Rightarrow \quad \boxed{\hat{Q}' = \hat{T}^\dagger\hat{Q}\hat{T}}$$

4.2.2 Translational Symmetry

A system is translationally invariant if the Hamiltonian is unchanged by the transformation, then

$$\hat{H}' = \hat{T}^\dagger\hat{H}\hat{T} = \hat{H} \quad \Rightarrow \quad \left[\hat{H}, \hat{T}\right] = 0$$

1. Discrete translation symmetry and Bloch's Theorem
2. Continuous translational symmetry and MomentumConservation

4.3 Conservation Laws

- First Definition: $\langle Q\rangle$ is independent of time
- Second Definition: The probability of getting any particular value is independent o f time

4.4 Parity

4.4.1 Parity in One Dimension

- $\hat{\Pi}(a)$ is a unitary operator

$$\hat{\Pi}(a)^{-1} = \hat{\Pi}(-a) = \hat{\Pi}(a)^\dagger$$

- $\hat{\Pi}$ is Hermitian

Inversion symmetry

$$\left[\hat{H}, \hat{\Pi}\right] = 0$$

Parity Conservation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\Pi\rangle = 0$$

4.4.2 Parity in Three Dimensions

4.4.3 Parity Selection Rules

4.5 Rotational Symmetry

4.5.1 Rotations About the z Axis

$$\hat{R}_z(\varphi) = \exp\left[-\frac{i\varphi}{\hbar}\hat{L}_z\right]$$

4.5.2 Rotations in Three Dimension

$$\boxed{\hat{R}_n(\varphi) = \exp\left[-\frac{i\varphi}{\hbar}\mathbf{n}\cdot\hat{\mathbf{L}}\right]}$$

4.6 Degeneracy

4.7 Rotational Selection Rules

4.7.1 Selection Rules for Scalar Operators

4.7.2 Selection Rules for Vector Operators

4.8 Translation in Time

generator of translations in time

$$\boxed{\hat{U}(t) = \exp\left[-\frac{it}{\hbar}\hat{H}\right]}$$

4.8.1 The Heisenberg Picture

4.8.2 Time-Translation Invaraince

Energy Conservation is a consequence of time-translation invar	aince

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{H} \right\rangle = 0$$

Chapter 5

Time-Independent Perturbation Theory

5.1 Nondegenerate Perturbation Theory

5.1.1 General Formulation

Perturbation theory is a systematic procedure for obtaining approximation solutions to the perturbed problem, by building on the known exact solutions to the unperturbed theory

$$H = H^0 + \lambda H'$$

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

- E_n^1: first-order correction to the nth eigenvalue
- ψ_n^1: first-order correction to the nth eigenfunction

Plugging into

$$H\psi_n = E_n\psi$$

we have

- to lowest order (λ^0)
$$H^0\psi_n^0 = E_n^0\psi_n^0$$
- to first order λ^1
$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$
- to second order λ^2
$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

5.1.2 First-Order Theory

$$\left\langle \psi_n^0 \middle| H^0\psi_n^1 \right\rangle + \left\langle \psi_n^0 \middle| H^0\psi_n^0 \right\rangle = E_n^0 \left\langle \psi_n^0 \middle| \psi_n^1 \right\rangle + E_n^1 \left\langle \psi_n^0 \middle| \psi_n^0 \right\rangle$$

$$\Rightarrow \qquad \boxed{E_n^1 = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^0 \right\rangle}$$

rewrite first-order wave function

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0 \qquad \leftarrow \qquad \psi_n^1 = \sum_{m\neq n} c_m^{(n)}\psi_m^0$$

Taking the inner product with ψ_l^0

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\left\langle\psi_l^0\middle|\psi_m^0\right\rangle = -\left\langle\psi_l^0\middle|H'\middle|\psi_n^0\right\rangle + E_n^1\left\langle\psi_n^0\middle|\psi_l^0\middle|\psi_n^0\right\rangle$$

If $l \neq m$

$$\Rightarrow \qquad \boxed{\psi_n^1 = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}\psi_m^0}$$

5.1.3 Second-Order Energies

$$\left\langle\psi_n^0\middle|H^0\psi_n^2\right\rangle + \left\langle\psi_n^0\middle|H'\psi_n^1\right\rangle = E_n^0\left\langle\psi_n^0\middle|\psi_n^2\right\rangle + E_n^1\left\langle\psi_n^0\middle|\psi_n^1\right\rangle + E_n^2\left\langle\psi_n^0\middle|\psi_n^0\right\rangle$$

$$\Rightarrow \qquad E_n^2 = \left\langle\psi_n^0\middle|H'\middle|\psi_n^1\right\rangle = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle\,\langle\psi_n^0|H'|\psi_m^0\rangle}{E_n^0 - E_m^0}$$

$$\Rightarrow \qquad \boxed{E_n^2 = \sum_{m\neq n}\frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}}$$

5.2 Degenerate Perturbation Theory

5.2.1 Two-Fold Degeneracy

Suppose that

$$H^0\psi_a^0 = E^0\psi_a^0, \qquad H^0\psi_b^0 = E^0\psi_b^0, \qquad \left\langle\psi_a^0\middle|\psi_b^0\right\rangle = 0$$

Note that

$$\psi_0 = \alpha\psi_a^0 + \beta\psi_b^0, \qquad H^0\psi^0 = E^0\psi^0$$

The fundamental result of degenerate perturbation theory

$$\boxed{E_\pm^1 = \frac{1}{2}\Big[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab|^2}}\Big]}$$

5.2.2 "Good" States

Theorem: Let A be a hermitian operator that commutes with H^0 and H'. If ψ_a^0 and ψ_b^0 (the degenerate eigenfunction of H^0) are also eigenfunctions of A, with distinct eigenvalues,

$$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_a^0 = \mu\nu_a^0, \quad \text{and } \mu \neq \nu$$

then ψ_a^0 and ψ_b^0 are the "good" states to use in perturbation theory.
Proof:

5.2.3 Higher-Order Degeneracy

5.3 The Fine Structure of Hydrogen

5.3.1 The Relativistic Correction

$$\begin{aligned} T &= \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2 \\ p &= \frac{mv}{\sqrt{1-(v/c)^1}} \end{aligned} \quad \Rightarrow$$

expanding in powers of small number (p/mc)

$$\begin{aligned} T =& \sqrt{p^2c^2 + m^2c^4} - mc^2 \\ =& mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots - 1\right] \\ =& \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots \end{aligned}$$

$$E_r^1 = \langle H_r' \rangle = -$$

5.4 The Zeeman Effect

5.5 Hyperfine Splitting in Hydrogen

Chapter 6

The Variational Principle

6.1 Theory

Variational principle

$$\boxed{E_{gs} \leqslant \langle\psi|H|\psi\rangle \equiv \langle H\rangle}$$

- Pick any normalized function ψ whatsoever
- E_{gs}: ground state energy
- Proof:

$$\psi = \sum_n c_n \psi_n, \qquad \text{with } H\psi_n = E_n \psi_n$$

$$1 = \sum_n |c_n|^2 \qquad \langle H\rangle = \sum_n E_n |c_n|^2$$

$$\because E_{gs} \leqslant E_n \qquad \therefore \langle H\rangle \geqslant E_{gs} \sum_n |c_n|^2 = E_{gs}$$

Examples:

- 1-d harmonic oscillator

$$\text{"trial wave function"}: \quad \psi(x) = A\mathrm{e}^{-bx^2} \qquad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

$$\frac{\mathrm{d}}{\mathrm{d}b}\langle H\rangle = \frac{\hbar^2}{2m} - \frac{m\omega}{8b^2} = 0 \qquad \Rightarrow b = \frac{m\omega}{2\hbar} \qquad \Rightarrow \langle H\rangle_{\min} = \frac{1}{2}\hbar\omega$$

- delta function potential

$$\text{"trial wave function"}: \quad \psi(x) = A\mathrm{e}^{-bx^2} \qquad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

$$\frac{\mathrm{d}}{\mathrm{d}b}\langle H\rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \qquad \Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4} \qquad \Rightarrow \langle H\rangle_{\min} = -\frac{m\alpha^2}{\pi\hbar^2}$$

6.2 The Ground State of Helium

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

The ground state energy measured in lab:

$$E_{gs} = -78.975\,\mathrm{eV} \qquad \text{experimental}$$

If ignore V_{ee}

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}\mathrm{e}^{-2(r_1+r_2)/a} \qquad \text{with } 8E_1 = -109\,\mathrm{eV}$$

$$\Rightarrow \quad H\psi_0 = (8E_1 + V_{ee})\psi_0 \qquad \Rightarrow \quad \langle H\rangle = 8E_1 + \langle V_{ee}\rangle$$

trial function

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3}\mathrm{e}^{-Z(r_1+r_2)/a}$$

- Z: effective nuclear charge, variational parameter

rewrite H

$$\begin{aligned} H = &-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) \\ &+ \frac{e^2}{4\pi\epsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right) \end{aligned}$$

$$\langle H\rangle = 2Z^2E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \langle V_{ee}\rangle$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{Z}{a} \qquad \langle V_{ee}\rangle = \frac{5Z}{8a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5Z}{4}E_1$$

$$\Rightarrow \quad \langle H\rangle = \left[-aZ^2 + (27/4)Z\right]E_1 \qquad \to \qquad \frac{\mathrm{d}}{\mathrm{d}Z}\langle H\rangle = 0$$

$$\Rightarrow \qquad Z = \frac{27}{16} \qquad \langle H\rangle = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 = -77.5\,\mathrm{eV}$$

6.3 The Hydrogen Molecule Ion

Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r} + \frac{1}{r'}\right)$$

Trial wave function

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}}\mathrm{e}^{-r/a}$$

6.4 The Hydrogen Molecule

Chapter 7

The WKB Approximation

Chapter 8

Scattering

Chapter 9

Quantum Dynamics

9.1 Two-level System

Suppose two states of (unperturbed) System

$$\hat{H}^0\psi_b = E_a\psi_a \qquad \hat{H}^0\psi_b = E_b\psi_b$$

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}, \qquad (i, j = a, b)$$

9.1.1 The Perturbed System

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b\hbar}$$

$$|c_a|^2 + |c_b|^2 = 1$$

Solve for $c_a(t)$ and $c_b(t)$

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \quad \text{where} \quad \hat{H} = \hat{H}^0 + \hat{H}'(t)$$

We find

$$c_a\Big(\hat{H}\psi_a\Big)e^{-iE_a t/\hbar} + c_b\Big(\hat{H}'\psi_b\Big)e^{-iE_b t/\hbar} = i\hbar\big(\dot{c}_a\psi_a e^{-iE_a t/\hbar} + \dot{c}_b\psi_b t/\hbar\big)$$

We define

$$H'_{ij} \equiv \langle\psi_i|\hat{H}'|\psi_j\rangle \qquad \Rightarrow \qquad \hat{H}'_{ji} = \big(H'_{ij}\big)^*$$

Take the inner product with ψ_a and ψ_b

$$\begin{cases} \dot{c}_a = -\frac{i}{\hbar}\Big[c_a\hat{H}'_{aa} + c_b\hat{H}'_{ab}e^{-i(E_b-E_a)t/\hbar}\Big] \\ \dot{c}_b = -\frac{i}{\hbar}\Big[c_a\hat{H}'_{bb} + c_b\hat{H}'_{ba}e^{i(E_b-E_a)t/\hbar}\Big] \end{cases}$$

$$\hat{H}'_{aa} = \hat{H}'_{bb} = 0 \qquad \Rightarrow \boxed{\begin{aligned} \dot{c}_a &= -\frac{i}{\hbar}\hat{H}'_{ab}e^{-i\omega_0 t}c_b \\ \dot{c}_a &= -\frac{i}{\hbar}\hat{H}'_{ba}e^{-i\omega_0 t}c_a \end{aligned}} \quad \omega_0 \equiv \frac{E_a - E_b}{\hbar}$$

9.1.2 Time-Dependent Perturbation Theory

Suppose the particles states out in the lower state:

$$c_a(0) = 1 \qquad c_b(0) = 0$$

Zeroth Order:

$$c_a^{(0)}(t) = 1 \qquad c_b^{(0)}(t) = 0$$

First Order:

$$\begin{aligned} \frac{\mathrm{d}c_a^{(1)}}{\mathrm{d}t} &= 0 \Rightarrow c_a(1)(t) = 1 \\ \frac{\mathrm{d}c_b^{(1)}}{\mathrm{d}t} &= -\frac{i}{\hbar}\hat{H}'_{ba}\mathrm{e}^{-i\omega_0 t} \Rightarrow c_b^{(1)}(t) = -\frac{i}{\hbar}\int_0^t \hat{H}'_{ba}(t')\mathrm{e}^{i\omega_0 t'}\mathrm{d}t' \end{aligned}$$

9.1.3 Sinusoidal Perturbations

Suppose

$$\hat{H}'(\mathbf{r}, t) = V(\mathbf{r})\cos(\omega t) \quad \Rightarrow \quad \begin{aligned} H'_{ab} &= V_{ab}\cos(\omega t) \\ V_{ab} &\equiv \langle\psi_a|V|\psi_b\rangle \end{aligned}$$

Assume

$$\omega_0 + \omega \gg |\omega_0 - \omega|$$

we have

$$\begin{aligned} c_b(t) \approx c_b^{(1)}(t) &= -\frac{iV_{ba}}{2\hbar}\int_0^t \left[\mathrm{e}^{i(\omega_0+\omega)t'} + \mathrm{e}^{i(\omega_0-\omega)t'}\right]\mathrm{d}t' \\ &= -\frac{V_{ba}}{2\hbar}\left[\frac{\mathrm{e}^{i(\omega_0+\omega)t} - 1}{\omega_0+\omega} + \frac{\mathrm{e}^{i(\omega_0-\omega)t} - 1}{\omega_0-\omega}\right] \\ &\approx -\frac{V_{ba}}{2\hbar}\frac{\mathrm{e}^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left[\mathrm{e}^{i(\omega_0-\omega)t/2} - \mathrm{e}^{-i(\omega_0-\omega)t/2}\right] \\ &= -i\frac{V_{ba}}{\hbar}\frac{\sin\left[(\omega_0-\omega)t/2\right]}{\omega_0-\omega}\mathrm{e}^{i(\omega_0-\omega)t/2} \end{aligned}$$

Transition probability

$$\boxed{P_{a\to b}(t) = |c_b(t)|^2 \approx \frac{|V_{ba}|^2}{\hbar^2}\frac{\sin^2\left[(\omega_0-\omega)t/2\right]}{(\omega_0-\omega)^2}}$$

9.2 Emission and Absortion of Radiationj

9.2.1 Electromagnetic Waves

The atom is exposed to a sinusoidally oscillating electric field

$$\mathbf{E} = E_0\cos(\omega t)\hat{k} \qquad H' = -qE_0 z\cos(\omega t)$$

$$\Rightarrow \quad H_{ba} = -\wp E_0\cos(\omega t), \quad \text{where } \wp \equiv q\langle\psi_b|z|\psi_a\rangle$$

in section 11.1.3, with

$$V_{ba} = -\wp E_0$$

9.2.2 Absortion, Stimulation Emission, and Spontaneous Emission

Absortion (start off in the lower state)

$$P_{a\to b}(t) = \left(\frac{|\wp|E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

- $c_a(0) = 1, c_b(0) = 0$
- the atom absorts energy $E_b - E_a = \hbar\omega_0$ from the electromagnetic field

Stimulation Emission (start off in the upper state)

$$P_{b\to a}(t) = |c_a(t)|^2 = P_{a\to b}(t)$$

- $c_a(0) = 0, c_b(0) = 1$
- The electromagnetic field gains energy $\hbar\omega_0$ form the atom

Spontaneous Emission

- An atom in the excited state makes a transition downward, with the release of a photon, but without any applied electromagnetic field to initate the process

9.2.3 Incoherent Perturbations

9.3 Spontaneous Emission

9.3.1 Einstein's A and B

9.3.2 The Life tiem of an Excites State

9.3.3 Selection Rules

9.4 Fermi's Golden Rule

9.5 The Adiabatic Approximation