

$$\Psi_a(r_1)\Psi_b(r_2) + \Psi_b(r_1)\Psi_a(r_2) \rightarrow \text{first excited wave function is the same so non-degenerate for Bosons}$$

## Bosons and Fermions

- Suppose two noninteracting particles  $\Psi(\vec{r}_1, \vec{r}_2) = \Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2)$
- however this assumes we can tell particle 1 and particle 2 apart, since we are dealing w/ probabilities this is no good

↳ Instead construct a wave function that is non-committal to which particle is in which state

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = A (\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) \pm \Psi_b(\vec{r}_1)\Psi_a(\vec{r}_2))$$

state of particle 1 at  $r_1$  can either be in  $\Psi_b$  or  $\Psi_a$ . Admits two kinds of identical particles (+ bosons) and (- fermions)

\* Bosons & Fermions are defined by spin so the connection to statistics seems strange, need relativistic

$$\text{Bosons: } \Psi_{+}(\vec{r}_1, \vec{r}_2) = \Psi_{+}(\vec{r}_2, \vec{r}_1) \quad (\text{symmetric})$$

$$\text{Fermions: } \Psi_{-}(\vec{r}_1, \vec{r}_2) = -\Psi_{-}(\vec{r}_2, \vec{r}_1) \quad (\text{antisymmetric})$$

- if  $\Psi_a = \Psi_b$ , two identical fermions cannot occupy the same state

$$\Psi_{-}(\vec{r}_1, \vec{r}_2) = A [\Psi_a(\vec{r}_1)\Psi_a(\vec{r}_2) - \Psi_a(\vec{r}_2)\Psi_a(\vec{r}_1)] = 0 \quad (\text{Pauli exclusion principle})$$

Example two non-interacting particles in the infinite well inf well states (one particle)  $\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$ ,  $E_n = n^2 K$ ,  $K = \frac{\pi^2 \hbar^2}{2m a^2}$

$$\text{If distinguishable: } \Psi_{n_1 n_2}(x_1, x_2) = \Psi_{n_1}(x_1)\Psi_{n_2}(x_2), E_{n_1 n_2} = (n_1^2 + n_2^2)K$$

$$\text{If identical Bosons: } \sqrt{\frac{2}{a}} \left[ \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{2\pi}{a}x_2\right) + \sin\left(\frac{2\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \right], E = 5K$$

Ground  $n_1=1, n_2=1$  (first excited but ground state is the same as distinguishable)  
1st excited  $n_1=1, n_2=2$  (vice versa)

$$\text{If identical Fermions: } \sqrt{\frac{2}{a}} \left[ \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{2\pi}{a}x_2\right) - \sin\left(\frac{2\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \right]$$

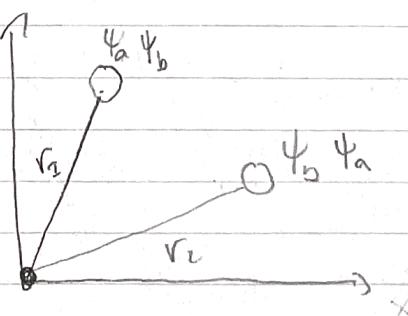
Its ground state is

$$5K$$

No Energy  $\approx 2K$

$$= A [\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) \pm \Psi_b(\vec{r}_1)\Psi_a(\vec{r}_2)]$$

non-committal as to what state both the particles are because it could be either one they are identical



Getting a sense for the symmetrization argument

[Symmetrization Argument]  $\Psi_{\pm}(r_1, r_2) = A [\Psi_a(r_1)\Psi_b(r_2) \pm \Psi_b(r_1)\Psi_a(r_2)]$

bosons + fermions -

\* looking at how the expectation value changes for distinguishable & indistinguishable particles  $\Psi_a + \Psi_b$  are orthogonal & normalized

Distinguishable  $\rightarrow \Psi(x_1, x_2) = \Psi_a(x_1)\Psi_b(x_2)$

Indistinguishable  $\rightarrow \Psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} [\Psi_a(x_1)\Psi_b(x_2) \pm \Psi_b(x_1)\Psi_a(x_2)]$

↳ [calculate the of square of separation distance]  $\rightarrow \langle (x_2 - x_1)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

Distinguishable  $\langle x_1^2 \rangle = \int x_1^2 |\Psi_a(x_1)|^2 dx_1 \int |\Psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$

$$\langle x_2^2 \rangle = \int |\Psi_a(x_1)|^2 dx_1 \int x_2^2 |\Psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

$$\langle x_1 x_2 \rangle = \int x_1 |\Psi_a(x_1)|^2 dx_1 \int x_2 |\Psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$$

So  $\langle (x_2 - x_1)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$

Identical Particles doing  $\Psi_{\pm}^* \Psi_{\pm}$

$$\langle x_1^2 \rangle = \frac{1}{2} \left[ \int x_1^2 |\Psi_a(x_1)|^2 dx_1 \int |\Psi_b(x_2)|^2 dx_2 + \int x_1^2 |\Psi_b(x_1)|^2 dx_1 \int |\Psi_a(x_2)|^2 dx_2 + \right. \\ \left. \pm \int x_1^2 \Psi_a(x_1)^* \Psi_b(x_2) dx_1 \int \Psi_b(x_2)^* \Psi_a(x_1) dx_2 \pm \int x_1^2 \Psi_b(x_1)^* \Psi_a(x_2) dx_1 \int \Psi_a(x_2)^* \Psi_b(x_1) dx_2 \right]$$

$$= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) = \langle x_1^2 \rangle$$

$$\langle x_1 x_2 \rangle = \frac{1}{2} \left[ \int x_1 |\Psi_a(x_1)|^2 dx_1 \int x_2 |\Psi_b(x_2)|^2 dx_2 + \int x_1 |\Psi_b(x_1)|^2 dx_1 \int x_2 |\Psi_a(x_2)|^2 dx_2 + \right. \\ \left. \pm \int x_1 \Psi_a(x_1)^* \Psi_b(x_2) dx_1 \int x_2 \Psi_b(x_2)^* \Psi_a(x_1) dx_2 \pm \int x_1 \Psi_b(x_1)^* \Psi_a(x_2) dx_1 \int x_2 \Psi_a(x_2)^* \Psi_b(x_1) dx_2 \right]$$

$$= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab})$$

$$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2 , \quad \langle x \rangle_{ab} = \int x \Psi_a(x)^* \Psi_b(x) dx$$

↳ finally  $\langle (x_2 - x_1)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2$

$$\hookrightarrow \langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle \mp 2|\langle x \rangle_{ab}|^2$$

for distinguishable particles bosons tend to be closer together fermions tend to be further apart

$\Psi_a$  represented the separated solution for one particle

Solution for one particle

## Identical Particles

Single particle:  $\Psi(\vec{r}, t)$

two particles:  $\Psi(\vec{r}_1, \vec{r}_2, t) \rightarrow$  wave function is dependent on the position of both particles  $V(\vec{r}_1, \vec{r}_2, t)$

↳ time evolution by  $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$ ,  $\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2)$

↳ probability:  $\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3 \vec{r}_1 d^3 \vec{r}_2 = 1$

time ind potentials:  $\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2) e^{-iEt/\hbar}$

↳ then:  $-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi \leftarrow$  hard to solve

1. Non-interacting particles, just subject to some external force  
 ex connected to two different springs

$$V(\vec{r}_1, \vec{r}_2) = V_1(\vec{r}_1) + V_2(\vec{r}_2)$$

then can be solved  
 by separation of variables  
 (using)

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2)$$

solve for  $\psi_a$   $\rightarrow -\frac{\hbar^2}{2m_1} \nabla_1^2 \psi_a(\vec{r}_1) + V_1(\vec{r}_1) \psi_a(\vec{r}_1) = E_a \psi_a(\vec{r}_1)$

$$E = E_a + E_b$$

solve for  $\psi_b$   $-\frac{\hbar^2}{2m_2} \nabla_2^2 \psi_b(\vec{r}_2) + V_2(\vec{r}_2) \psi_b(\vec{r}_2) = E_b \psi_b(\vec{r}_2)$

Total Wave function  $\Psi(\vec{r}_1, \vec{r}_2, t) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) e^{-i(E_a+E_b)t/\hbar}$   
 $= \psi_a(\vec{r}_1) e^{-iE_a t/\hbar} \psi_b(\vec{r}_2) e^{-iE_b t/\hbar} = \Psi_a(\vec{r}_1, t) \Psi_b(\vec{r}_2, t)$

depend on  $\vec{r}_1$       depend on  $\vec{r}_2$       depend on  $\vec{r}_1$       depend on  $\vec{r}_2$

$$\boxed{\text{Ex}} \quad \Psi(\vec{r}_1, \vec{r}_2, t) = \frac{3}{5} \Psi_a(\vec{r}_1, t) \Psi_b(\vec{r}_2, t) + \frac{4}{5} \Psi_c(\vec{r}_1, t) \Psi_d(\vec{r}_2, t)$$

~~$\Psi_a$  basis function for particle 1,  $\vec{r}_1$~~        ~~$\Psi_d$  basis function for particle 2,  $\vec{r}_2$~~

- state of particle 1 depends on the state of particle 2

↳ Energy of particle  $\rightarrow E_a$  or  $E_c$

entangled

then particle 2's energy is  $E_b$       then particle 2's energy is  $E_d$   
 $(\text{prob } 9/25)$        $(\text{prob } 16/25)$

- 2. instead of independent potentials, what if the potential only depended on the distance between them?

$$V(\vec{r}_1, \vec{r}_2) \rightarrow V(|\vec{r}_1 - \vec{r}_2|)$$

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

$\uparrow$  potential between electrons

Number of states =  $\frac{\text{number of electrons}}{2}$   
 ↓  
 Each  $\mathbf{k}$  is a state

## Free Electron Gas Overview

in inf well potential (box)

$$\hookrightarrow E_{nx,ny,nz} = \frac{\hbar^2 \pi^2}{2m} \left( \left(\frac{n_x}{\ell_x}\right)^2 + \left(\frac{n_y}{\ell_y}\right)^2 + \left(\frac{n_z}{\ell_z}\right)^2 \right) = \frac{\hbar^2 k^2}{2m} : k_x = \frac{n_x \pi}{\ell_x}, k_y = \frac{n_y \pi}{\ell_y}, k_z = \frac{n_z \pi}{\ell_z}$$

↳ [each  $k$  value represents a state that an electron could be in, only 2 electrons per state]

$$\hookrightarrow \begin{bmatrix} \text{Volume } V \\ \text{k-space} \end{bmatrix} \rightarrow k_x \cdot k_y \cdot k_z = \frac{\ell_x^3}{\ell_x \cdot \ell_y \cdot \ell_z} = \frac{\pi^3}{V} \leftarrow \begin{array}{l} \text{Volume of one state} \\ \text{where 2 electrons can be} \end{array}$$

$$\frac{1}{8} \left( \frac{4}{3} \pi k_F^3 \right) = \frac{N_d}{2} \left( \frac{\pi^3}{V} \right)$$

Volume of all states      number of states      Volume of one shell

$$\rightarrow k_F = \left( 3 \pi^2 \frac{N_d}{V} \right)^{1/3}$$

$\frac{N_d}{V}$  = free electron density (number of free electrons per unit volume)

$$\text{Fermi Energy} : E_F = \frac{\hbar^2}{2m} \left( 3 \pi^2 \frac{N_d}{V} \right)^{2/3} \leftarrow \begin{array}{l} \text{(energy at the highest energy} \\ \text{electrons)} \end{array}$$

### Calculating Total Energy!

$$\frac{1}{8} (4\pi k^2) dk \rightarrow \begin{bmatrix} \text{Volume of a} \\ \text{shell in k-space} \end{bmatrix}, \quad \begin{array}{l} \text{to find the number} \\ \text{of electrons (not total } N_d \text{)} \end{array}$$

$$\hookrightarrow 2 \frac{\frac{1}{2} \pi k^2 dk}{\pi^3/V} = \text{number of electrons in this shell in k-space} = \frac{V}{\pi^2} k^2 dk$$

$$\begin{bmatrix} \text{Energy of one} \\ \text{state is just} \end{bmatrix} \rightarrow E = \frac{\hbar^2 \pi^2}{2m} k^2, \quad \begin{bmatrix} \text{Energy of all} \\ \text{states} \\ \text{inside our shell} \end{bmatrix} \rightarrow dE = \left( \frac{\hbar^2 \pi^2}{2m} k^2 \right) \left( \frac{V}{\pi^2} k^2 dk \right)$$

$$E_{tot} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2}{10\pi^2 m} (3\pi^2 N_d)^{5/3} V^{-2/3}$$

little bit of energy little bit of shell

$$\text{Power calc: } dE_{tot} = -\frac{2}{3} \frac{\hbar^2}{10\pi^2 m} (3\pi^2 N_d)^{5/3} V^{-5/3} dV = -\frac{2}{3} E_{tot} \frac{dV}{V}$$

$$P = \frac{2}{3} \frac{E_{tot}}{V} = \frac{(3\pi^2)^{2/3}}{5m} \hbar^2 \left( \frac{N_d}{V} \right)^{5/3}$$

# Solids

- Valence electrons become delocalized & roam around the metal
- No longer subject to the Coulomb field but combined potential of entire lattice
- Sommerfeld: primitive model that ignores all forces except the confining boundaries (electron gas)

## Free Electron Gas

(Imagine an electron experiencing)  
 (no forces at all except at walls)  $\rightarrow V = \begin{cases} 0 & 0 < x < l_x, 0 < y < l_y, 0 < z < l_z \\ \infty & \text{elsewhere} \end{cases}$

$$\hookrightarrow \left[ \begin{array}{l} \text{Schrodinger} \\ \text{Equation} \end{array} \right] \rightarrow -\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi \rightarrow \text{separate} \rightarrow -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X, -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y, \frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z$$

$$\hookrightarrow \text{let } k_x = \frac{\sqrt{2mE_x}}{\hbar}, k_y = \frac{\sqrt{2mE_y}}{\hbar}, k_z = \frac{\sqrt{2mE_z}}{\hbar}$$

## General Solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z)$$

$\hookrightarrow$  [Using  $X(l_x), Y(l_y), Z(l_z) = 0$ ]  
 [On the sin solutions]

$$\left| \begin{array}{l} \text{Boundary Conditions} \\ X(0) = 0, X(l_x) = 0 \\ Y(0) = 0, Y(l_y) = 0 \\ Z(0) = 0, Z(l_z) = 0 \end{array} \right. \quad \left. \begin{array}{l} V = \infty \text{ here} \\ \text{so no chance of finding particle} \end{array} \right. \quad \begin{array}{l} \text{using } X(0), Y(0), Z(0) \\ B_x = 0, B_y = 0, B_z = 0 \end{array}$$

$$k_x l_x = n_x \pi, n_x = 1, 2, 3, \dots$$

$$k_y l_y = n_y \pi, n_y = 1, 2, 3, \dots$$

$$k_z l_z = n_z \pi, n_z = 1, 2, 3, \dots$$

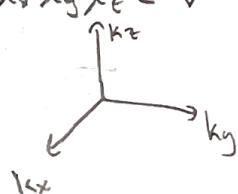
## Wave Function (Normalized)

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right), E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$$

$$\text{let: } \vec{k} = \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix} = \begin{bmatrix} n_x \pi / l_x \\ n_y \pi / l_y \\ n_z \pi / l_z \end{bmatrix} \rightarrow |\vec{k}|^2 = \frac{n_x^2 \pi^2}{l_x^2} + \frac{n_y^2 \pi^2}{l_y^2} + \frac{n_z^2 \pi^2}{l_z^2} \rightarrow E_{n_x n_y n_z} = \frac{\hbar^2 k^2}{2m}$$

Normal value  $\rightarrow l_x l_y l_z = V$

[Imagine in the  $k$  space]



$$\rightarrow \underbrace{k_x k_y k_z}_{\Delta k_x = 1} = \frac{\pi}{l_x} \frac{\pi}{l_y} \frac{\pi}{l_z} = \frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \quad (\text{volume in } k\text{-space})$$

- We have  $N$  electrons ~~each~~ w/ d free electrons
- ↳ If electrons were bosons all the electrons could settle in the ground state
- ↳ But electrons are fermions, so you can only have two electrons in each state

$$||\mathbf{k}||^2 = \frac{n_x^2 \pi^2}{l_x^2} + \frac{n_y^2 \pi^2}{l_y^2} + \frac{n_z^2 \pi^2}{l_z^2}, \quad k_x = \frac{n_x \pi}{l_x}, \quad k_y = \frac{n_y \pi}{l_y}, \quad k_z = \frac{n_z \pi}{l_z}$$

↑  $\mathbf{k}$   
 (Kx, Ky, Kz) → and hence  $n_x$   
 Each point  
 represents a  
 distinct 2 particle  
 state

only positive  
 $\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x}\right) \sin\left(\frac{n_y \pi}{l_y}\right) \sin\left(\frac{n_z \pi}{l_z}\right)$

Each state in the  $\mathbf{k}$  space occupies a  
 volume  $\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$  in this  $\mathbf{k}$ -space  
 ← physical volume

Ground state:  $\psi_{1,1,1} \rightarrow$   
 $k_x$

$N_d = \text{total number of free electrons}$  so  $\frac{N_d}{2}$  is the number of pairs of electrons

$$\left(\frac{N_d}{2}\right) \cdot \left(\frac{\pi^3}{V}\right) = (\text{number of pairs of } e^-) \cdot (\text{volume of one state of our well}) = \text{total volume of all states of each pair of electrons}$$

- Electrons will pile in and fill all the states until there's no more to fill,  $\psi_{1,1,1}, \psi_{1,1,2}, \psi_{1,2,2}, \dots$
- There's a boundary between filled states & unfilled states.
- makes sphere be lowest energy config, w/ no preference
- so this sphere in  $\mathbf{k}$ -space that represents all of our states is the same as

↳ it represents all the states for each pair, each has a volume,

↳ our radius is  $K_{\text{Fermi}}$  = final radius or state

$$\frac{1}{8} \left( \frac{4}{3} \pi k_F^3 \right) = \frac{N_d}{2} \left( \frac{\pi^3}{V} \right) \rightarrow k_F = \left( 3 \rho \pi^2 \right)^{1/3}, \quad \rho \equiv \frac{N_d}{V} = \frac{H \text{ of free electrons}}{\text{unit volume}}$$

↳  $E_F = \frac{\hbar^2}{2m} k_F^2$  = energy at the outer most states, <sup>↑ Fermi surface</sup>

$$E_F = \frac{\hbar^2}{2m} \left( 3 \rho \pi^2 \right)^{2/3}$$

Continued

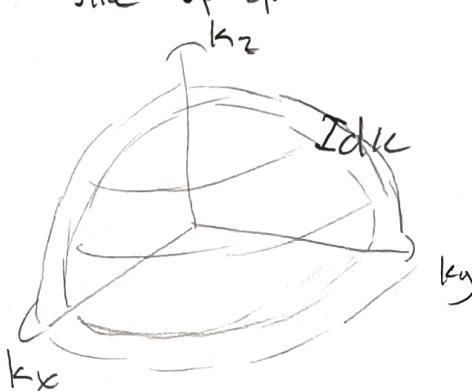
Found:  $k_F = (3\pi^2)^{1/3}$ ,  $P = \frac{Nd}{V}$ ,  $K_F =$  furthest out states,  
highest energy states

$$E_F = \frac{\hbar^2}{2m} (3\pi^2)^{2/3}$$

Lets find total Energy of of the electron gas;

need to get energy for all states, so entire volume in k-space  
but each path in k-space represents a state for a pair of e-

• slice up sphere into  $\frac{1}{8}(4\pi k^2) dk$



How many electron states are in the shell?

$$\frac{\pi^3}{V} = \text{volume of one state}$$

$$2 \cdot \frac{1}{\pi^3/V} \cdot \frac{1}{8}(4\pi k^2) dk \leftarrow \begin{array}{l} \text{as if we need} \\ \text{over } \frac{\pi^3}{V} \\ \text{for} \end{array}$$

2 for each electron

$$= \frac{V}{\pi^2} k^2 dk \quad \text{and} \quad \text{Energy of 1 state} = \frac{\hbar^2 k^2}{2m}$$

= number of electron states or # electrons

$$\rightarrow \text{so total energy in slice} \rightarrow dE = \left(\frac{\hbar^2 k^2}{2m}\right) \left(\frac{V}{\pi^2} k^2 dk\right)$$

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m} \int k^4 dk = \frac{k^2 k_F^5 V}{10\pi^2 m} = \frac{k^2 (3\pi^2 N d)^{5/3}}{10\pi^2 m} V^{-2/3}$$

Recall:  $dE = dW = PdV \rightarrow$  if box expands it decreases in energy

$$dE_{\text{tot}} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 N d)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{\text{tot}} \frac{dV}{V} \quad \text{but } P = \frac{dE}{dV}$$

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} = \frac{2}{3} \frac{\hbar^2 k_F^5}{3 \cdot 10\pi^2 m} \frac{1}{V} \frac{(3\pi^2)^{2/3} \hbar^2}{5m} P^{5/3}, \quad P = \frac{Nd}{V}$$

$$\frac{1}{8} \frac{4}{3} \pi k_F^3 = \frac{Nd}{2} \left(\frac{\pi^3}{V}\right)$$

Instead of total volume, its slice

$$\frac{1}{8} \frac{4}{3} \pi k_F^3 = \frac{Nd}{\pi^3/V} \underbrace{\text{number of electron states}}$$

## Band Structure, Dirac Comb, Periodic Potentials

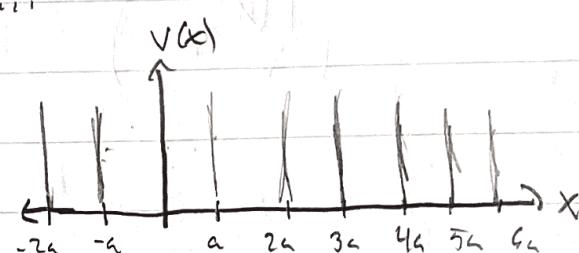
•  $V(x+a) = V(x)$

• Bloch's Theorem:  $\psi(x+a) = e^{iqa} \psi(x)$  (note:  $|\psi(x+a)|^2 = |\psi(x)|^2$ )

↳  $\psi(x+Na) = \psi(x)$  ← compare we say the solid repeats itself, or after the end of the solid, it just starts again,  $N \approx 10^{23}$  per m<sup>3</sup>

$$\psi(x+Na) = e^{iqNa} \psi(x) = \psi(x) \rightarrow e^{iqNa} - 1 = 0 \text{ or } Ng/a = 2\pi n$$

↳  $q = \frac{2\pi n}{Na}$ ,  $n = 0, \pm 1, \pm 2, \dots$



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

In  $0 < x < a$ :  $V=0$  so:  $\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi$   $0 < x < a$

[general solution] →  $\psi(x) = A\sin(kx) + B\cos(kx)$   $0 < x < a$   
[to two diff of B]

In  $-a < x < 0$ :  $\psi(x-a) = e^{iq(a)} \psi(x)$  ↪ can't just plug in back there aren't the same x, when solved delta well

↳ need  $x' = x+a$  ← shift all values by a, →  $\psi(x) = e^{-iqa} \psi(x+a)$

Boundary conditions

1)  $\left. \frac{d\psi_L}{dx} \right|_{x=0} - \left. \frac{d\psi_R}{dx} \right|_{x=0} = \frac{2ma}{\hbar^2} \psi(0)$  and  $\psi_R(0) = \psi_L(0)$

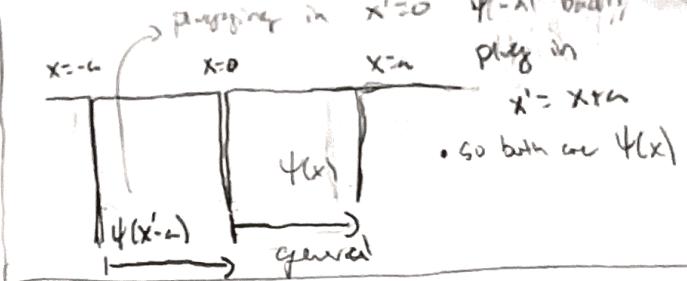
2)  $e^{-iqa} (\psi_L(ka) + \psi_R(ka)) = 0 + B \rightarrow A\sin(ka) = (e^{iqa} - \cos(ka)) B$

1)  $\rightarrow kA - e^{-iqa} k(\psi_L(ka) - \psi_R(ka)) = \frac{2ma}{\hbar^2} B$

↳ algebra →  $\cos(qa) = \cos(ka) + \frac{ma}{\hbar^2 k} \sin(ka)$

## Band Structure

- improving on the last model by including potential of the atoms
- evenly spaced atoms are periodic



## Bloch's Theorem (proof later)

for a potential  $\rightarrow V(x+a) = V(x)$ , solves the Schrödinger equation  $\rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$ , thus  $\psi(x+a) = e^{iqa}\psi(x)$

$\rightarrow \psi(x)$  is not periodic,  $|\psi|^2 \rightarrow |\psi(x+a)|^2 = |\psi(x)|^2$ , can depend on every

\* A real solid has edges, which renders Bloch's theorem useless

\* wrap x-axis around in a circle

\*  $N$  = number of atoms = number of periods

$\rightarrow$  impose:  $\psi(x+Na) = \psi(x) \rightarrow e^{iNqa} \psi(x) = \psi(x)$  since

$\rightarrow \psi(x)(e^{iNqa} - 1) = 0$ ,  $e^{iNqa} = 1$  or  $Nqa = 2\pi n$ ,  $n=0, n=\pm 1, n=\pm 2$

Once we solve one  $\psi(x)$ , we can use Bloch theorem to get the rest:  $\psi(x+a) = e^{iqa}\psi(x)$

Our Potential:  $V(x) = \alpha \sum_{j=0}^{N-1} \delta(x-ja)$  ~~if griffiths weird we use a rectangle~~ ~~as come from~~  
 $V(x)$  ~~as come from~~  
  
 nuclei rest here  
 $\rightarrow$  in region  $0 < x < a$   $\rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi$ ,  $k \equiv \sqrt{\frac{2mE}{\hbar^2}}$   
 $\rightarrow \psi(x) = A\sin(kx) + B\cos(kx)$   $0 < x < a$   
 $\psi(x-a) = e^{-ika}\psi(x)$   
 $\text{let } x' = x+a$   
 $\psi(x) = e^{iqa}\psi(x+a)$

$\psi$  must be continuous on the boundaries next to  $a$   $\rightarrow$  in the region  $-a < x < 0$   $\rightarrow \psi(x) = e^{iqa}(A\sin(k(x+a)) + B\cos(k(x+a)))$

$\left[ \text{at } x=0 \psi \right]$   $\rightarrow e^{iqa}(A\sin(ka) + B\cos(ka)) = 0 + B$   $\left[ \text{and recall the derivative discontinuity relation} \right] \rightarrow \left. \frac{d\psi}{dx} \right|_{x=0} - \left. \frac{d\psi}{dx} \right|_{x=0} = \frac{2ma}{\hbar^2} \psi(0)$

$\rightarrow kA - e^{iqa}k(A\cos(ka) - B\sin(ka)) = \frac{2ma}{\hbar^2}$   $\left[ \text{solve for } A\sin(ka) \right] \rightarrow A\sin(ka) = (e^{iqa} - \cos(ka))B$

Plug into here  $\left[ [e^{iqa} - \cos(ka)][1 - e^{iqa}\cos(ka)] + e^{iqa}\sin^2(ka) = \frac{2ma}{\hbar^2 k} \sin(ka) \right]$

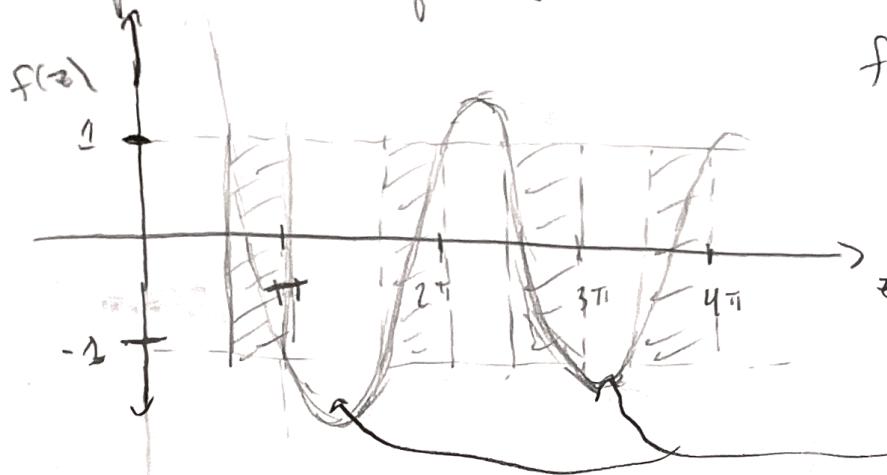
$\left[ \text{simply to } \right] \left[ \cos(qa) = (\cos(ka) + \frac{ma}{\hbar^2 k} \sin(ka)) \right] \rightarrow \frac{z=ka}{\beta = \frac{ma}{\hbar^2}} \rightarrow f(z) = \cos(z) + \beta \frac{\sin(z)}{z}$

$f(z)$

$$(\cos(qa)) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka) \leftarrow \text{determines the possible values of } k, \text{ and hence the allowed energies}$$

$$\hookrightarrow f(z) = (\cos(z) + \beta \frac{\sin(z)}{z}) \leftarrow z \rightarrow k, k - \text{s allowed vals}$$

$\cos(qa)$  has  $\neq$  equal  $f(z)$



$$f(z) = \cos(qa)$$

can only go  
between 1 and -1  
so when  $f(z)$  is  
outside of  
1, -1, there is no  
solutn

& gaps represent forbidden energies

$$qa = \frac{2\pi n}{N}, N \text{ is large number}$$

$n$  is integer

$n=0 \rightarrow \cos(0)=1$  so a  
horizontal line at  $f(z)=1$

$\left[ n=1 \rightarrow \cos\left(\frac{2\pi}{N}\right) \text{ so a} \right]$   
horizontal line just above 0  $\rightarrow$

$\rightarrow \cos\left(\frac{2\pi n}{N}\right)$ , each  $n$  is an allowed  
energy  
|| \* dont forget \*

$$f(z)$$

$$\cos\left(\frac{2\pi n}{N}\right); n=\frac{N}{2} \rightarrow \cos(\pi)=-1, n=N-1 \approx \cos(2\pi)=1$$

$$n=0 \rightarrow \cos(0)=1$$

as  $n \rightarrow \infty$  such a small number starts out  
that the lines are so close together.  
Eventually,  $n=N/2$  and block recycles

$\hookrightarrow$  consequently, there are  $N$  states in each band  $\leftarrow n=0 \rightarrow n=\frac{N}{2} \rightarrow n=N$

So far: We only have 1 electron per atom,  $d=1$

Pauli Exclusion: only two electrons can occupy a given spatial state

$d=1$  will half fill the first band

$d=2$  will completely fill the first band

$d=3$  will half fill the second band

because there are  $Nd$  electrons

$\hookrightarrow$  there are  $N$  states in each band

$\hookrightarrow d=1 \rightarrow N \cdot 1 = N$  free electrons, 2 can be in same state so it fills  $\frac{N}{2}$  states or half a band

[Partly filled band]  $\rightarrow$  very little energy to excite electron so they will just flow (conductor)

[Fully filled band]  $\rightarrow$  has to jump the forbidden zone, lots of energy to excite electrons (insulator)

(make gap narrow)  
so thermal energy  
(can make the temp)

$\rightarrow$  semi conductor, band gaps of 4eV or less

## Time Ind Perturbation Theory

Start w/ some solved:  $H^0 \Psi_n^0 = E_n^0 \Psi_n^0$

Perturb the potential:  $H \Psi_n = E_n \Psi_n \quad \leftarrow H = H^0 + \lambda H'$

[expand]  $\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots$  now plug everything in  
 [and E]  $E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$

[Collect same order terms]  $\rightarrow H^0 \Psi_n^0 + \lambda^1 (H^0 \Psi_n^1 + H^1 \Psi_n^0) + \dots = E_n^0 \Psi_n^0 + \lambda^1 (E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0) + \dots$   
 lowest order      first order

First Order:  $H^0 \Psi_n^1 + H^1 \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0$

[take inner product w/  $\langle \Psi_n^0 |$ ]  $\rightarrow \langle \Psi_n^0 | H^0 \Psi_n^1 \rangle + \langle \Psi_n^0 | H^1 \Psi_n^0 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle + E_n^1 \langle \Psi_n^0 | \Psi_n^0 \rangle$   
 $= E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle$  (cancel)

[So First Order correction]  $\rightarrow E_n^1 = \langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle$  (want to know) (know) (know)

Wave Function Correction: Start w/  $(H^0 - E_n^0) \Psi_n^1 = -(H^1 - E_n^1) \Psi_n^0$

Observe:  $\Psi_n^1 = \sum_m C_m \Psi_m^0 \rightarrow \text{plug in} \sum_m (E_m^0 - E_n^0) C_m \Psi_m^0 = -(H^1 - E_n^1) \Psi_n^0$

[take inner product w/  $\langle \Psi_n^0 |$ ]  $\sum_m (E_m^0 - E_n^0) C_m \langle \Psi_n^0 | \Psi_m^0 \rangle = -\langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle + E_n^1 \langle \Psi_n^0 | \Psi_n^0 \rangle$

- if  $m=n$ , we recover  $E_n^1$  eq, LHS=0,  $\langle \Psi_n^0 | \Psi_n^0 \rangle = 1$

- if  $m \neq n$   $\langle \Psi_n^0 | \Psi_m^0 \rangle = 0$  unless  $m=l$  then has 1

$\hookrightarrow (E_l^0 - E_n^0) C_l = -\langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle \rightarrow C_l = \frac{\langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle}{E_l^0 - E_n^0}$

$\hookrightarrow \Psi_n^1 = \sum_m \frac{\langle \Psi_m^0 | H^1 | \Psi_n^0 \rangle}{(E_n^0 - E_m^0)} \Psi_m^0$

## Time Independent Perturbation Theory

Suppose the time-ind SE was solved  $\rightarrow H^0 \Psi_n^0 = E_n^0 \Psi_n^0$ ,  $\Psi_n^0$  forms a complete set of orthonormal eigenfunctions  $\langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{nm}$ , w/ corresponding  $E_n^0$

Now perturb the potential slightly, goal is to find the new solution  $\rightarrow H \Psi_n = E_n \Psi_n$  ← new solution after perturbation  
\* won't be able to solve exactly for this perturbed system so perturbation theory allows us to find approx solutions \*

### The Beginning

$$H = H^0 + \lambda H' \quad , \quad \lambda = \text{small number}$$

(small perturbation) (first order)

Power series of  $\Psi_n$ ,  $E_n$ : expanded in  $\lambda$ ,

$$\begin{aligned} \Psi_n &= \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \end{aligned} \quad \left. \begin{array}{l} \text{the most general power series, where} \\ \Psi_n^k \text{ represent the higher order terms} \\ \lambda \text{ is some small number (for now)} \end{array} \right\}$$

Plug into  $H \Psi_n = E_n \Psi_n$ :

$$(H_0 + \lambda H')(\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots)$$

Collect powers of  $\lambda$ : ( $\lambda$  tells what order the series is)

$$H^0 \Psi_n^0 + \lambda (H^0 \Psi_n^1 + H' \Psi_n^0) + \lambda^2 (H^0 \Psi_n^2 + H' \Psi_n^1) + \dots =$$

$$E_n^0 \Psi_n^0 + \lambda (E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0) + \lambda^2 (E_n^0 \Psi_n^2 + E_n^1 \Psi_n^1 + E_n^2 \Psi_n^0) + \dots$$

can get rid of  $\lambda$  now as it's a constant, just used to keep track of orders

Lowest order:  $\lambda^0$ ;  $H^0 \Psi_n^0 = E_n^0 \Psi_n^0$  (nothing new)

First order:  $\lambda^1$ ;  $H^0 \Psi_n^1 + H' \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0$  etc... for higher order

take inner product w/  $\langle \Psi_n^0 |$

$$\langle \Psi_n^0 | H^0 \Psi_n^1 \rangle + \langle \Psi_n^0 | H' \Psi_n^0 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle + E_n^1 \langle \Psi_n^0 | \Psi_n^0 \rangle$$

those cancel now

$$\zeta = \langle H^0 \Psi_n^0 | \Psi_n^1 \rangle = \langle E_n^0 \Psi_n^0 | \Psi_n^1 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle = 1$$

$$\hookrightarrow E_n^1 = \langle \Psi_n^0 | H' \Psi_n^0 \rangle \stackrel{!}{=} \langle \Psi_n^0 | H' | \Psi_n^0 \rangle = E_n^1$$

\* Says the first order correction to energy is the expectation value of the perturbation in the state

## Ex 1

- rotating an inf well by  $V_0$ :  $H = V_0$  (no kinetic energy perturbation?)  
 b)  $E_n' = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \rightarrow$  corrected energy levels are  $E_n' \approx E_n^0 + V_0$   
 b) the corrected energies are just lifted by an amount  $V_0$ , (also exact answer)  
 rotating an inf well by  $V_0$   $\rightarrow E_n' = \frac{2V_0}{\pi} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}$   
 but only half way!  
 b) In this case every energy level is lifted by  $V_0/2$ , not exact result but is reasonable for first order approx.

What about the first order correction to the wave function?

$$H^0 \psi_n^0 + H' \psi_n^0 = E_n^0 \psi_n^0 + E_n' \psi_n^0 \rightarrow (H^0 - E_n^0) \psi_n^0 = -(H' - E_n') \psi_n^0$$

differentiation  
eq → what we want to know

inhomogeneous diff eq for  $\psi_n'$

$\psi_n^0$  = the unperturbed wave functions const. in a complete set

thus we can rewrite  $\psi_n'$  as a linear combination of them (Fourier):

$$\psi_n' = \sum_{m \neq n} C_m \psi_m^0$$

if  $m=n$ ,  $\alpha \psi_n^0$  also satisfies  $\psi_n' + \alpha \psi_n^0$  also satisfies this too! for any  $\alpha$ : to get rid of  $\psi_n^0$  term

Moreover look at  $\psi_n'$ :

$\psi_n = \psi_n^0 + \lambda \psi_n' + \dots$  if  $\psi_n'$  has a  $\psi_n^0$  component, pull out and add w/ first term,  $\psi_n^0$

b) letting  $C_{m=n} \psi_m^0 \rightarrow C_{m=n} = 0$ , ensures  $\psi_n'$  is normalized to first order

b)  $\langle \psi_n | \psi_n' \rangle = \langle \psi_n^0 | \psi_n' \rangle + \lambda (\langle \psi_n^0 | \psi_n^0 \rangle + \langle \psi_n^0 | \psi_n' \rangle) + \dots$  as  $\psi_n'$  has no  $\psi_n^0$  component  
 $\downarrow$  so rest have to be 0.

Put boxed eq into diff eq:

$$\sum_{m \neq n} (E_m^0 - E_n^0) C_m \psi_m^0 = - (H' - E_n^0) \psi_n^0 \quad \text{take inner product w/ } \langle \psi_n^0 |$$

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

$\downarrow$  if  $l=n$ , we have orthogonal states so LHS = 0 then  $\uparrow = 1$  and we recover

if  $n \neq l$ ,  $\langle \psi_n^0 | \psi_m^0 \rangle = 0$  unless  $m=l$  then it's 1

$$(E_l^0 - E_n^0) C_l = - \langle \psi_n^0 | H' | \psi_n^0 \rangle + 0 \quad \text{last term is 0 b/c } l \neq n$$

$$C_l = \frac{\langle \psi_n^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_l^0}$$

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

if energy is degenerate then we have to do another approach

# Degenerate Perturbation Theory

Suppose:

$$H^0 \Psi_a^0 = E^0 \Psi_a^0, \quad H^0 \Psi_b^0 = E^0 \Psi_b^0, \quad \langle \Psi_a^0 | \Psi_b^0 \rangle = 0$$

↳ [and we can have]  $\Psi^0 = \alpha \Psi_a^0 + \beta \Psi_b^0$  and  $H^0 \Psi^0 = E^0 \Psi^0$   
[the following]

[Ex]  $H^0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 (x^2 + y^2)$  w/ perturbation  $H^1 = \epsilon m \omega^2 xy$

↳ this hamiltonian has degenerate energies  $E^0 = 2\hbar\omega$  w/  
 $\Psi_a^0 = \Psi_a(x) \Psi_a(y) = \sqrt{\frac{2}{\pi}} \frac{m\omega}{n} y e^{-\frac{m\omega}{2n}(x^2+y^2)}$   
 $\Psi_b^0 = \Psi_b(x) \Psi_b(y) = \sqrt{\frac{2}{\pi}} \frac{m\omega}{k} x e^{-\frac{m\omega}{2n}(x^2+y^2)}$

Solve:

$$H\Psi = E\Psi, \quad \Psi = \alpha \Psi_a + \beta \Psi_b, \quad H = H^0 + \lambda H^1 \text{ and } \Psi = \Psi^0 + \lambda \Psi^1 + \lambda^2 \Psi^2 + \dots$$

↳ [plug into Schrödinger eq]  $\cancel{H^0 \Psi^0 + \lambda (H^1 \Psi^0 + H^0 \Psi^1) + \dots = E^0 \Psi^0 + \lambda (E^0 \Psi^0 + E^0 \Psi^1) + \dots}$

↳ [First order correction]  $\cancel{H^0 \Psi^1 + H^1 \Psi^0 = E^0 \Psi^1 + E^1 \Psi^0}$  now do  $\langle \Psi_a^0 |$

↳  $\langle \Psi_a^0 | H^0 \Psi^1 \rangle + \langle \Psi_a^0 | H^1 \Psi^0 \rangle = E^0 \langle \Psi_a^0 | \Psi^1 \rangle + E^1 \langle \Psi_a^0 | \Psi^0 \rangle$

Now plug in  $\Psi = \alpha \Psi_a^0 + \beta \Psi_b^0$ :  $\langle \Psi_a^0 | H^1 (\alpha \Psi_a^0 + \beta \Psi_b^0) \rangle = E^1 \langle \Psi_a^0 | \alpha \Psi_a^0 + \beta \Psi_b^0 \rangle$

$\rightarrow \underbrace{\alpha \langle \Psi_a^0 | H^1 | \Psi_a^0 \rangle}_{W_{aa}} + \underbrace{\beta \langle \Psi_a^0 | H^1 | \Psi_b^0 \rangle}_{W_{ab}} = \alpha E^1$

↳  $\boxed{\alpha W_{aa} + \beta W_{ab} = \alpha E^1}, \quad W_{ij} = \langle \Psi_i^0 | H^1 | \Psi_j^0 \rangle$

↳ If we do  $\langle \Psi_b^0 | \rightarrow \boxed{\alpha W_{ba} + \beta W_{bb} = \beta E^1}$

↳  $\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \in \mathbb{R}^2$

Solve eigenvalue eq

$$\begin{pmatrix} \omega_{aa} - E^1 & \omega_{ab} \\ \omega_{ba} & \omega_{bb} - E^1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \rightarrow \text{Solve the determinant}$$

$$\hookrightarrow (\omega_{aa} - E^1)(\omega_{bb} - E^1) - (\omega_{ab})^2 = 0, \quad \omega_{ab}^* = \omega_{ba}$$

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

$\hookrightarrow$  if  $\omega_{ab} = 0$  then  $E_{\pm}^1 = 0$  in both cases w/ eigenvectors  $(1), (0)$   
and you don't have degeneracy