Week 1 Notes

I. Bra-ket Notation

A. Eigenstates → kets $|\psi\rangle \longleftrightarrow \psi$ wavefunctions

$\langle\psi| \longleftrightarrow \psi^*$

$\langle\psi|\psi\rangle = 1$ Normalization

B. Matrices / Operators

$$A|\psi\rangle = |\psi'\rangle \qquad B|\psi\rangle = |\psi''\rangle$$

In general $AB \neq BA$

$$[A,B] = AB - BA \qquad \text{Commutator of } A \,\&\, B$$

C. Projectors

if $|\psi\rangle\langle\phi| = A$

$$A|\chi\rangle = |\psi\rangle\underbrace{\langle\phi|\chi\rangle}_{\text{complex }\#}$$

$$P_\psi = |\psi\rangle\langle\psi|$$

$$P_\psi|\phi\rangle = |\psi\rangle\langle\psi|\phi\rangle \qquad \text{Projector Operators}$$

$$P_\psi^2 = P_\psi P_\psi = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = P_\psi$$

D. Orthonormal Sets of Eigenvectors

$$\langle u_i|u_j\rangle = \delta_{ij} \qquad 1 = \sum_i |u_i\rangle\langle u_i|$$

$$|\psi\rangle = \sum_i c_i|u_i\rangle$$

$$|\psi\rangle = 1\,|\psi\rangle = \sum_i |u_i\rangle\langle u_i|\psi\rangle$$

$$= \sum_i c_i|u_i\rangle$$

$$c_i = \langle u_i|\psi\rangle$$

E. Representations

kets :

$$\begin{pmatrix} \langle u_1 | \psi \rangle \\ \langle u_2 | \psi \rangle \\ \vdots \\ \langle u_i | \psi \rangle \\ \vdots \end{pmatrix} \rightarrow |\psi\rangle$$

bras :

$$\begin{pmatrix} \langle \phi | u_1 \rangle & \langle \phi | u_2 \rangle & \ldots & \langle \phi | u_i \rangle & \ldots \end{pmatrix}$$

Operators:

$$A_{ij} = \langle u_i | A | u_j \rangle$$

$$\begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1j} \\ A_{21} & \ddots & & \\ \vdots & & \ddots & \\ A_{i1} & & & A_{ij} \end{pmatrix}$$

F. Eigenvectors

$$A|\psi\rangle = \lambda |\psi\rangle$$

$A = A^{+}$ Hermitian operators :

$$\langle \phi | A | \psi \rangle^* = \langle \psi | A | \phi \rangle$$

$$\langle \psi | A | \psi \rangle = \lambda \langle \psi | \psi \rangle$$

$$\langle \psi | A | \psi \rangle^* = \langle \psi | A^{+} | \psi \rangle = \langle \psi | A | \psi \rangle$$

$\underline{\lambda \text{ real}}$.

G. Postulates of Q.M.

see Atkins & C-T III.

H. Schrodinger Eqn.:

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

$\mathcal{H}$ = Hamiltonian

Scalar Potential: $\mathcal{H}(r,p) = \frac{p^2}{2m} + V(r)$

$$\langle A\rangle_\psi = \langle\psi|A|\psi\rangle$$

I. Conservation of Probability

$$\frac{d}{dt}\langle\psi(t)|\psi(t)\rangle = \left[\frac{d}{dt}\langle\psi(t)|\right]|\psi(t)\rangle + \langle\psi(t)|\left[\frac{d}{dt}|\psi(t)\rangle\right]$$

$$\underbrace{\left[\frac{d}{dt}\langle\psi(t)|\right]}_{= -\frac{1}{i\hbar}\langle\psi(t)|\mathcal{H}(t)} \qquad \underbrace{\left[\frac{d}{dt}|\psi(t)\rangle\right]}_{= \frac{1}{i\hbar}H(t)|\psi(t)\rangle}$$

$$= -\frac{1}{i\hbar}\langle\psi(t)|\mathcal{H}(t)|\psi(t)\rangle + \frac{1}{i\hbar}\langle\psi(t)|\mathcal{H}|\psi(t)\rangle$$

$$\frac{d}{dt}\langle\psi(t)|\psi(t)\rangle = 0$$

J. Evolution of the Expectation Value

$$\langle A\rangle(t) = \langle\psi(t)|A|\psi(t)\rangle$$

$$\frac{d}{dt}\langle\psi|A|\psi\rangle = \left[\frac{d}{dt}\langle\psi|\right]A|\psi\rangle + \langle\psi|A\left[\frac{d}{dt}|\psi\rangle\right] + \langle\psi|\overset{0}{\cancel{\frac{\partial A}{\partial t}}}|\psi\rangle$$

$$= \frac{1}{i\hbar}\langle\psi|(AH - HA)|\psi\rangle = \frac{1}{i\hbar}\langle[A, H(t)]\rangle$$

Handout A

Density Matrix Formalism:

1) Define $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$.

where $|\psi(t)\rangle = \sum_n c_n(t)\,|n\rangle$ in the $|n\rangle$ basis

Note that:

$$\langle p|\psi(t)\rangle = \sum_n c_n(t)\langle p|n\rangle$$

$$\langle p|\psi(t)\rangle = c_p(t)$$

2) Since $|\psi(t)\rangle$ is normalized:

$$\langle\psi(t)|\psi(t)\rangle = 1$$

$$1 = \sum_n \langle\psi(t)|n\rangle\langle n|\psi(t)\rangle$$

$$= \sum_n \langle n|\psi(t)\rangle\langle\psi(t)|n\rangle$$

$$= \sum_n \langle n|\rho(t)|n\rangle$$

$$\boxed{1 = \mathrm{Tr}\,\rho(t)}$$

3) Expectation Value of an operator A:

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \sum_{n,p}\langle\psi|n\rangle\langle n|A|p\rangle\langle p|\psi\rangle$$

$$= \sum_{n,p}\langle n|A|p\rangle\langle p|\psi\rangle\langle\psi|n\rangle$$

$$\langle A\rangle = \sum_n \langle n|A\rho(t)|n\rangle = \underline{\underline{\mathrm{Tr}\{A\rho\}}}$$

In thermal equilibrium at temperature T,

$$\rho = Z^{-1} e^{-H/kT} \quad \text{where } Z = \mathrm{Tr}\{e^{-H/kT}\}$$

Consider the basis $|n\rangle$ which is the eigenbasis of $\mathcal{H}$:

$$\mathcal{H}|n\rangle = E_n |n\rangle$$

$$\rho_{np} = Z^{-1}\langle n| e^{-\mathcal{H}/kT}|p\rangle = Z^{-1} e^{-E_n/kT}\delta_{np}$$

only $\rho_{nn} \neq 0$.

Thus:

$$\langle A\rangle = \mathrm{Tr}(\rho A) = Z^{-1}\sum_n A_{nn} e^{-E_n/kT}$$

and the energy, $\langle E\rangle$, is given by

$$\langle E\rangle = \frac{\sum_n E_n e^{-E_n/kT}}{\sum_n e^{-E_n/kT}}$$

Simple Harmonic Oscillator in Thermal Equilibrium:

$$Z = \sum_{n=0}^{\infty} \langle n | e^{-\mathcal{H}/kT} | n \rangle$$

$$= \sum_{n=0}^{\infty} e^{-\hbar\omega(n+\frac{1}{2})/kT} \qquad \text{in the energy representation}$$

$$= e^{-\hbar\omega/2kT} \left[1 + e^{-\hbar\omega/kT} + e^{-2\hbar\omega/kT} + \cdots \right]$$

$$Z = \frac{e^{-\hbar\omega/2kT}}{1 - e^{-\hbar\omega/kT}}$$

$$\langle H \rangle = \mathrm{Tr}\,(H\rho) = Z^{-1}\, \mathrm{Tr}\,(\mathcal{H} e^{-\mathcal{H}/kT})$$

$$= Z^{-1} \sum_{n=0}^{\infty} \hbar\omega(n+\tfrac{1}{2})\, e^{-\hbar\omega(n+\frac{1}{2})/kT}$$

$$\langle H \rangle = kT^2 \frac{1}{Z} \frac{dZ}{dT} \qquad \left[\text{since } \frac{dZ}{dT} = \frac{1}{kT^2} \sum_{n=0}^{\infty} \hbar\omega(n+\tfrac{1}{2})\, e^{-\hbar\omega(n+\frac{1}{2})/kT}\right.$$

with ~~much~~ some math, one can show

$$\langle H \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

Time Evolution of the Density Operator

$$\frac{d}{dt}\rho(t) = \left(\frac{d}{dt}|\psi(t)\rangle\right)\langle\psi(t)| + |\psi(t)\rangle\left(\frac{d}{dt}\langle\psi(t)|\right)$$

$$= \frac{1}{i\hbar}\mathcal{H}(t)\,|\psi(t)\rangle\langle\psi(t)| + \frac{1}{-i\hbar}|\psi(t)\rangle\langle\psi(t)|\,\mathcal{H}(t)$$

$$\frac{d\rho(t)}{dt} = \frac{1}{i\hbar}\left[\mathcal{H}\rho - \rho\mathcal{H}\right] = \frac{1}{i\hbar}[\mathcal{H},\rho]$$

Spin 1/2 Particles:

I. States in the S_z representation: $|+\rangle$ & $|-\rangle$

$$S_z|+\rangle = +\frac{\hbar}{2}|+\rangle$$

$$S_z|-\rangle = -\frac{\hbar}{2}|-\rangle$$

These are a C S C.O. and $\langle+|+\rangle = \langle-|-\rangle = 1$, $\langle+|-\rangle = 0$
and

$$\underline{1} = |+\rangle\langle+| + |-\rangle\langle-|$$

In the $|\pm\rangle$ bases

$$S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \qquad S_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$

$$\underline{S} = \hat{i}S_x + \hat{j}S_y + \hat{k}S_z$$ $\underline{S}$ is a vector.

The magnitude of $\underline{S}$ is given by $\sqrt{|\underline{S}\cdot\underline{S}|}$

II Spin 1/2 in a magnetic field.

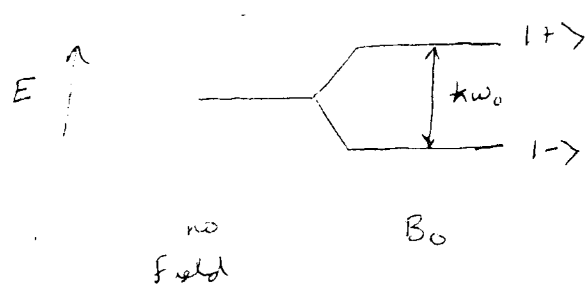
gyromagnetic ratio

$$\mathcal{H} = -\underline{m}\cdot\underline{B} = -\gamma\,\underline{S}\cdot\underline{B}$$

If $\underline{B}$ is in the z direction, $\underline{B} = \hat{k}B_0$

$$\mathcal{H} = -\gamma B_0 S_z = \omega_0 S_z \qquad \omega_0 = -\gamma B_0$$

$$\mathcal{H}|+\rangle = +\frac{\hbar\omega_0}{2}|+\rangle, \quad \mathcal{H}|-\rangle = -\frac{\hbar\omega_0}{2}|-\rangle$$



This is called an Energy Level Diagram.

III General Two Level System

$$\mathcal{H}_0 |\phi_1\rangle = E_1 |\phi_1\rangle$$
$$\mathcal{H}_0 |\phi_2\rangle = E_2 |\phi_2\rangle$$

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \qquad i, j = 1, 2$$

Consider $\mathcal{H} = \mathcal{H}_0 + W$

where W in the $|\phi\rangle$ representation is given by

$$W = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix} \qquad W_{12} = W_{21}^* \quad (W \text{ is Hermitian})$$

The new states that are eigenvectors of $\mathcal{H}$ are $|\pm\rangle$

$$\mathcal{H} = \begin{pmatrix} E_1 + W_{11} & W_{12} \\ W_{21} & E_2 + W_{22} \end{pmatrix} \qquad \text{in the } |\phi\rangle \text{ rep.}$$

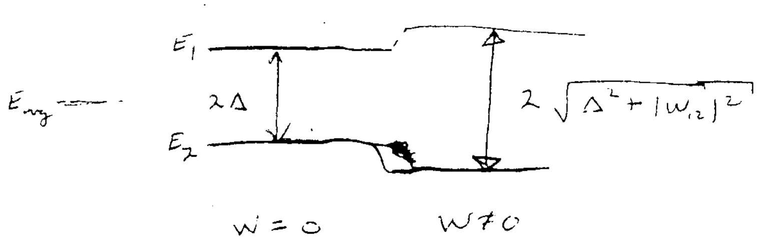
Diagonalization leads to

$$E_+ = \tfrac{1}{2}(E_1 + W_{11} + E_2 + W_{22}) + \tfrac{1}{2}\sqrt{(E_1 + W_{11} - E_2 - W_{22})^2 + 4|W_{12}|^2}$$

$$E_- = \tfrac{1}{2}(E_1 + W_{11} + E_2 + W_{22}) - \tfrac{1}{2}\sqrt{(E_1 + W_{11} - E_2 - W_{22})^2 + 4|W_{12}|^2}$$

If $W_{11} - W_{22} = 0$, then $E_{Avg} \equiv \tfrac{1}{2}(E_1 + E_2)$ & $\Delta = \tfrac{1}{2}(E_1 - E_2)$ and

$$E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{12}|^2}$$



As $\Delta \to 0$, W_{12} becomes more important. This is an "avoided crossing."

Note that $|\phi_1\rangle$ + $|\phi_2\rangle$ are no longer eigenstates of $\mathcal{H}$.

Quantum Mechanical Harmonic Oscillator:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}Kx^2 \qquad [x,p] = xp - px = i\hbar$$

① $E_K > 0$.

In the energy representation

$$\langle k|\mathcal{H}|l\rangle = E_K\,\delta_{kl}$$
$$= \sum_j \frac{1}{2m}\langle k|p|j\rangle\langle j|p|l\rangle + \frac{1}{2}K\langle k|x|j\rangle\langle j|x|l\rangle$$

if $k=l$, then

$$E_K = \sum_j \frac{1}{2m}|\langle k|p|j\rangle|^2 + \frac{1}{2}|\langle k|x|j\rangle|^2$$

Since the R.H.S of this eqn is all positive, $E_K \geq 0$.
$E_K = 0$ if and only if $\langle k|p|j\rangle$ & $\langle k|x|j\rangle$ are zero for all j
But then

$$\langle k|xp-px|k\rangle = i\hbar$$
$$= \sum_j \langle k|x|j\rangle\langle j|p|k\rangle - \langle k|p|j\rangle\langle j|x|k\rangle$$

would be zero. Therefore, it must be true that $E_K > 0$.

② The eigenvalues are evenly spaced by $\hbar\omega$.

Consider $[x,\mathcal{H}]$ and $[p,\mathcal{H}]$

$$[x, \mathcal{H}] = \frac{x\,p^2}{2m} - \frac{p^2 x}{2m} + \tfrac{1}{2}k\,\underbrace{\cancel{(x^3 - x^3)}}_{\to 0}$$

Since $px = xp - i\hbar$ & $xp = px + i\hbar$:

$$[x, \mathcal{H}] = \frac{(px + i\hbar)p}{2m} - \frac{p\,(xp - i\hbar)}{2m} = \frac{i\hbar}{m}p + \underbrace{\cancel{\frac{pxp - pxp}{2m}}}_{\to 0}$$

$$\boxed{[x, \mathcal{H}] = \frac{i\hbar}{m}p}$$

Similarly, $\boxed{[p, \mathcal{H}] = -i\hbar K x}$.

Now in the energy representation again:

$$\langle k|[x,\mathcal{H}]|l\rangle = \sum_j \langle k|x|j\rangle\langle j|\mathcal{H}|l\rangle - \langle k|\mathcal{H}|j\rangle\langle j|x|l\rangle$$

$$= \sum_j \langle k|x|j\rangle E_j \langle j|l\rangle - \langle k|j\rangle E_j \langle j|x|l\rangle$$

$$\boxed{\frac{i\hbar}{m}\langle k|p|l\rangle = (E_l - E_k)\langle k|x|l\rangle} \qquad (a)$$

Similarly, from $[p, \mathcal{H}]$ it happens that

$$\boxed{-i\hbar K\langle k|x|l\rangle = (E_l - E_k)\langle k|p|l\rangle} \qquad (b)$$

Plug $\langle k|x|l\rangle$ from (b) into (a):

$$\frac{(E_\ell - E_k)^2}{-i\hbar K} \langle k|p|\ell\rangle = \frac{i\hbar}{m} \langle k|p|\ell\rangle$$

Thus either $\langle k|p|\ell\rangle = 0$ or

$$E_\ell - E_k = \pm \hbar\sqrt{\frac{K}{m}} = \pm \hbar\omega \qquad \omega^2 \equiv \frac{K}{m}$$

$\therefore$ the eigenvalues are evenly spaced by $\hbar\omega$.

3 The energy of the ground state, $|0\rangle$, is $\frac{1}{2}\hbar\omega$.

Multiply eqn (a) by $-im\omega$ & add it to eqn. (b):

$$-im\omega\,(E_\ell - E_k)\langle k|x|\ell\rangle = \frac{i\hbar}{m}(-im\omega)\langle k|p|\ell\rangle = \hbar\omega\langle k|p|\ell\rangle$$

$$(E_\ell - E_k)\langle k|p|\ell\rangle + (E_\ell - E_k)\langle k|-im\omega x|\ell\rangle$$
$$= -i\hbar K\langle k|x|\ell\rangle + \hbar\omega\langle k|p|\ell\rangle$$

Since $K = m\omega^2$, $-i\hbar K\langle k|x|\ell\rangle = \hbar\omega\langle k|-im\omega x|\ell\rangle$, &

$$(E_\ell - E_k)\langle k|p - im\omega x|\ell\rangle = \hbar\omega\langle k|p - im\omega x|\ell\rangle$$

OR, $$(E_\ell - E_k - \hbar\omega)\langle k|p - im\omega x|\ell\rangle = 0$$

Thus $\langle k|p - im\omega x|\ell\rangle \neq 0$ only if $E_k = E_\ell - \hbar\omega$.

Thus this operator, $\boxed{p - im\omega x}$, when operating on ket $|\ell\rangle$ gives back the ket $|k = \ell - 1\rangle$ with an energy lower than E_ℓ by $\hbar\omega$. Similarly, the operator $\boxed{p + im\omega x}$ raises the state of ℓ to $\ell + 1$.

Repeated operation of $p - im\omega x$ on $|\ell\rangle$ will eventually yield the ground state, which must yield a 0:

$$(p - im\omega x)|0\rangle = 0$$

Operate upon this equation by the raising operator:

$$(p + im\omega x)(p - im\omega x)|0\rangle = 0$$

$$(p^2 + m^2\omega^2x^2 + im\omega\underbrace{(xp - px)}_{i\hbar})|0\rangle = 0$$

$$(p^2 + m^2\omega^2x^2 - m\omega\hbar)|0\rangle = 0$$

$$2m\left(\frac{p^2}{2m} + \frac{m\omega^2x^2}{2} - \frac{\hbar\omega}{2}\right)|0\rangle = 0$$

$$2m\left(\mathcal{H} - \frac{\hbar\omega}{2}\right)|0\rangle = 0$$

$$\therefore \quad \mathcal{H}|0\rangle = \tfrac{1}{2}\hbar\omega|0\rangle$$

& $\underline{E_0 = \tfrac{1}{2}\hbar\omega}$. This is the zero point energy, and differs from the classical result

In Summary — for the eigenbasis $|n\rangle$

$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) \qquad n = 0, 1, 2 ..$$

We can define dimensionless operators:

$$\boxed{\begin{aligned} a &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\, x + i\,\frac{1}{\sqrt{m\hbar\omega}}\, p\right) \\ a^+ &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\, x - i\,\frac{1}{\sqrt{m\hbar\omega}}\, p\right) \end{aligned}}$$

Such that $\quad [a, a^+] = 1$

$$\boxed{\mathcal{H} = \hbar\omega\left(a^+ a + \tfrac{1}{2}\right) = \hbar\omega\left(\hat{N} + \tfrac{1}{2}\right)}$$

&

$a|n\rangle = \sqrt{n}\,|n-1\rangle$ — lowering operator $(a|0\rangle = 0$

$a^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$ — raising operator

$N|n\rangle = n\,|n\rangle$ — number operator