or

$$\langle\psi|(\hat{x}_1-\hat{x}_2)^2|\psi\rangle = \langle a|\hat{x}^2|a\rangle + \langle b|\hat{x}^2|b\rangle - 2\langle a|\hat{x}|a\rangle\langle b|\hat{x}|b\rangle + 2|\langle b|\hat{x}|a\rangle|^2$$

fermion case

boson case

$$\langle\psi|(\hat{x}_1-\hat{x}_2)^2|\psi\rangle = \langle a|\hat{x}^2|a\rangle + \langle b|\hat{x}^2|b\rangle - 2\langle a|\hat{x}|a\rangle\langle b|\hat{x}|b\rangle - 2|\langle b|\hat{x}|a\rangle|^2$$

opposite sign (same calc)

$$\langle(\hat{x}_1-\hat{x}_2)^2\rangle_{\text{fermion}} - \langle(\hat{x}_1-\hat{x}_2)^2\rangle_{\text{boson}}$$

$$= 4|\langle b|\hat{x}|a\rangle|^2 \geq 0$$

the fermions are "pushed appart" relative to the bosons

but note there was no force between them in Hamiltonian

Non interacting particles interact thru exchange

- when $|\langle b|\hat{x}|a\rangle|^2 \ll \langle a|\hat{x}^2|a\rangle$ exchange doesn't matter

— the real case

· fermions have spin as well as space

· bosons can have spin

— full ~~st~~ state has spinor and spatial wavefunction

Exchange ($\hat{P}$) means exchange everything not just space

eg basis states for single spin $\frac{1}{2}$

particle state $|r_0 \; m_0\rangle$ ~~[illegible]~~

2 particle states (distinguishable)

$$|r_1 m_1 \; r_2 m_2\rangle$$

Now $\hat{P} |r_1 m_1 \; r_2 m_2\rangle = |r_2 m_2 \; r_1 m_1\rangle$

if identical $|r_1 m_1 \; r_2 m_2\rangle = -|r_2 m_2 \; r_1 m_1\rangle$

what is $|r_1 m_2 \; r_2 m_1\rangle$ not imediately related to above unless $m_1 = m_2$

e.g. 2 spin $\frac{1}{2}$ particles

$\psi_a \, \chi_a$ $\qquad$ $\psi_b \, \chi_b$

space spin $\qquad$ space spin

Combine $\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(r_1)\psi_a(r_2)\right]\left[\chi_a^{(1)}\chi_b^{(2)} \mp \chi_b^1 \chi_a^2\right]$

space - spin (sym - anti) or anti - sym

more generally $\left[\psi(r_1, r_2) \pm \psi(r_2, r_1)\right]\left[\chi_a^1 \chi_b^2 \mp \chi_b^1 \chi_a^2\right]$

space $\qquad$ spin

Note if space is symmetric then spin antisym
but anti-sym means total $|S=0\rangle$

if space is anti-symmetric then spin sym
which means total spin $|S=1\rangle$

Consider He atom : two electrons
if two electrons are $|S=0\rangle$ (para helium)
has symmetric space wave functions
(both electrons can be in same state
spatially

Now lowest energy has both electron in lowest orbital ; space is symmetric and spin is anti sym ($s=0$)

ortho He has greater energy than para

- Periodic table

Free fermi gas (cond. mat. phys, astrophys ...)

- 1-d ; N fermions in box of length L.
- $V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & \text{otherwise} \end{cases}$ keeps in particular
- no interactions between fermions
- ignore spin for now

single particle levels $E_{single} = \frac{\hbar^2 k^2}{2m}$ $kL = j\pi$ $j = 1, 2, \ldots$

$E = \sum_{j=1}^{N} \frac{\hbar^2 (j\frac{\pi}{L})}{2m}$ for $N >> 1$ $\sum_{j=1}^{N} \longrightarrow \int_0^N dj$

(up to $1/N$ corrections)

change variables $k = \frac{j\pi}{L}$ $dj = \frac{L}{\pi} dk$ $k_F L = N\pi$

$$E \simeq \int_0^N dj \frac{\hbar^2 (\frac{j\pi}{L})}{2m} = \frac{L}{\pi} \int_0^{k_F} dk \frac{\hbar^2 k^2}{2m} = \frac{L}{2\pi} \int_{-k_F}^{k_F} dk \frac{\hbar^2 k^2}{2m} = \frac{L}{\pi} \frac{\hbar^2 k_F^3}{6m}$$

$\mathcal{E} = \frac{E}{L}$ more useful

$\mathcal{E} = \frac{1}{\pi} \frac{\hbar^2 k_F^3}{6m}$ particle density $\lambda = \frac{N}{L} = \frac{k_F}{\pi}$

$\mathcal{E} = \pi^2 \hbar^2 \lambda^3$

. Do in a 3-d box all sides $= L$

. include spin

$$E = \overset{\text{spins}}{2} \sum_{j_x, j_y, j_z} \frac{\hbar^2\left[\left(\frac{\pi}{L} j_x\right)^2 + \left(\frac{\pi}{L} j_y\right)^2 + \left(\frac{\pi}{L} j_z\right)^2\right]}{2m}$$

all j's > 0

(how many in each j — chose to minimize E)

which j's to include; those which minimize E

assume $N >> 1$

$$E = 2 \int dj_x\, dj_y\, dj_z \frac{\hbar^2 \left(\frac{\pi}{L}\right)^2 (j_x^2 + j_y^2 + j_z^2)}{2m}$$

$$= 2 \frac{L^3}{\pi^3} \int dk_x\, dk_y\, dk_z \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} = 2 \frac{V}{\pi^3} \int dk_x dk_y dk_z \frac{\hbar^2 k^2}{2m}$$

Minimum energy ~~state~~ of fixed number include all single particle states with $k^2 < k_F^2$

$$E = 2 \frac{L^3}{\pi^3} \int dk_x\, dk_y\, dk_z\, \Theta(k_F^2 - k^2) \underbrace{\Theta(k_x)\Theta(k_y)\Theta(k_z)}_{k_x > 0 \; k_y > 0 \; k_z > 0} \frac{\hbar^2 k^2}{2m}$$

$$= \frac{2 L^3}{8 \pi^3} \int dk_x\, dk_y\, dk_z\, \Theta(k_F^2 - k^2) \frac{\hbar^2 k^2}{2m}$$

k_x, k_y, k_z have no fixed sign

Jacobean for spherical

$$= \frac{2 L^3}{(2\pi)^3} \int_0^{k_F} 4\pi k^2\, dk \frac{\hbar^2 k^2}{2m} = \frac{2 L^3}{(2\pi^2)} \frac{\hbar^2}{2m} \int_0^{k_F} dk\, k^4 = \frac{2 L^3 \hbar^2}{(2\pi^2)(10m)} k_F^5$$

$$= \frac{L^3}{\pi^2} \frac{\hbar^2 k_F^5}{10 m}$$

total particle number

$$N = \overset{\text{spin}}{2} \sum_{\nu_x \nu_y \nu_z} 1$$

same as E calculation without $\frac{\hbar^2 k^2}{2m}$ so do same steps

$$= \frac{L^3}{\pi^2} \int_0^{k_f} dk\, k^2 = \frac{L^3 k_f^3}{3\pi^2}$$

More useful

$$\mathcal{E} = \frac{E}{vol} = \frac{\hbar^2 k_f^5}{10\pi^2 m}$$

$$\rho = \frac{N}{vol} = \frac{k_f^3}{3\pi^2} \quad \text{or} \quad k_f = (3\pi^2 \rho)^{\frac{1}{3}}$$

$$\text{so} \quad \mathcal{E} = \frac{3^{5/3} \pi^{4/3} \hbar^2 \rho^{5/3}}{10 m}$$

Now in thermo

pressure

$$P = -\frac{dE}{dV}\bigg|_{\text{fixed } N} \qquad \text{analog to } \vec{F} = -\vec{\nabla} V$$

$$E = \left(\frac{3^{5/3}\pi^{4/3}\hbar^2}{10 m}\right) \rho^{5/3} V = \left(\frac{3^{5/3}\pi^{4/3}\hbar^2}{10 m}\right) \frac{N^{5/3}}{V^{5/3}} V = \left(\frac{3^{5/3}\pi^{4/3}\hbar^2}{10 m}\right) N^{5/3} V^{-2/3}$$

$$\frac{\partial E}{\partial V}\bigg|_N = \left(\frac{3^{5/3}\pi^{4/3}\hbar^2}{10 m}\right) N^{5/3} \left(-\frac{2}{3}\right) V^{-\frac{5}{3}} = -\frac{2}{3} \frac{\left(\frac{3^{5/3}\pi^{4/3}\hbar^2}{2m}\right) N^{5/3} V^{-2/3}}{V} = -\frac{2}{3}\frac{E}{V}$$

this is the "degeneracy pressure"

Less spherical Cow approx for electrons in metal.

- electron-electron interactions neglected
- electrons interact with a periodic potential due to crystal with nuclei & bound electrons

1st consider 1-particle in periodic potential; for ~~simplest~~ simplicity 1st do 1 dimension

$$V(x+a) = V(x) \qquad \text{periodicity}$$

$$\hat{H} = \cancel{\quad} \; -\frac{\hat{p}^2}{2m} + V(\hat{x})$$

Does periodicity tell us anything about spectrum?

Yes! Intuitive argument $\boxed{\psi_n(x+a) = e^{i\phi_n}\psi_n(x)}$

the world looks the same shifted by a

Define a finite translation operator

$$\hat{D}\,|x\rangle = \hat{D}\,|x-a\rangle$$

Now it is easy to see that $\hat{D}$ is a unitary

$$|\psi\rangle = \int dx\, |x\rangle\langle x|\psi\rangle = \int dx\, |x\rangle \psi(x)$$

so $\hat{D}|\psi\rangle = \int dx\, \hat{D}|x\rangle\langle x|\psi\rangle = \int dx\, |x-a\rangle\psi(x)$ but x is dummy let $y = x-a$ $x = y+a$

$$= \int dy\, |y\rangle \psi(y+a)$$

$$= \int dx\, |x\rangle \psi(x+a)$$

so $\langle\psi|\hat{D}^\dagger = \left(\hat{D}|\psi\rangle\right)^\dagger = \int dx'\, \psi^*(x'+a)\langle x'|$

$$\langle\psi|\hat{D}^\dagger D|\psi\rangle = \int dx'\, dx\, \psi^*(x'+a) \underbrace{\langle x'|x\rangle}_{\delta(x'-x)} \psi(x+a)$$

$$= \int_{-\infty}^{\infty} dx\, \psi^*(x+a)\psi(x+a) \quad \text{let } y = x+a,\ dy = dx$$

$$= \int_{-\infty}^{\infty} dy\, \psi^*(y)\psi(y) = 1$$

$\therefore$ $D^\dagger D = \mathbb{1}$ since this true for all $|\psi\rangle$

therefore D is unitary

Now principal claim

$$[D, \hat{H}] = 0$$

Proof : several steps

claim $\hat{D}^+ \hat{x} \hat{D} = \hat{x} + a$

proof $\hat{D}^+ \hat{x} \hat{D} |x\rangle \; D^+ \hat{x} |x+a\rangle = \hat{D}^+ (x+a) |x+a\rangle = (x+a) \hat{D}^+ |x+a\rangle = (x+a)|$

but the operator which has as an eigenstate $|x\rangle$ with eigenvalue $x+a$ is $\hat{x}+a$ Q.E.D

claim $\hat{D}^+ \hat{x}^n \hat{D} = (\hat{x}+a)^n$

proof $\hat{D}^+ \hat{x}^n D = \underbrace{\hat{D}^+ \hat{x} \underbrace{D^+ D}_{=1} \hat{x} D^+ D \hat{x} D \cdots D^+ \hat{x} D}_{n \text{ times}} = \underbrace{(\hat{x}+a)(\hat{x}+a) \cdots (\hat{x}+a)}_{n \text{ times}}$

claim $\hat{D}^+ f(\hat{x}) D = f(\hat{x}+a)$

proof: expand $f(\hat{x})$ is a Taylor Series $f(\hat{x}) = \sum_n c_n \hat{x}^n$

$\hat{D}^+ f(\hat{x}) D = \sum_n c_n \hat{D}^+ \hat{x}^n D = \sum_n c_n (\hat{x}+a)^n = f(\hat{x}+a)$

So consider

$\hat{D}^+ \hat{H} \hat{D}$ with a periodic potential $V(\hat{x}+a) = V(\hat{x})$

$= \hat{D}^+ \frac{\hat{p}^2}{2m} \hat{D} + \underbrace{\hat{D}^+ V(\hat{x}) \hat{D}}$

$= V(\hat{x}+a)$

$= V(\hat{x})$

Now consider $\langle\psi|\hat{O}^{+}\frac{\hat{p}^2}{2m}\hat{O}|\psi\rangle$

$= \int dx\, \psi^*(x+a)\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x+a)$ let $y=x+a$

$= \int dy\, \psi^*(y)\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi(y)$

$= \langle\psi|\frac{\hat{p}^2}{2m}|\psi\rangle$

true for all $|\psi\rangle$ so

$\hat{O}^{+}\frac{\hat{p}^2}{2m}\hat{O} = \frac{\hat{p}^2}{2m}$

or

$$\boxed{\hat{O}^{+}\hat{H}\hat{O} = \hat{H}}$$

mult on left by $\hat{O}$

$\hat{H}\hat{O} = \hat{O}\hat{H}$

or

$$\boxed{[\hat{H},\hat{O}] = 0}$$

Now $[\hat{H}, \hat{O}] = 0$ so eigen vectors of $\hat{H}$ are simultaneously eigenvectors of $\hat{O}$ (if $\hat{H}$ has degeneracy we can always arrange this; otherwise automatic)

Now $\hat{O}$ is unitary and thus has eigenvalues which are pure phases

proof: diagonalize $\hat{O}$ get $\begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots\ \lambda_n \end{pmatrix}$ where λ is eigen vector

diagonalize $\hat{O}^+$ get $\begin{pmatrix} \lambda_1^* & & \\ & \lambda_2^* & \\ 0 & & \ddots\ \lambda_n^* \end{pmatrix}$

so $\hat{O}^+ \hat{O} = \begin{pmatrix} \lambda_1^*\lambda_1 & & 0 \\ & \lambda_2^*\lambda_2 & \\ 0 & & \lambda_n^*\lambda_n \end{pmatrix} = \begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & 1 \end{pmatrix}$ since $\hat{O}^+\hat{O} = \mathbb{1}$

so $\lambda_n^* \lambda_n = 1$ or $\lambda_j = e^{i\phi_j}$

all eigenvalues of $\hat{O}$ are phases

suppose $|\psi_n\rangle$ is an eigenstate of $\hat{H}$
it is also an eigenstate of $\hat{O}$

$\hat{O}|\psi_n\rangle = e^{i\phi_n}|\psi_n\rangle$

so $\langle x|\hat{O}|\psi_n\rangle = \psi_n(x+a)$

but $\langle x|\hat{O}|\psi_n\rangle = e^{i\phi_n}\langle x|\psi_n\rangle = e^{i\phi_n}\psi_n(x)$

so $\psi_n(x+a) = e^{i\phi_n}\psi_n(x)$

Note $\psi_n(x+2a) = e^{2i\phi_n}\psi_n(x)$

$\psi_n(x+Na) = e^{iN\phi_n}\psi_n(x)$

cute way to write this

if $\psi(x)$ is an eigenstate of $\hat{H}$
then

$$\boxed{\psi(x) = e^{ikx}\, u(x) \qquad \text{where} \quad u(x+a) = u(x)}$$

Bloch's theorem

$$\psi(x+a) = e^{ika} e^{ikx} u(x+a) = e^{ika}\, \psi(x)$$

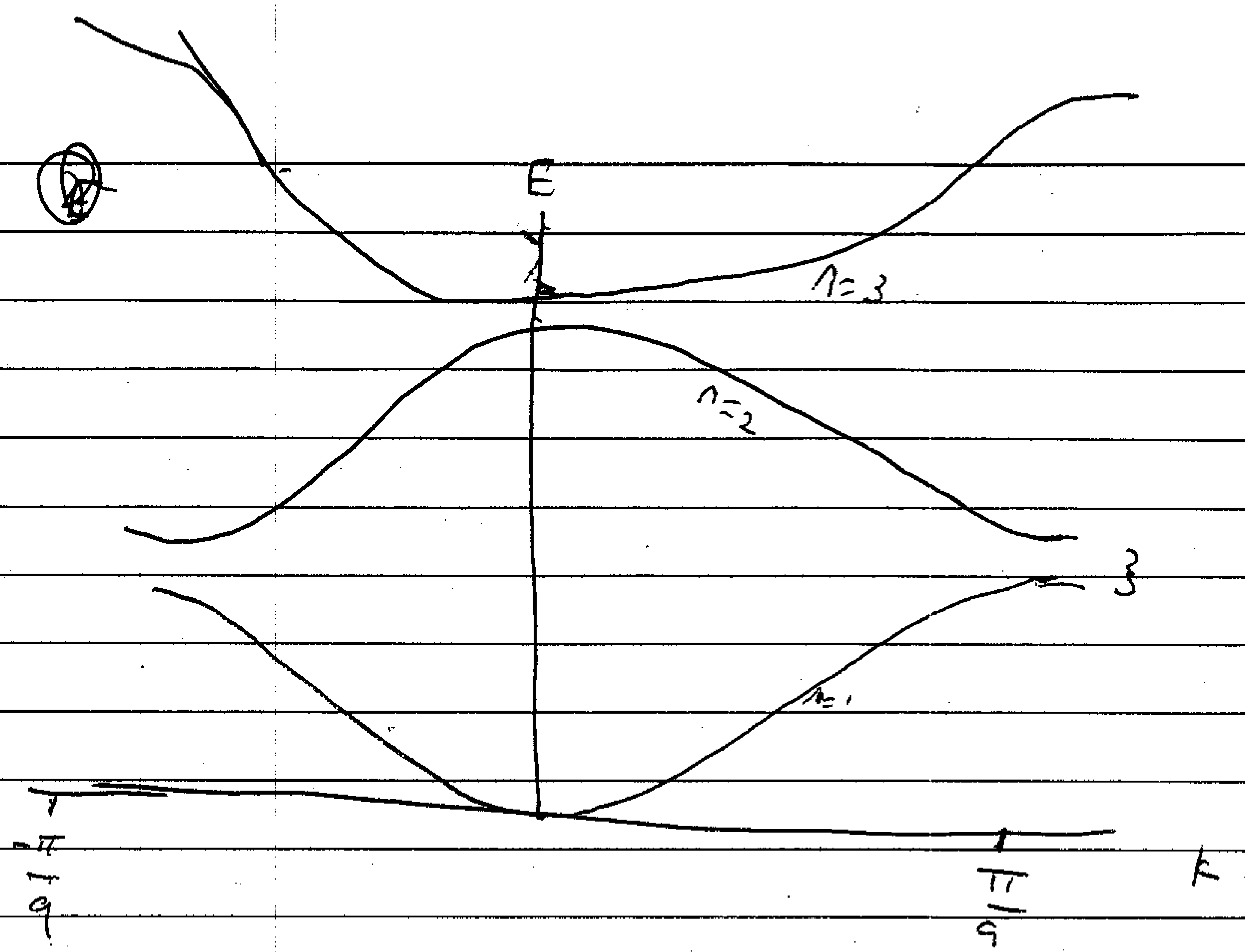
call $\phi = ka$ and this is previous form

$\hbar k$ is called the crystal momentum ~~[illegible]~~

- k is continuous ; not info is contained in
wave function not normalized

$-\frac{\pi}{a} < k < \frac{\pi}{a}$ (then it repeats)

- this cannot be all info (plane waves have no way to fix k in a finite band)
so eigenvectors have two labels
k, n where n is discrete
and k continuous



etc.

Note my picture has gaps
E cannot take all values

let us do an example to see
how this works

Kronig – Penney model.

$$V(x) = -\alpha \sum_j \delta(x - ja)$$

periodically placed δ (attractive)

toy model but illustrates point

for x not at δ function

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

or

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi$$

$$\psi(x) = A\sin(kx) + B\cos(kx) \qquad \text{for} \qquad 0 < x < a$$

$$\psi(x-a) = e^{-iKa}\psi(x) \qquad \text{Bloch}$$

so for $-a < x < 0$

crystal mom.

$$\psi(x) = e^{-iKa}\psi(x+a) = e^{-iKa}\left[A\sin(k(x+a)) + B\cos(k(x+a))\right]$$

~~at $x=0$~~ function cont.

$$B = e^{-iKa}\left[A\sin(ka) + B\cos(ka)\right]$$

integrate both sides of Schrodinger eq.

$$\int_{-\epsilon}^{\epsilon}\left(-\frac{\hbar^2}{2m}\frac{\partial\psi}{\partial x} - \alpha\delta(x)\psi\right)dx = \int_{-\epsilon}^{\epsilon}E\psi = 0$$

$$-\frac{\hbar^2}{2m}(\psi'_+ - \psi'_-) = \alpha\psi(0)$$

so $\quad \psi_+' - \psi_-' = \frac{-2m\alpha}{\hbar^2} \psi(0)$

$$k A - e^{-iKa} k \left[A\cos(ka) - B\sin(ka) \right] = \frac{-2m\alpha}{\hbar^2} B$$

$\Big\downarrow$ algebra

$$\cos(Ka) = \cos(ka) - \frac{m\alpha}{\hbar^2 k} \sin(ka)$$

LHS bounded $\quad -1 < \cos(Ka) < 1$

this bound prevents solutions for some k's (i.e. some E's) giving gaps

Study RHS near $ka = n\pi$

$$\cos(ka) = (-1)^n + \mathcal{O}\left((ka - n\pi)^2\right) \qquad \text{Taylor}$$

$$\sin(ka) = (-1)^n (ka - n\pi) + \mathcal{O}\left((ka - n\pi)^2\right)$$

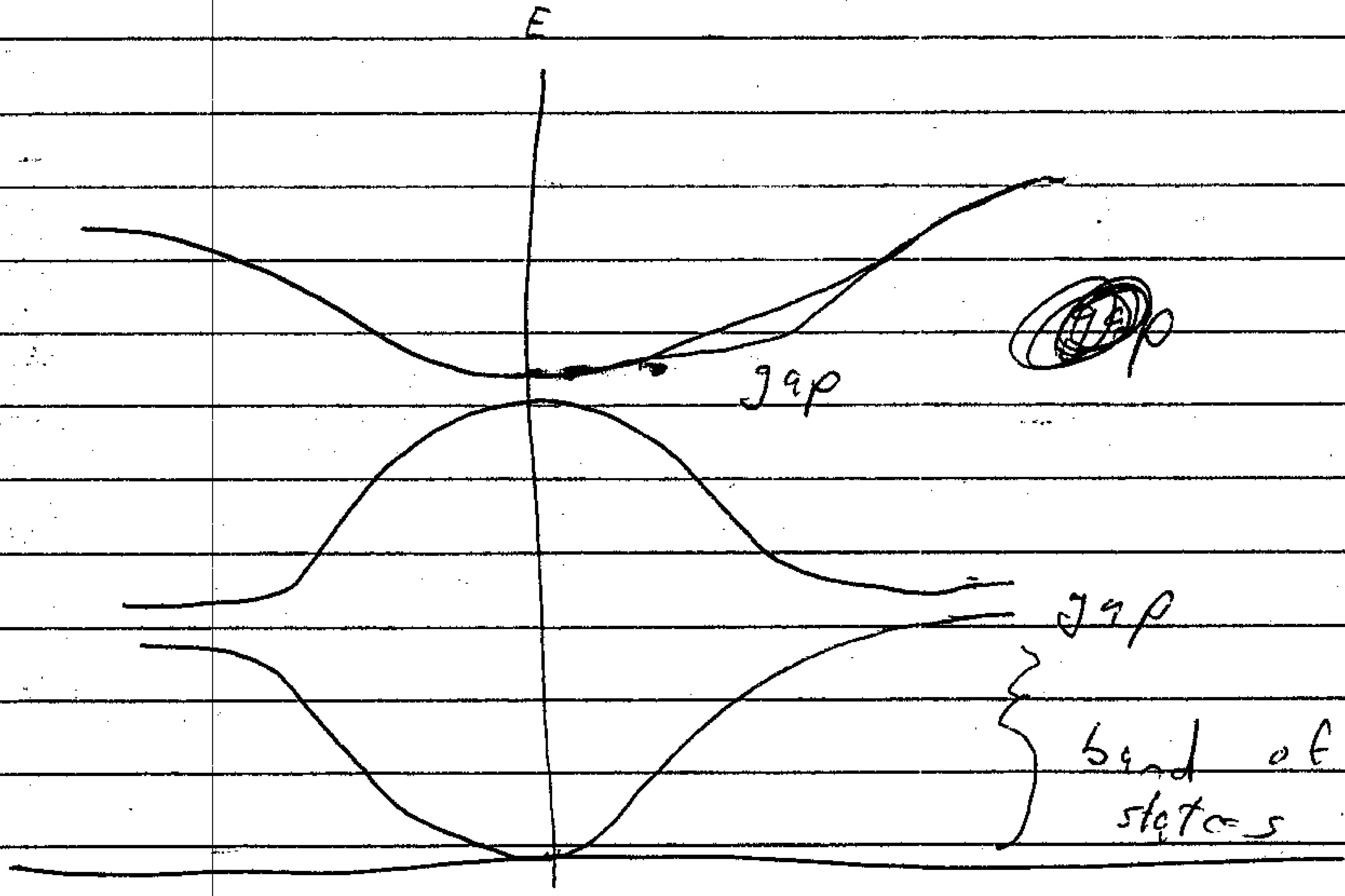
$$\frac{\sin(ka)}{ka} = (-1)^n \frac{(ka - n\pi)}{n\pi} + \mathcal{O}\left((ka - n\pi)^2\right)$$

$$= (-1)^n \left(\frac{ka}{n\pi} - 1 \right) + \mathcal{O}(ka - n\pi)^2$$

$$rhs = (-1)^n \left[1 \; 4 \frac{m\alpha}{\hbar^2} \underbrace{\left(1 - \frac{ka}{n\pi}\right)}_{> 0} + O((ka - n\pi)^3) \right]$$

so near $ka \approx n\pi$ $\quad |rhs| > 1$

but $|lhs| < 1$ so no solution



conductors & insulators

if E_f (the fermi energy)
lies within a band
the you need ~~e~~ essentially no energy to
excite an electron from ground state
conductor

if E_f is at band gap
insulator

Pert theory —

suppose $\hat{H} = \hat{H}_0 + \hat{H}'$

where we know how to find eigenvectors and eigenvalues of $\hat{H}_0$ and $\hat{H}'$ is "small" we want a method to approximately find eigenvector and eigenvalues of $\hat{H}$. Method should be systematic (get better as we work harder and converge on exact answer). Example spin effects in hydrogen atom

Method: perturbation theory

condition H' is "small" what does this mean we shall see later. Here just assume "small"

write

$H = H_0 + \lambda H'$ λ is a smallness parameter we will keep it to keep track of order of smallness and then set to unity at end

since λ mults H' and H' is small anything proportional to $\lambda^2 \sim H'^2$ and is very small etc.

work in the eign basis of $\hat{H}_0$; this the problem we know.

$$\hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \qquad \langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{m,n}$$

want to solve $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad \hat{H} = \hat{H}_0 + \lambda\hat{H}'$

trick write everything as a Taylor series in λ

small, very small, etc

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

plug in

$$\left(\hat{H}_0 + \lambda\hat{H}'\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2 \psi_n^{(2)} + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right)$$

equate powers of λ; since eq holds for all λ should hold order by order

$$\hat{H}_0|\psi_n^{(0)}\rangle + \lambda\left(\hat{H}'|\psi_n^{(0)}\rangle + \hat{H}_0|\psi_n^{(1)}\rangle\right) + \lambda^2\left(\hat{H}'|\psi_n^{(1)}\rangle + \hat{H}_0|\psi_n^{(2)}\rangle\right) + \cdots$$

$$= E_n|\psi_n^{(0)}\rangle + \lambda\left(E_n^{(1)}|\psi_n^{(0)}\rangle + E_n^{(0)}|\psi_n^{(1)}\rangle\right) + \lambda^2\left(E_n^{(2)}|\psi_n^{(0)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(0)}|\psi_n^{(2)}\rangle\right.$$

$+ \cdots$

equating powers of λ:

i) $\hat{H}_0 |\psi_n^{(0)}\rangle = E_n |\psi_n^{(0)}\rangle$

ii) $\hat{H}' |\psi_n^{(0)}\rangle + \hat{H}_0 |\psi_n^{(1)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle$

iii) $\hat{H}' |\psi_n^{(1)}\rangle + \hat{H}_0 |\psi_n^{(2)}\rangle = E_n^{(2)} |\psi_n^{(0)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(0)} |\psi_n^{(2)}\rangle$

+ higher order equations (we will neglect this here but could be included for higher accuracy

Now we can set $\lambda = 1$ so

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + \cdots$$

equation i) is trivially true

equation ii) $\hat{H}' |\psi_n^{(0)}\rangle + \hat{H}_0 |\psi_n^{(1)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle$

right multiply by $\langle\psi_n^{(0)}|$

$$\langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle + \underbrace{\langle\psi_n^{(0)}|\hat{H}_0}_{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle}|\psi_n^{(1)}\rangle = E_n^{(1)} \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(0)} \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$$

$$\underset{1}{\parallel}$$

or $\quad E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$

shift in energy is just expectation value of the shift in $\hat{H}$ in the <u>old</u> state.

what about $|\psi_n^{(1)}\rangle$

$$|\psi_n^{(1)}\rangle = \sum_m{}' c_{nm} |\psi_m^0\rangle$$ our job is to find $c_{n,m}$

claim $c_{nn} = 0$ proof

$1 = \langle \psi_n | \psi_n \rangle$ but $|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + O(\lambda^2)$

$$1 = \left(\langle \psi_n^{(0)}| + \lambda \psi_n^{(1)} + \dots\right)\left(|\psi_n^{(0)}\rangle + \lambda \psi_n^{(1)} + \dots\right)$$

$$= \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{1} + \lambda \underbrace{\left(\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle\right)}_{=0} + O(\lambda^2)$$

so $|\psi_n^{(1)}\rangle$ is orthogonal to $|\psi_n^{(0)}\rangle$ $\quad c_{nn} = 0$

to find c_{nm} take ii) and right multiply by $\langle \psi_m^{(0)}|$

$c_{nm} = \langle \psi_m^0 | \psi_n^{(1)} \rangle$

~~but ii) gives~~

$$\langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle + \overbrace{\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle}^{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle} = E_n^{(1)}\cancel{\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle} + E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$$

or $$\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle = \left(E_n^{(0)} - E_m^{(0)}\right)\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$$

$$= \left(E_n^{(0)} - E_m^{(1)}\right) C_{nm}$$

so $$C_{nm} = \frac{\langle\psi_m^{(0)}|H'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

or

$$|\psi_n^{(1)}\rangle = \sum_m C_{nm}|\psi_m^{(0)}\rangle$$

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

Let us return to question of How small $\hat{H}'$ must be.

claim $$\frac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_n^{(0)}} \ll 1$$ for all relevant m,n

Finally let's look at $E^{(2)}$

take eq. iii) and left mult by $\langle\psi_n^{(0)}|$

$$\langle\psi_n^{(0)}|H'|\psi_n^{(1)}\rangle + \underbrace{\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle}_{E_n^0 \langle\psi_n^{(0)}|\psi_n^{(2)}\rangle} =$$

$$E_n^{(2)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(1)}\cancel{\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle} + E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle$$

so

$$E_n^{(2)} = \langle\psi_n^{(0)}|H'|\psi_n^{(1)}\rangle$$

$$= \langle\psi_n^{(0)}|H'\sum_{m\neq n}\frac{|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|H'|\psi_n^{(0)}\rangle}{E_n-E_m}$$

$$= \sum_{m\neq n}\frac{\langle\psi_n^{0}|H'|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|H'|\psi_n^{0}\rangle}{E_n-E_m}$$

Note for ground state

$E_0^{(2)} \leq 0$ since $E_m > E_0$

Higher order calculations possible but get tedious

Summary:

$H = H_0 + H'$

$$E_n = E_n^{(0)} + \langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | H' | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{E_n - E_m}$$

$$+ \mathcal{O}(H'^3)$$

$$|\Psi_n\rangle = |\Psi_n^{(0)}\rangle + \sum_{m \neq n} \frac{|\Psi_m^{(0)}\rangle \langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{E_n - E_m} + \mathcal{O}(H'^2)$$

Examples: suppose I put a "small" δ function of strength α in middle of H.O.

$$\hat{H} = \underbrace{\frac{1}{2}\frac{\hat{p}^2}{m} + \frac{1}{2} k \hat{x}^2}_{H_0} + \underbrace{\alpha \delta(x)}_{H'}$$

what is ground state Energy

$E_0^{(0)} = \frac{1}{2}\hbar\omega \qquad \omega = \sqrt{\frac{k}{m}}$

$$E_0^{(1)} = \langle \Psi^{(0)} | \alpha \delta(\hat{x}) | \Psi^{(0)} \rangle = \alpha \int dx\, \Psi_0^{*(0)}(x)\, \delta(x)\, \Psi(x) = \alpha\, \Psi_0^{*(0)}(0)\, \Psi_0^{(0)}(0)$$

but $\Psi_0^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{\hbar}}$

so $E_n^{(1)} = \alpha\left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{2}}$

units check

or

$$E \approx \hbar\omega/_2 + \alpha\left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{2}} + \cdots$$

what about second order

$$E_0^{(2)} = \sum_n \frac{\langle\psi_0|H'|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|H'|\psi_0\rangle}{E_0^{(0)} - E_0^{(n)}}$$

now $E_0^0 - E_0^{(n)} = \cancel{\quad} = -n\hbar\omega$

$$\langle\psi_n^{(0)}|H'|\psi_0^{(0)}\rangle = \int dx\, \psi_n^{(0)}(x)\, \alpha\,\delta(x)\, \psi_0^{(0)} = \alpha\, \psi_n^{(0)*}(0)\psi_0^{(0)}(0)$$

look up h.o. wave function

$$\psi_n^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}\, x\right) e^{-\frac{m\omega x^2}{\hbar}}$$

so

$$\psi_n^{(0)}(0) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(0)$$

Note $H_n(0) = 0$ for all odd n

even n

$H_0(0) = 1$ $\quad H_2(0) = -2$ $\quad H_4(0) = 12$ $\quad \ldots$

$$E_0^{(2)} = \sum_n \left(\frac{m\omega}{\pi\hbar}\right) \frac{|H_n(0)|^2}{n!\,2^n} \frac{\alpha^2}{-n\hbar\omega}$$

$$= -\frac{\alpha^2 m}{\pi\hbar^2} \sum_{n=1}^{\infty} \frac{|H_n(0)|^2}{n!\,2^n}$$

mathematica

$\approx .68$

dimensions
check

so

$$E \approx \frac{\hbar\omega}{2} + \alpha\left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{2}} - .68\left(\frac{\alpha^2 m}{\pi\hbar^2}\right) + \cdots$$

Note pattern

0^{th} order easy
1^{st} order more work
2^{nd} order lots of work

work more + more to get less and less

Example:

anharmonic oscillator

$$\hat{H} = \underbrace{\frac{1}{2}\frac{\hat{p}^2}{m} + \frac{1}{2}k\hat{x}^2}_{H_0} + \underbrace{\alpha\hat{x}^4}_{H'}$$

Ground state

$$E_0^{(0)} = \frac{1}{2}\hbar\omega$$

$$E_0^{(1)} = \langle\psi_0^{(0)}|\alpha\hat{x}^4|\psi_0^{(0)}\rangle$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(b + b^\dagger) \qquad b|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$b^\dagger|n+1\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$\hat{x}^4 = \frac{\hbar^2}{9m^2\omega^2}(b + b^\dagger)^4$$

$$= \frac{\hbar^2}{4m^2\omega^2}\Big(\cancel{b^4} + \cancel{b^2 b^\dagger b} + \cancel{b^3 b^\dagger} + b^2 b^{\dagger 2} + b^\dagger b\,[illegible] + \cancel{b^\dagger b b^\dagger b} + b^\dagger b b b^\dagger + \cancel{b^\dagger b b^{\dagger 2}}$$
$$+ \cancel{b b^\dagger b^2} + b b^\dagger b^\dagger b + b b^\dagger b b^\dagger + \cancel{b b^{\dagger 3}} + b^{\dagger 2} b^2 + \cancel{b^{\dagger 3} b} + \cancel{b^{\dagger 2} b b^\dagger} + \cancel{b^{\dagger 4}}\Big)$$

only terms with same number of b's as $b^\dagger$'s contribute

$$\langle\psi_0|\hat{x}^4|\psi_0\rangle = \frac{\hbar^2}{4m\omega^2}(2 + 0 + 1 + 0 + 0 + 0)$$

$$= \frac{3\hbar^2}{4m\omega^2}$$

so $$E = \frac{1}{2}\hbar\omega + \frac{3\alpha\hbar^2}{4m\omega^2} + \ldots$$

Example $\hat{V} = \begin{cases} \infty & x<0 \\ a\cos(\pi x/L) & 0<x<L \\ \infty & x>0 \end{cases}$

so it is an ∞ square well with cos perturbation

$\hat{H}_0 \psi_n(x) = E_n^{(0)} \psi_n(x)$ $\qquad \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ from 0 to L

$H' = a \cos\left(\frac{\pi x}{L}\right)$ $\qquad E_n = \frac{\hbar^2 \left(\frac{n\pi}{L}\right)^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$

$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} + \dots$

$$E_1^{(1)} = \int_0^L dx \; \psi_1^{(0)}(x) \, a\cos\left(\frac{\pi x}{L}\right) \psi(x)$$

$$= \int_0^L dx \; \frac{2a}{L} \sin^2\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right)$$

$$= \int_0^L dx \; \frac{2}{L} \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right)$$

$$= \frac{a}{L} \int_0^L dx \; \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) = 0$$

$$E_1^{(2)} = \sum_{n \neq 1} \frac{\left|\langle \psi_1 | H' | \psi_n \rangle\right|^2}{E_1^{(0)} - E_n^{(0)}}$$

Now $\langle \psi_1 | H' | \psi_n \rangle$

$$= \int_0^L dx \left(\frac{2}{L}\right) \sin\left(\frac{\pi x}{L}\right) q \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right)$$

$$= \frac{q}{L}\int_0^L dx \, \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right)$$

$$= \delta_{n,2} \left(\frac{q}{L}\right) \frac{L}{2} = \frac{q}{2}\delta_{n2}$$

$$E_1^{(2)} = \frac{\left(\frac{q}{2}\right)^2}{E_1^{(0)} - E_2^{(0)}} = \frac{\left(\frac{q}{2}\right)^2}{\frac{\hbar^2 \pi^2}{2mL^2}(1-4)} = \frac{-q^2 m L^2}{6 \hbar^2 \pi^2}$$

$$E = \frac{\hbar^2 \pi^2}{2mL^2} - \frac{q^2 m L^2}{6\pi^2 \hbar^2} + O(q^3)$$

Standard Pert theory generally fails when there are degenerate states

(exception: degeneracy is due to symmetry and pert. has same symmetry as H_0 then $\langle \psi_a | H' | \psi_b \rangle = 0$ for degenerate a, b)

Consider for simplicity two degenerate states $|\psi_a^0\rangle$ $|\psi_b^0\rangle$

$$H_0 |\psi_a\rangle = E^0 |\psi_a\rangle$$
$$H_0 |\psi_b\rangle = E^0 |\psi_b\rangle$$

Note any linear combo is also degenerate

$$|\psi^0\rangle = \alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle$$

$$\hat{H}_0 |\psi^0\rangle = E |\psi^{(0)}\rangle$$

Now claim $H = H_0 + H'$ generally will not have degeneracy [if H' has different symmetry]

key point danger is due to terms which go like $\dfrac{\langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle}{E_a^{(0)} - E_b^{(0)}}$ which diverge trick: pick 2 linear combo's of $|\psi_a^{(0)}\rangle$ and $|\psi_b^{(0)}\rangle$ as new states

call them $|\psi_\pm^{(0)}\rangle$ bad notation I'll follow book

$|\psi_+^{(0)}\rangle = \alpha_+ |\psi_a\rangle + \beta_+ |\psi_b\rangle$ $\quad |\alpha|^2 + |\beta|^2 = 1$

$|\psi_-^{(0)}\rangle = \alpha_- |\psi_a\rangle + \beta_- |\psi_b\rangle$

with $\langle\psi_+^{(0)}|\psi_-^{(0)}\rangle = 0$

and with $\langle\psi_+^{(0)}|H'|\psi_-^{(0)}\rangle = 0$

these are "good" states

1st order pert works directly with good states

$E_\pm^{(1)} = \langle\psi_\pm^{(0)}|H'|\psi_\pm^{(0)}\rangle$

so how do I find $|\psi_\pm\rangle$

answer $|\psi_\pm\rangle$ are eigenstates of H' ! in 2x2 basis

Note eigenstates are orthogonal so satisfies boxed conditions

In that case

$E_\pm^{(1)}$ are just the eigenvalues of H' in the 2×2 space of degenerate levels

define: $W_{aa} = \langle \psi_a^{(0)} | H' | \psi_a^{(0)} \rangle$

$W_{ab} = \langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle$

$W_{ba} = \langle \psi_b^{(0)} | H' | \psi_a^{(0)} \rangle = W_{ab}^*$

$W_{bb} = \langle \psi_b^{(0)} | H' | \psi_b^{(0)} \rangle$

eigenvalues : $\mathrm{Det}\begin{pmatrix} W_{aa} - E_\pm^{(1)} & W_{ab} \\ W_{ba} & W_{bb} - E_\pm^{(1)} \end{pmatrix} = 0$

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

~~$H = \lambda H'$~~

Generalization to more than two degenerate states: n state

- "good" linear combos : eigenstates of H' in n-state degenerate basis

- $E^{(1)}$ are the eigenvalues

Example — 2-d h.o. oscillator
with perturbation

$$H_0 = \frac{1}{2}k(\hat{x}^2 + \hat{y}^2) + \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m}$$

$$H' = \alpha xy$$

unperturbed eigenstates

$|n_x, n_y\rangle$ $\quad \hat{H}_0 |n_x, n_y\rangle = \hbar\omega(n_x + n_y + 1)|n_x, n_y\rangle$

Note total energy $= \hbar\omega(N+1)$ $\quad N = n_x + n_y$

N is degenerate for $N > 0$

$N=1$ $\quad n_x = 1\ n_y = 0$ or $n_y = 1\ n_x = 0$ $\quad$ doubly

$N=2$ $\quad n_x = 2\ n_y = 0$ $\quad n_x = 1\ n_y = 1$ $\quad n_x = 0\ n_y = 2$ $\quad$ triple

etc.

lets look at $N=1$ states. what does perturbation do to them

$|a\rangle = |1,0\rangle \quad |b\rangle = |0,1\rangle$ $\quad W_{aa} = \langle 1,0|\hat{H}'|1,0\rangle = \alpha\langle 1,0|\hat{x}\hat{y}|1,0\rangle$

$= \alpha\langle 1|x|1\rangle\langle 0|y|0\rangle = 0$

$W_{bb} = 0$ similarly $\quad$ x space $\quad$ y-space

$W_{ab} = \langle 1,0|\hat{H}'|0\,1\rangle = \alpha\langle 1\,0|\hat{x}\hat{y}|0\,1\rangle = \alpha\langle 1|\hat{x}|0\rangle\langle 0|\hat{y}|1\rangle$

now Q $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(b+b^{\dagger})$

so $\langle 1|\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}$ $\qquad \langle 0|\hat{y}|1\rangle = \langle 1|\hat{x}|0\rangle^{*}$

or

$$W_{ab} = \alpha \frac{\hbar}{2m\omega}$$

so

$$W = \begin{pmatrix} 0 & \alpha\frac{\hbar}{2m\omega} \\ \alpha\frac{\hbar}{2m\omega} & 0 \end{pmatrix}$$

eigen value $E^{W}_{\pm} = \pm\,\alpha\frac{\hbar}{2m\omega}$ easy to get

"good" eigen statate $\begin{pmatrix} 1/\sqrt{2} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$ $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$

$|\psi_+\rangle = \frac{1}{\sqrt{2}}|a\rangle + \frac{1}{\sqrt{2}}|b\rangle$ $\qquad |\psi_-\rangle = \frac{1}{\sqrt{2}}|\psi_a\rangle - \frac{1}{\sqrt{2}}|b\rangle$

Example –

Fine structure of Hydrogen

$H_0 = \frac{-\nabla^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$ we've solved this

perturbations : many types

two largest "fine structure"

two types of effects here

– relativity (splits states of same n and different l)

– spin-orbit (splits states of same l but different $\vec{J} = \vec{l} + \vec{s}$

lowest relativistic effect

$$H = \frac{p^2}{2m} + V$$

but this is non rel

relativistically

rest energy

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

$$= mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] =$$

$$= mc^2\left(1 + \frac{1}{2}\left(\frac{p^2}{mc}\right) - \frac{1}{2}\left(\frac{p}{mc}\right)^4 + \dots\right)$$

leading corr

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

treat as H'

claim: we can compute this using non-degenerate pert. theory in $n\,l\,m$ basis

automatically diagonalized in this basis — why?

L's don't mix but what about the n's, you can check important Hydrogen

so

$$E^{(1)}_{rel} = \langle n l m | \frac{\hat{p}^4}{8m c^2} | n l m \rangle$$

there is a trick Here

$$\left(\frac{\hat{p}^2}{2m} + \hat{V} \right) |n l m\rangle = E^{\circ}_{nl} |n l m\rangle$$

so

$$p^2 |n l m\rangle = (2m E_{nl} - 2m V) |n l m\rangle$$

$$\hat{p}^4 |n l m\rangle = 4m (E_{nl} - V)^2 |n l m\rangle$$

we know this

$$\langle n l m | \hat{p}^4 | n l m \rangle = 4m \Big(E^{\circ 2}_{nl} + E^{\circ}_{nl} \langle n l m | V | n l m \rangle + \langle n l m | \hat{V}^2 | n l m \rangle \Big)$$

"simple matter to evaluate

E°_{nl} is known

algebra

$$\langle V \rangle = \frac{e^2}{4\pi\epsilon_0} \langle 1/r \rangle = \frac{e^2}{4\pi\epsilon_0} \frac{1}{n^2 a}$$

$$\langle V^2 \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+\frac{1}{2}) n^3 a^2}$$

Combining fields

$$E_r^{(1)} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right]$$

valid by itself for pionic atom
pion is spin zero

another effect of same size due to spin orbit

Darwin term

claim $\quad H' = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\ \vec{L}\cdot\vec{S}$

derivation :

- From Dirac equation in non-rel reduction
  best method

- intuitive moving ~~charge~~ electron
  in proton's E field gives $\vec{B}$ which
  interacts with S

$$\vec{B} = \frac{\vec{v}_e \times \vec{E}}{c^2}$$

1st non rel (see Purcell)

$$|E| = \frac{e}{4\pi\epsilon_0 r^2}$$

$$|V| = \frac{L}{mr}$$

so as seen by electron

$$B = \frac{e\, L}{4\pi\epsilon_0 c^2 m r^3}$$

classical

$$\mu = g\left(\frac{q}{2m}\right)S = -g\frac{e}{2m}S = \frac{e}{m}S$$

recall factor of 2 from "g-factor"

$$H' = \mu \cdot B = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\, S \cdot L$$

unfortunately this is not right there is an additional factor of $\frac{1}{2}$ due to "Thomas ~~[illegible]~~ Precession"

Note $H' = -\mu \cdot B$ only is valid for an inertial frame but here electron is non-inertial. The derivation is subtle but gives $\frac{1}{2}$

$$H' = \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2}\frac{1}{r^3}\,\vec{S}\cdot\vec{L}$$

Now again we have degenerate pert. theory need to choose "good" basis.

Claim $\hat{L}^2$ still good quantum number
but $\hat{L}^2$ is ~~not~~ good too but ~~m~~
~~m~~ However m_l is not

$H' \sim \vec{L} \cdot \vec{S}$. does not commute with L_z
but does commute with J^2, J_z
where $\vec{J} = \vec{L} + \vec{S}$

$$J = L + \tfrac{1}{2}$$
$$\phantom{J = {}} L - \tfrac{1}{2}$$

$$E'_{so} = \langle H' \rangle = \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2}\langle L \cdot S\rangle\left\langle\frac{1}{r^3}\right\rangle$$

now $\left\langle \frac{1}{r^3} \right\rangle \overset{\text{algebra}}{=} \dfrac{1}{l(l+\frac{1}{2})(l+1)\,n^3a^3}$

$$\langle \hat{L}\cdot\hat{S}\rangle = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

$$= \frac{1}{2}\left(j(j+1) - (l)(l+1) - \frac{1}{4}\right)$$