Formularium Quantum Mechanics

0 Braket notation and Hilbert spaces

Commuting operators share an eigenbasis:

$$[A, B] = 0 \wedge A\,|\phi_i\rangle = a_i\,|\phi_i\rangle \implies B\,|\phi_i\rangle = b_i\,|\phi_i\rangle \tag{1}$$

A set of kets $\{\ |\,\psi_i\rangle\ \}$ is an orthonormal and complete basis of a Hilbert space if:

$$\langle\psi_i\,|\,\psi_j\rangle = \delta_{ij} \qquad\qquad \sum_i |\psi_i\rangle\langle\psi_i| = \mathbb{1} \tag{2}$$

Fourier transform between momentum and position representations:

$$\Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3/2} \int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\Phi(\mathbf{p}, t)d\mathbf{p} \tag{3}$$

$$\Phi(\mathbf{p}, t) = (2\pi\hbar)^{-3/2} \int e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\Psi(\mathbf{r}, t)d\mathbf{r} \tag{4}$$

1 The Formalism of QM

The Fourier transform factor:

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{5}$$

Scalar product:

$$\langle\Psi_1|\Psi_2\rangle = \int \Psi_1^*(\mathbf{r})\Psi_2(\mathbf{r})d\mathbf{r} \tag{6}$$

Adjoint of an operator:

$$\langle X\,|\,A\Psi\rangle = \left\langle A^\dagger X\,\middle|\,\Psi\right\rangle \tag{7}$$

Hermitian operator:

$$\langle X\,|\,A\Psi\rangle = \langle AX\,|\,\Psi\rangle \tag{8}$$

Adjoint of function of a Hermitian operator:

$$(f(A))^\dagger = f^*(A) \tag{9}$$

Unitary operator:

$$UU^\dagger = \mathbb{1} \tag{10}$$

Closure relation:

$$\sum_n \psi_n^*(\mathbf{r}')\psi_n(\mathbf{r}) = \delta(\mathbf{r}' - \mathbf{r}) \tag{11}$$

$$\sum_n |\psi_n\rangle\,\langle\psi_n| = \mathbb{1} \tag{12}$$

Canonical commutation relation:

$$[x_i, p_j] = i\hbar\mathbb{1}\delta_{ij} \tag{13}$$

Uncertainty principle:

$$\Delta A\Delta B \geq \frac{1}{2}|\,\langle[A, B]\rangle\,| \tag{14}$$

Time evolution of expectation value:

$$i\hbar \frac{\mathrm{d}\langle \mathcal{O} \rangle}{\mathrm{d}t} = \langle [\mathcal{O}, H] \rangle + i\hbar \left\langle \frac{\partial \mathcal{O}}{\partial t} \right\rangle \tag{15}$$

Ehrenfest Theorem:

$$m\frac{\mathrm{d}\langle \mathbf{r} \rangle}{\mathrm{d}t} = \langle \mathbf{p} \rangle \tag{16}$$

$$\frac{\mathrm{d}\langle \mathbf{p} \rangle}{\mathrm{d}t} = -\langle \nabla V \rangle \tag{17}$$

Momentum operator in position representation

$$\mathbf{p} \to -i\hbar \boldsymbol{\nabla} \tag{18}$$

Position operator in momentum representation

$$\mathbf{r} \to i\hbar \boldsymbol{\nabla}_{\mathbf{p}} \tag{19}$$

Commutation of H and $\mathbf{r}$

$$[\mathbf{r}, H] = \frac{i\hbar}{m}\mathbf{p} \tag{20}$$

Commutator algebra

antisymmetry

$[A, B] = -[B, A]$

bilinearity, product rules

$[A, B + C] = [A, B] + [A, C]$

$[A, BC] = [A, B]C + B[A, C]$

$[AB, C] = A[B, C] + [A, C]B$

Jacobi identity

$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

Operator translation

$$U_T(\mathbf{a}) = \exp\left(-\frac{i}{\hbar}\mathbf{a} \cdot \mathbf{P}_{op}\right) \tag{21}$$

2 Free Particle

TISE and TDSE:

$$H|\psi\rangle = E(p)|\psi\rangle \tag{22}$$

$$H|\Psi(t)\rangle = i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} \tag{23}$$

Useful integrals ($a, J \in \mathbb{R}_0$):

$$\int \mathrm{d}x e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}} \tag{24}$$

$$\int \mathrm{d}x e^{-\frac{1}{2}ax^2 + Jx} = \sqrt{\frac{2\pi}{a}} e^{\frac{J^2}{2a}} \tag{25}$$

$$\int \mathrm{d}x e^{-\frac{1}{2}ax^2 + iJx} = \sqrt{\frac{2\pi}{a}} e^{-\frac{J^2}{2a}} \tag{26}$$

$$\int \mathrm{d}x x^2 e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}} \frac{1}{a} \tag{27}$$

General form of a wavepacket:

$$|\Psi(t)\rangle = \int \mathrm{d}p \phi(p) e^{-iHt/\hbar} |p\rangle \tag{28}$$

3 Generators and Bound State (SHO!)

Virial Theorem ($H|\psi_E\rangle = E|\psi_E\rangle$):

$$2\langle T \rangle_{\psi_E} = \langle \mathbf{r} \cdot \nabla V \rangle_{\psi_E} \tag{29}$$

Variations of states and operators under infitesimal unitary transformations

$$U(\delta\theta) = \mathbb{1} + i\delta\theta F$$

$$|\Psi\rangle \to |\Psi'\rangle = U(\delta\theta)\,|\Psi\rangle \qquad \delta\,|\Psi\rangle = i\delta\theta F\,|\Psi\rangle \tag{30}$$

$$A \to A' = U(\delta\theta) A U(\delta\theta)^\dagger \qquad \delta A = i\delta\theta[F, A] \tag{31}$$

1D SHO and ladder operators:

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2 = H = \hbar\omega(a^\dagger a + \frac{1}{2})$$

$$a = \frac{1}{\sqrt{2}}\Big(\sqrt{\frac{m\omega}{\hbar}}x + i\frac{p}{\sqrt{m\omega\hbar}}\Big) \tag{32}$$

$$[a, a^\dagger] = \mathbb{1} \quad [N, a^\dagger] = a^\dagger \quad [N, a] = -a \tag{33}$$

$$a^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{34}$$

$$a\,|n\rangle = \sqrt{n}\,|n-1\rangle \tag{35}$$

$$N\,|n\rangle = a^\dagger a\,|n\rangle = n\,|n\rangle \tag{36}$$

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}\,|0\rangle \tag{37}$$

4 Addition of Angular Momentum

Angular momentum in position representation:

$$\mathbf{L} = -i\hbar(\mathbf{r} \times \boldsymbol{\nabla}) \tag{38}$$

Commutation relations:

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \tag{39}$$

Rotation operator:

$$U_{\hat{\mathbf{n}}}(\alpha) = \exp\left(-\frac{i}{\hbar}\alpha\hat{\mathbf{n}}\cdot\mathbf{L}\right) \tag{40}$$

Raising and lowering operators:

$$J_\pm = J_x \pm iJ_y \tag{41}$$

Generic facts about angular momentum:

$$\begin{aligned}
\mathbf{J}^2\,|jm\rangle &= j(j+1)\hbar^2\,|jm\rangle \\
J_z\,|jm\rangle &= m\hbar\,|jm\rangle \\
J_\pm\,|jm\rangle &= \sqrt{j(j+1) - m(m\pm 1)}\hbar\,|j, m\pm 1\rangle \\
m &= -j, \ldots, j \\
J_\pm J_\mp &= \mathbf{J}^2 - J_z^2 \pm \hbar J_z \\
[J_+, J_-] &= 2\hbar J_z \\
[J_z, J_\pm] &= \pm\hbar J_\pm
\end{aligned}$$

Clebsch-Gordan coefficients:

$$\begin{aligned}
|j_1 m_1 j_2 m_2\rangle &= |j_1 m_1\rangle \otimes |j_2 m_2\rangle \\
|j_1 j_2 j m\rangle &= \sum_{m_1=-j_1}^{+j_1}\sum_{m_2=-j_2}^{+j_2} C_{jm}^{m_1 m_2}\,|j_1 m_1 j_2 m_2\rangle \\
C_{jm}^{m_1 m_2} &= \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle \\
m &= m_1 + m_2 \\
j &= |j_1 - j_2|, \ldots, j_1 + j_2
\end{aligned}$$

Pauli matrices $S_a = \frac{\hbar}{2}\sigma_a$ for spin 1/2:

$$\begin{aligned}
\sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
\sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
\sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
\mathbf{S}^2 &= \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\end{aligned}$$

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

For spin 1 particles:

$$\mathbf{S}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$S_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

$$S_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Basis vectors:

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

General form of operators on two Hilbert Spaces:

$$\mathbf{S} = \mathbf{S}^{(1)} \otimes \mathbb{1}^{(2)} + \mathbb{1}^{(1)} \otimes \mathbf{S}^{(2)} \tag{42}$$

5 3D Potentials

Hamiltonian for a charged particle in electromagnetic field ($\mathbf{B} = \nabla \times \mathbf{A}$, $\mathbf{E} = -\nabla\phi$):

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi \tag{43}$$

General solution of an infinite square well ($V = 0,\ \mathbf{r} \in [0, L_x] \times [0, L_y] \times [0, L_z],\ V = +\infty$, elsewhere)

$$\psi(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{44}$$

With energy

$$E = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_y^2}{L_y^2}\right), \quad n_i = 1, 2, \ldots \tag{45}$$

3D SHO Hamiltonian

$$H = \frac{1}{2m}\mathbf{p}^2 + \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2 \tag{46}$$

6 Hydrogen & time-independent perturbation theory

Fine structure constant

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} \approx 1/137 \tag{47}$$

Bohr radius

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \tag{48}$$

General radius

$$a = \frac{m}{\mu} a_0 \tag{49}$$

(Unperturbed) energy levels

$$E_n^{(0)} = -\frac{e^2}{4\pi\epsilon_0 a}\frac{Z^2}{2n^2} = -\frac{\mu c^2}{2}\frac{(Z\alpha)^2}{n^2} \tag{50}$$

Non-degenerate: First & second order energy correction

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle \equiv H'_{nn} \tag{51}$$

$$E_n^{(2)} = \sum_{n \neq k} \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{52}$$

First order correction to wavefunction

$$\psi_n^{(1)} = \sum_{l \neq n} \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} \psi_l^{(0)} \tag{53}$$

Degenerate: First order correction

$$E_{nr}^{(1)} = \widetilde{H}'_{nr,nr} \tag{54}$$

where

$$\widetilde{H}'_{nr,ns} = \left\langle \chi_{nr}^{(0)} \middle| H' \middle| \chi_{ns}^{(0)} \right\rangle \tag{55}$$

$$H'_{nr,ns} = \left\langle \psi_{nr}^{(0)} \middle| H' \middle| \psi_{ns}^{(0)} \right\rangle \tag{56}$$

$$\chi_{nr}^{(0)} = \sum_{s=1}^{\alpha} c_{rs} \psi_{ns}^{(0)} \tag{57}$$

$$\tag{58}$$

7 Variational method and WKB

Variational method:

$$\langle \phi | H | \phi \rangle \geq E_{\text{ground state}} \tag{59}$$

WKB for bound state

$$\frac{1}{\pi} \int_{x_1}^{x_2} \frac{p(x)}{\hbar} dx = n + \frac{1}{2} \tag{60}$$

Where x_1 and x_2 are the classical turning points, and the momentum is given by:

$$p(x) = \sqrt{2m(E - V(x))}$$

8 Time dependent perturbation theory

First order transition amplitude:

$$H = H_0 + H'(t) \tag{61}$$

$$\mathcal{A}_{f \leftarrow i}^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \mathrm{d}t' \, \langle f | e^{iH_0 t'/\hbar} H'(t') e^{-iH_0 t'/\hbar} | i \rangle \tag{62}$$

$$P_{f \leftarrow i}(t) = |\mathcal{A}_{f \leftarrow i}(t)|^2 \tag{63}$$

$$\Gamma_{f \leftarrow i} = \frac{\mathrm{d}P_{f \leftarrow i}(t)}{\mathrm{d}t} = \lim_{t \to \infty} \frac{P_{f \leftarrow i}(t)}{t} \tag{64}$$

9 Assorti

Various terms you can add to the Hamiltonian:

$$\text{Electric field:} \quad H' = -qEz \tag{65}$$

$$\text{Magnetic field:} \quad H' = -\boldsymbol{\mu}_{L,S} \cdot \mathbf{B} = -g_{L,S}\frac{q}{2m}\mathbf{B} \cdot (\mathbf{L} \text{ or } \mathbf{S}) \tag{66}$$

$$\text{LS coupling:} \quad H' = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{-Zq^2}{4\pi\epsilon_0 r}\right)\mathbf{L} \cdot \mathbf{S} \tag{67}$$

Super-useful formula:

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) \tag{68}$$

Selection rules for dipole transitions:

$$\Delta l = \pm 1 \quad \Delta m_l = 0, \pm 1 \quad \Delta m_s = 0 \tag{69}$$

Laplacian in spherical coordinates:

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}f\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}f\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}f \tag{70}$$