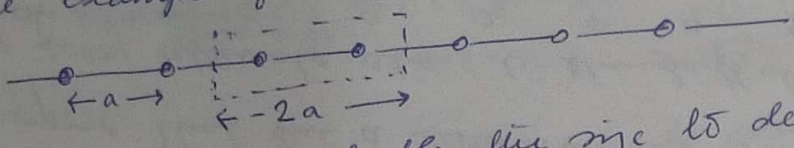


25/1/2018

lec 11. Systems with a band gap: Periodic Distortion

Brillouin Zone Folding: Suppose we intentionally lower the symmetry of a system by redefining the unit cell or by introducing a symmetry breaking distortion. How can we relate the electronic states of the high and the low symmetry systems?

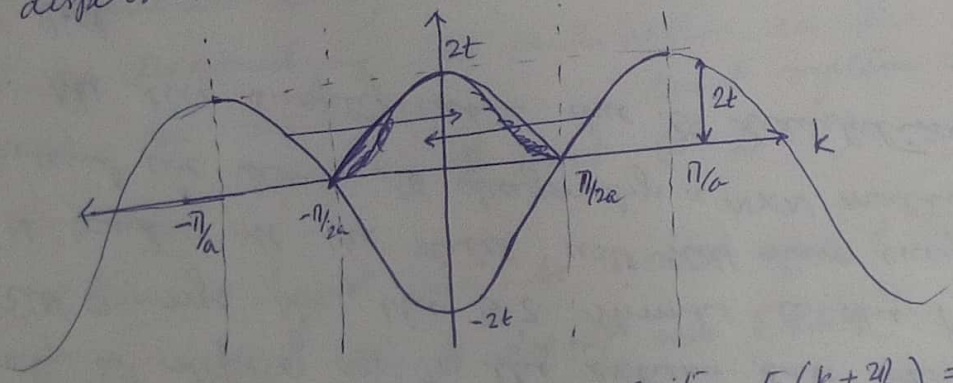
Consider the example of simple 1-d chain with lattice spacing a



We can use a unit cell of double the size to describe the same periodic lattice. The choice of the unit cell is somewhat arbitrary. But the electronic energies & states should be the same. Indeed, this is the case.

~~But we~~ we know the answer in this case. For the case of lattice space we defined a B.Z. between $-\pi/a$ & π/a & ~~got~~ the dispersion

$$E(k) = \tilde{E}_0 - 2t \cos(ka) \quad (194)$$



And the energies have the periodicity $E(k + \frac{2\pi}{a}) = E(k)$ (195)
 Now, with the doubled unit cell the dispersion relation remains the same but the periodicity of the B.Z. & the energy periodicity is halved

$$E(k + \pi/a) = E(k) \quad (196)$$

But this can only be possible if we define 2 bands instead of one: the first is the ~~energy~~ band from $-\pi/2a$ to $\pi/2a$, and the second from $\pi/2a$ to π/a on the RHS & from $-\pi/a$ to $-\pi/2a$ on the LHS. These latter then need to be rigidly translated by the new reciprocal lattice vectors $\pm \pi/a$, to

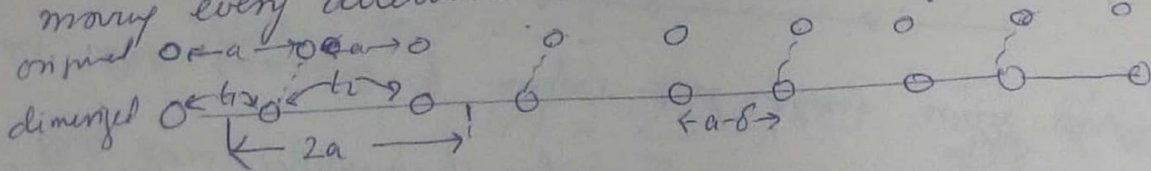
Bring them in to the new B.Z. Thus, we get a system with 2 bands instead of 1. This also makes sense as the basis per unit cell is now of size 2 $\Rightarrow H$ is 2×2 .

Needless to say, the energies are unchanged and to use a or $2a$ as periodicity is immaterial practically. However, dealing with 2 bands instead of 1 is computationally more intensive and hence not favorable. We can continue this procedure by increasing the periodicity in steps of a . In the extreme case when we consider a unit cell of size Na , the B.Z. shrinks to the Γ point and we get N bands. All the states will still have energies between $-2t$ & $2t$, and we have to diagonalize a $N \times N$ matrix to determine them. All the simplification due to translational symmetry is then lost.

This procedure of redefining the BZ and remapping the ~~above~~ states is called BZ folding. An unfolding procedure can also be similarly defined.

Dimerization of Linear Chain & the Peierls Theorem

Now let's suppose that due to a distortion, the 1-d lattice dimerizes by moving every alternate atom to the left by an amount δ .



Consequently, the hopping integrals will change to t_1 & t_2 instead of t . ($t_1 > t_2$, say)

The new Hamiltonian can be written as:

$$H = H^0 + W \quad \rightarrow (197)$$

The new Hamiltonian can be written as:

$$H = H^0 + W \quad \rightarrow (197)$$

$H^0 \rightarrow$ original ~~Hamiltonian~~ Hamiltonian, periodicity a

$W \rightarrow$ symmetry breaking perturbation, periodicity $2a$.

W can be written in terms of t_1, t_2 & t .

$$\left(W = \sum_{n=0,2,\dots} | \psi_n \rangle (t_1 - t) \langle \psi_{n+1} | - \sum_{n=1,3,\dots} | \psi_n \rangle (t_2 - t) \langle \psi_{n+1} | + h.c. \right) \rightarrow (198)$$

If the distortion is small its effect can be estimated by (time-indp.) perturbation theory. For a non-degenerate level we have:

$$E_n = E_n^0 + \langle \psi_n^0 | W | \psi_n^0 \rangle + \sum'_m \frac{|\langle \psi_n^0 | W | \psi_m^0 \rangle|^2}{E_n^0 - E_m^0} + \dots$$

where $H^0 | \psi_n^0 \rangle = E_n^0 | \psi_n^0 \rangle$ (199)

For a degenerate level, to lowest order, the effect is found by diagonalizing the perturbation in the degenerate subspace. For instance, for a 2-level system one obtains:

$$E_{\pm} = E_m^0 \pm |W_{12}| \quad (\text{at } \Delta=0) \quad \rightarrow (200)$$

The problem at hand can be viewed as a 2-level problem at every \vec{k} pt since the H doesn't mix \vec{k} pts. The 2-levels are the 2 bands, $E_1^0(k)$ & $E_2^0(k)$. The first order perturbation theory expression for such a system's energy is given by the Hamiltonian:

$$\begin{bmatrix} E_1^0(k) & W_{12} \\ W_{21} & E_2^0(k) \end{bmatrix} \quad \rightarrow (201)$$

$$\Rightarrow E_{\pm} = E_m^0 \pm \sqrt{\Delta^2 + |W_{12}|^2} \quad \rightarrow (202)$$

when $\Delta = \frac{E_1^0(k) - E_2^0(k)}{2}$, $E_m = \frac{E_1^0 + E_2^0}{2}$ — (203)

If the 2 levels are degenerate, we have $\Delta = 0$ and we

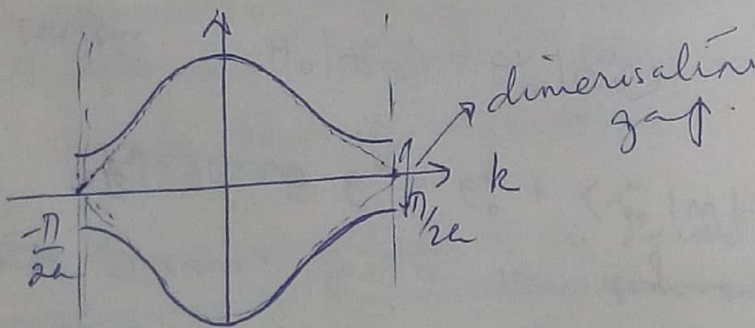
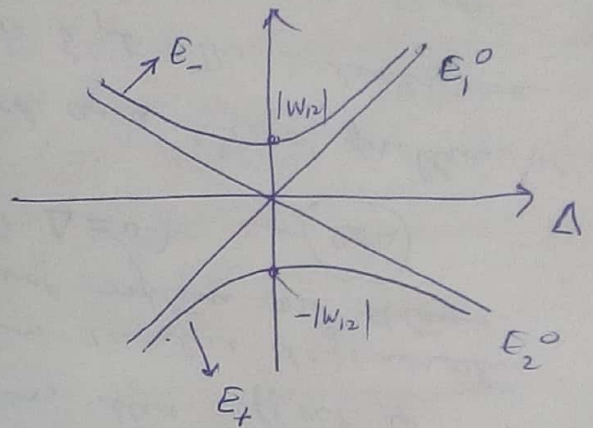
get $E_{\pm} = E_m \pm |W_{12}|$ — (204)

We have assumed $W_{11} = W_{22} = 0$

For small δ , we can write $t_1 = t + \delta t'$, $t_2 = t - \delta t'$ — (205)

In this case, the assumptions regarding W are true.

So a gap opens up at the BZ boundaries where there was a degeneracy between the 2 bands.



We can also solve this problem exactly in the TBM.

We construct the Bloch sums:

$$|\Psi_{\mathbf{R}, \mathbf{k}}\rangle = \sum_{\mathbf{R}, n} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{a}_n)} \left(c_1^{(v)}(\mathbf{k}) |\Psi_{n,1}\rangle + c_2^{(v)}(\mathbf{k}) |\Psi_{n,2}\rangle \right)$$

where $|\Psi_{n,i}\rangle \rightarrow$ AO on the n^{th} unit cell i^{th} basis atom.
 $v \rightarrow$ band index.

With this ~~assatz~~ ansatz we can solve the TB Hamiltonian to

$$\text{get: } \tilde{E}_\nu(k) = (-1)^{\nu+1} \left[(t_1 - t_2)^2 + 4t_1 t_2 \cos^2(ka) \right]^{1/2} \quad \nu=1,2. \quad (207)$$

w.r.t. the onsite energy \tilde{E}_0 .

Once again it is seen that a band-gap opens up at $k = \pm \frac{\pi}{2a}$, of size $E_g = 2|t_1 - t_2|$. — (208)

If the no. of electrons per atom is one (half-filling), the original undistorted chain has a Fermi wavevector of magnitude $k_F = \frac{\pi}{2a}$. Upon ~~distortion~~ dimerization the band gap opens at this wavevector. The lower band is completely filled while the upper is empty.

The electronic energy of the dimerized chain is lower than the undistorted one. We can write:

$$\tilde{E}_\nu(k) = (-1)^{\nu+1} 2t \sqrt{\cos^2(ka) + \left(\frac{\delta t'}{t}\right)^2 \sin^2(ka)} \quad (209)$$

w/ $\delta t'$ defined in (205)

Energy of undimerized lattice:

$$\begin{aligned} \tilde{E}_u &= \sum_{k < k_F} 2 \times \tilde{E}(k) \rightarrow \frac{Na}{2\pi} \times 2 \int_{-\pi/2a}^{\pi/2a} dk \cdot -2t \cos(ka) \quad (N \rightarrow \infty) \\ &= -\frac{2Nat}{\pi} \int_{-\pi/2a}^{\pi/2a} \cos(ka) \quad (210) \end{aligned}$$

Energy of dimerized lattice

$$\tilde{E}_d = \frac{2 \times Na}{2\pi} \int_{-\pi/2a}^{\pi/2a} -2t \sqrt{\cos^2(ka) + \left(\frac{\delta t'}{t}\right)^2 \sin^2(ka)} \quad (211)$$

lec 12. ~~Pert~~ Density of states

Pearls' Distortion, Elastic energy cost.

there is an elastic ^{strain} energy cost associated w/ the dimerization.

$$E_{\text{strain}} = \sum_n \frac{1}{2} \alpha \delta_n^2$$

$$= \frac{N \alpha}{4} \delta^2 \quad (\text{for dimerized lattice}) \quad (210)$$

$\delta_n = \frac{\delta}{2} (1 + (-1)^n)$

From solution of the dimerized chain we can write.

$$\tilde{E}_+(k) = - \sqrt{\Delta(k)^2 + W(k)^2} \quad (205)$$

where

$$\Delta(k) = \frac{E_-(k) - E_+(k)}{2}$$

$$W(k) = W_0 \sin^2(ka)$$

$$W_0 = 2qt$$

(206)

Now the ^{electron} energy diff. between ~~the~~ undimerized & dimerized chain can be shown to behave like $\propto q^2 \ln(q)$ (for small q) (207)

The distortion of the chain entails an elastic energy cost w/ which will appear as

$$E_{\text{elas}} = \sum_n \frac{1}{2} \alpha \delta_n^2$$

$$= \frac{N \alpha}{4} \delta^2 \quad (208)$$

$\delta_n = \frac{\delta}{2} (1 + (-1)^n)$

As $\delta \sim \delta$ in our approx, this means that the elastic energy cost goes as q^2 per electron.

∴ For small q , the stability ~~is~~ in electronic energy will dominate over the elastic energy cost. Hence, a one dimensional chain of atoms with one electron per site will always be unstable to dimerisation \rightarrow Peierls' theorem.

There can actually be a Peierls' transition. As temperature rises, a 2nd order phase transition occurs at temperature T_p given by

$$k_B T_p \approx \Delta \quad \text{--- (209)}$$

Related phenomena - Charge density wave, Spin-Peierls transition.

Density of states:

General case:-

We've seen that the B.Z. is spanned by $\vec{b}_1, \vec{b}_2, \vec{b}_3$
 \rightarrow The volume of the B.Z. is given by $\Omega_{BZ} = |\vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3| = \frac{(2\pi)^3}{\text{unit cell vol.}}$ --- (210)

with N \vec{k} vectors

Space allowed per k -vector is: $\frac{1}{N} \frac{(2\pi)^3}{\Omega} = \frac{(2\pi)^3}{V}$ --- (211)

\rightarrow total vol. of crystal.

Since $N \rightarrow$ large the distribution of k -points becomes continuous and any B.Z. sum can be converted into an integral:

$$\sum_{\vec{k} \in BZ} = \frac{V}{(2\pi)^3} \int d\vec{k} \quad \text{--- (212)}$$

⊗ For instance the total energy in a ^{single band} system. ($2e^-$ /atom)

$$E_{tot} = 2 \sum_{\vec{k} \in BZ} E(\vec{k}) = 2 \frac{(2\pi)^3}{(2\pi)^3} \frac{V}{(2\pi)^3} \int d\vec{k} E(\vec{k}) \quad \text{--- (213)}$$

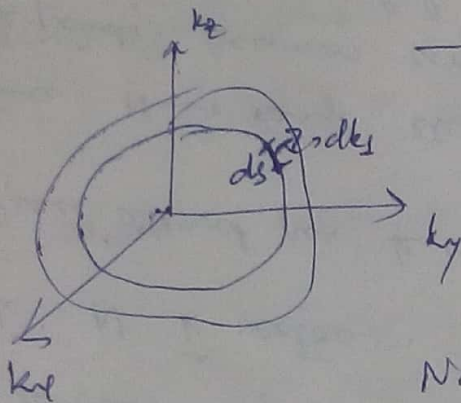
These sums often become more convenient if done over energies
 So we introduce Density of States:

$$D(E) = 2 \sum_{\vec{k} \in \text{BZ}} \delta(E - E(\vec{k})) \quad \text{--- (214)}$$

or more generally,

$$D(E) = 2 \sum_{n, \vec{k}} \delta(E - E_n(\vec{k})) \quad \text{--- (215)}$$

$$\Rightarrow 2 \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\vec{k} \delta(E - E(\vec{k})) \quad \text{--- (216)}$$



This is basically counting all states in the shell region shown in the figure. (2 iso surfaces at E & $E + dE$)

Note

$$\delta(E - E(\vec{k})) = \frac{\Theta(E + dE - E(\vec{k})) - \Theta(E - E(\vec{k}))}{dE} \quad \text{--- (217)}$$

It can also be calculated as an integral over the surface $S(E)$ of the volumes of the cylinders formed by base area dS & height dk_{\perp} where dk_{\perp} is \perp to the surface at \vec{k} .
 i.e. the volumes $dS dk_{\perp}$

$$\begin{aligned} \text{Now, } E(\vec{k} + d\vec{k}) &= E(\vec{k}) + d\vec{k} \cdot \nabla_{\vec{k}} E(\vec{k}) \\ &= E(\vec{k}) + dk_{\perp} |\nabla_{\vec{k}} E(\vec{k})| \quad \text{--- (218)} \end{aligned}$$

$$\text{or } dE = dk_{\perp} |\nabla_{\vec{k}} E(\vec{k})| \quad \because \nabla_{\vec{k}} E \perp E(\vec{k})$$

$$\Rightarrow dk_{\perp} = \frac{dE}{|\nabla_{\vec{k}} E(\vec{k})|} \quad \text{--- (219)}$$

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Lee 13. Density of States (d) & Free-electron theory

Thus,

$$D(E) = \frac{2V}{(2\pi)^3} \int_{S(E)} \frac{dS dk}{dE} = \frac{2V}{(2\pi)^3} \int \frac{dS}{|\nabla_k E(\mathbf{k})|} \quad (220)$$

The pts where $|\nabla_k E(\mathbf{k})| = 0$ are called critical points. It is seen that $D(E)$ is singular ^{at these pts} and its evaluation cannot be performed by a numerical integration easily. Analytic evaluation at the critical pts can, however, be done.

$$\text{Let } E(\mathbf{k}) = E_c \pm \frac{\hbar^2 k_x^2}{2m_x} \pm \frac{\hbar^2 k_y^2}{2m_y} \pm \frac{\hbar^2 k_z^2}{2m_z} \quad (221)$$

↑ Effective masses.

where $m_x, m_y, m_z > 0$ is a convention employed. This is a Taylor expansion about the critical pts.

We can classify the critical pts as:

- M_0 (0 negative signs) = minimum
- M_3 (3 negative signs) = maximum
- M_1, M_2 (1 or 2 negative signs) = saddle pt.

In 1D only M_0 & M_2 (max) can occur. In 2D, M_0, M_1 & M_2 can occur. In 3D M_0, M_1, M_2 & M_3 can occur.

The singularities corresponding to the critical pts are also called van Hove singularities.

Van Hove Theorem: In each dimensionality at least one of all the possible critical pts. must occur.

Using (221) in (220) we have

$$D(E) = \frac{2V}{(2\pi)^3} \int d\vec{k} \delta \left(E_c \pm \sum_x \frac{\hbar^2 k_x^2}{2m_x} - E \right) \quad (222)$$

We can evaluate these integrals by using

$$\delta[f(x)] = \sum_n \frac{\delta(x-x_n)}{|f'(x_n)|} \quad \text{--- (223)}$$

where x_n are simple zeros of $f(x)$

For instance for M_0 at energy E_0 in 1D one has.

$$D(E) = 2 \left(\frac{L}{2\pi} \right) \int \delta(E_0 + \frac{\hbar^2 k^2}{2m_p} - E) dk_x$$

$$= \frac{2\sqrt{2m_p}}{\pi \hbar} \int \delta(E_0 + q_x^2 - E) dq_x \quad \text{--- (224)}$$

$q_x = \frac{\hbar}{\sqrt{2m_p}} k_x$

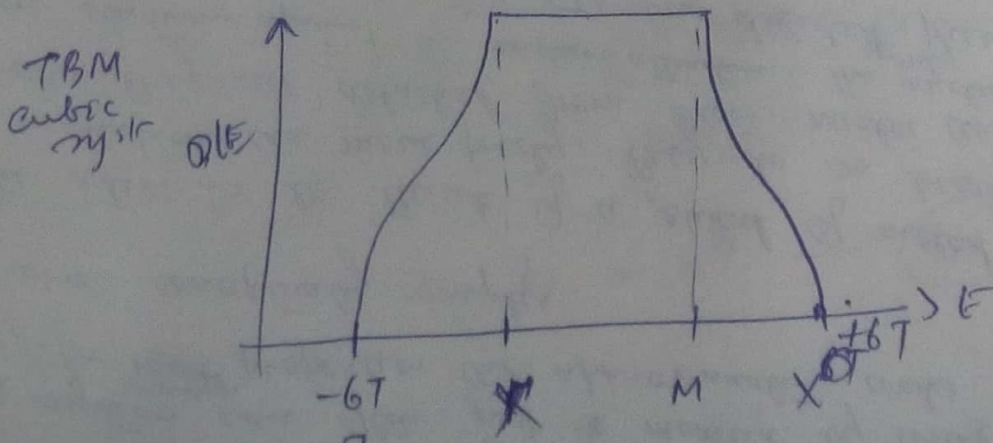
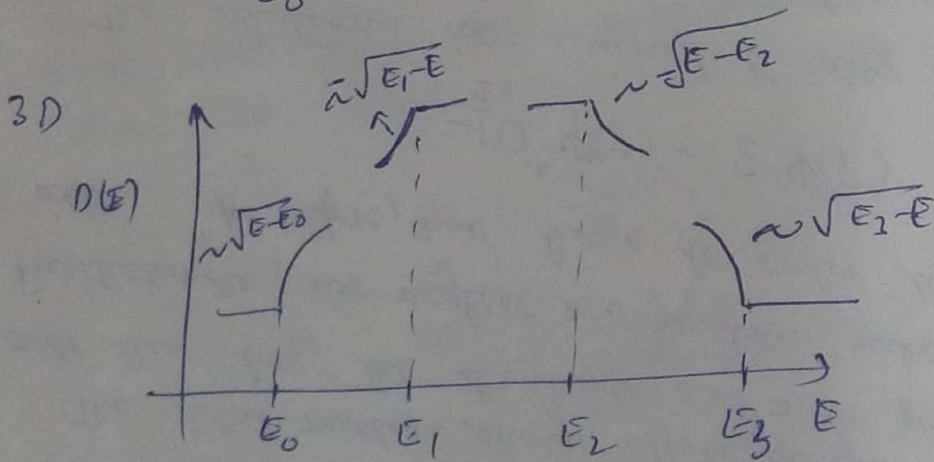
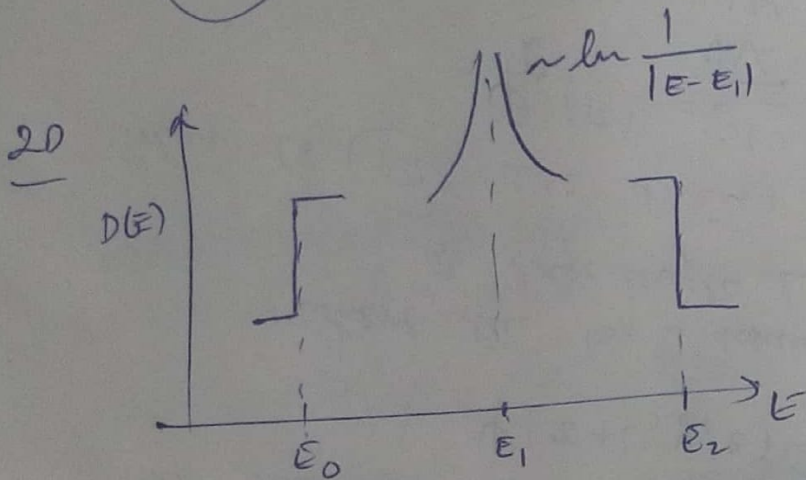
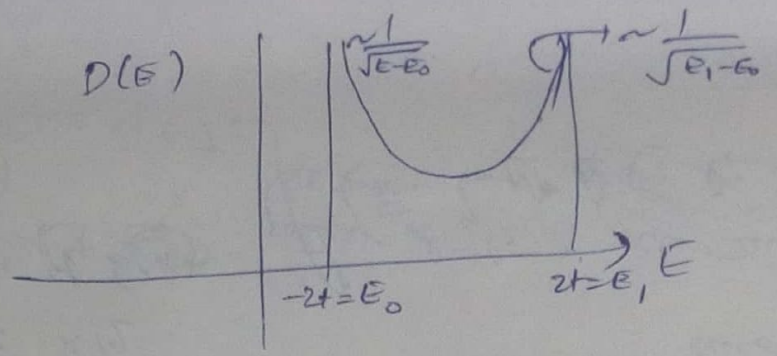
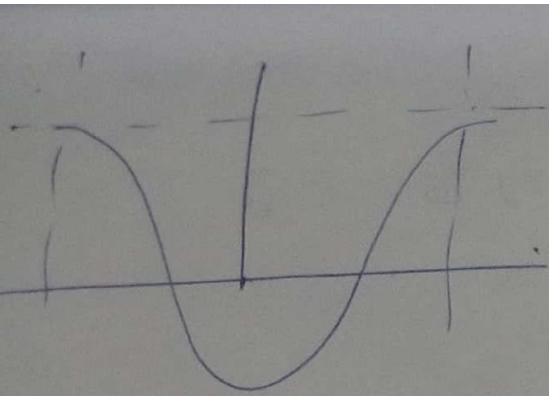
Roots are $q_{x_0} = \pm \sqrt{E - E_0}$ --- (225)

$$\therefore D(E) = \frac{L\sqrt{2m_p}}{\pi \hbar} \int \left[\frac{\delta(q_x - \sqrt{E - E_0})}{2\sqrt{E - E_0}} + \frac{\delta(q_x + \sqrt{E - E_0})}{2\sqrt{E - E_0}} \right] dq_x$$

$$= \frac{L\sqrt{2m_p}}{\pi \hbar} \frac{1}{\sqrt{E - E_0}} \quad (\text{wt } E > E_0) \quad \text{--- (225)}$$

Similarly for M_1

$$D(E) = L \frac{\sqrt{2m_p}}{\pi \hbar} \frac{1}{\sqrt{E_1 - E}} \quad \text{wt } E < E_1 \quad \text{--- (226)}$$



Free electrons

Metallic systems can often just be modeled by using free electron approximation. Actually, for ~~most~~ ^{many} properties the approximation works better than tight-binding. It is also conceptually simpler.

The idea is to think of a chunk of metal as a box in which valence electrons can move freely. They do so because for all practical purposes they are detached from their nuclei and are screened by the core electrons against the nuclear attraction. The nuclear charge still manages to keep the electrons in the box but ~~the~~ ^{only} presents a featureless constant background (neutralizing) potential.

The total nuclear charge is thought of being uniformly smeared over the box. The valence e's move freely through this "jellium". Furthermore, we neglect e-e repulsion making the e's independent as well. As before, we have to solve the one e Schrodinger Eqn.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = \epsilon \psi(\vec{r}) \quad \text{--- (227)}$$

The solutions are assumed to obey periodic B.C.

$$\psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L) = \psi(x, y, z) \quad \text{--- (228)}$$

where the box is assumed to be cubic & of edge length L.

Solns to (227) are then:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \quad \text{--- (229)}$$

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \quad \text{(atomic units used)}$$

$$\vec{k} = \frac{2\pi}{L} (l_1, l_2, l_3)$$

where $l_i \in \mathbb{I}$

where l_1, l_2, l_3 are integers between $-\frac{N}{2}$ and $\frac{N}{2}$.

if there are N ^{atoms} ~~atoms~~ _{electrons} in the system the average density of e's is $n = \frac{N}{V} = \frac{N}{L^3}$ — (230)

Each \vec{k} state is occupied by 2 e's of opposite spin.

Each \vec{k} pt has a volume of $\frac{(2\pi)^3}{V} \Rightarrow \frac{V}{(2\pi)^3}$ k pts per unit vol. of reciprocal space.

As $L \rightarrow \infty$ k pts become continuously distributed.

~~Density of states~~ since $E(\vec{k}) \equiv E(k)$, there is a large degeneracy associated w/ a wave vector k . If the highest occupied states have an energy $E_F = \frac{\hbar^2 k_F^2}{2m}$ — (231)

$k_F \rightarrow$ Fermi wavevector
 $k_F \rightarrow$ Fermi momentum
 $k_F \rightarrow$ Fermi velocity in a.u.

~~then we can write # of states in a~~
 then the Fermi surface is a sphere of radius k_F in Reciprocal space.

$$\therefore N = \frac{4}{3} \pi k_F^3 \times \frac{V}{(2\pi)^3} \times 2 \quad \text{--- (232)}$$

$$\text{or } n = \frac{1}{3\pi^2} k_F^3 \quad \text{--- (233)}$$

if the valency of each atom is Z and the no. of atoms is M then $n = M \cdot Z$ — (234)

$$\text{or } k_F = \left(3\pi^2 M \cdot Z \right)^{1/3} \quad \text{--- (235)}$$

$$= \left(3\pi^2 n \right)^{1/3}$$

$$\text{i.e. } k_F \sim n^{1/3} \quad \text{--- (236)}$$

$k_F \sim 0.01c$
 $E_F \sim 1.5 - 15 \text{ eV}$
 Due to Pauli exclusion principle

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Lec. 14, Free-electron theory (contd)

What about the density of states?

$$\frac{D(E)}{V} = \frac{2}{(2\pi)^3} \int_{S(E)} \frac{dS}{|\nabla_k E(k)|} \quad \text{--- (237)}$$

Here $S(E)$ is the surface of a sphere of radius $k = \sqrt{2E}$
 $\Rightarrow dS = k^2 d\Omega$

$$|\nabla_k E(k)| = |\vec{k}| = \sqrt{2E}$$

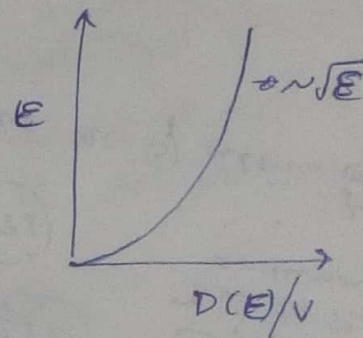
$$\therefore D(E) = \frac{2V}{(2\pi)^3} \int_{\Omega} \frac{(2E)^{3/2} d\Omega}{\sqrt{2E}} = \frac{V \sqrt{2E}}{\pi^2} \quad \text{--- (238)}$$

Total energy of system:

$$E_{\text{tot}} = \int_0^{E_F} dE D(E) E$$

$$= \frac{V\sqrt{2}}{\pi^2} \int_0^{E_F} dE E^{3/2} = \frac{2\sqrt{2}}{5\pi^2} V E_F^{5/2} \quad \text{--- (239)}$$

$$= \frac{2\sqrt{2}}{5\pi^2} \times V \times k_F^{5/2} \times \frac{1}{2^{5/2}} = \frac{V}{10\pi^2} (3\pi^2 n)^{5/3}$$



energy per unit volume $= \frac{E_{\text{tot}}}{V} = C n^{5/3} \quad \text{--- (239)}$

Also, energy per electron $= \frac{3E_F}{5} \quad \text{--- (240)}$

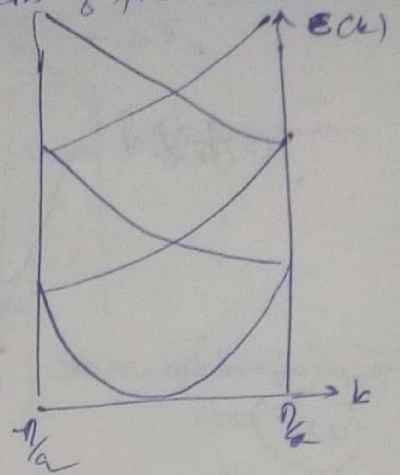
Scity radius $r_s \equiv 1/n^{1/3} \quad \text{--- (241)}$

To accommodate the notion of periodicity we did at first only talk about BZ. ~~finding~~ why gives the reduced BZ representation of free electron

This yields several degeneracies.

The periodic crystal potential can be treated as a perturbation on the uniform background $\rightarrow \hat{V}$.

$$\therefore E(\vec{k}) = E^0(\vec{k}) + \langle \vec{k} | \hat{V} | \vec{k} \rangle + \sum_{\vec{k}'} \frac{|\langle \vec{k} | \hat{V} | \vec{k}' \rangle|^2}{E_{\vec{k}}^0 - E_{\vec{k}'}^0} \quad (242)$$



Now, $V(\vec{r})$ has periodicity a in each dir. (say)

So we can write it in a Fourier series:

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \quad (243)$$

where $\vec{G} = \frac{2\pi}{a} (h, k, l)$ $\xrightarrow{\text{integers}}$ Reciprocal Lattice vector

$$\therefore \langle \vec{k} | \hat{V} | \vec{k}' \rangle = \frac{1}{V} \sum_{\vec{G}} V(\vec{G}) \int_V d\vec{r} e^{i(\vec{k}' + \vec{G} - \vec{k}) \cdot \vec{r}}$$

$$= \sum_{\vec{G}} V(\vec{G}) \delta(\vec{k}' + \vec{G} - \vec{k}) \quad (244)$$

$$= V_0 \delta(\vec{k}' - \vec{k}) + \sum_{\vec{G} \neq 0} V(\vec{G}) \delta(\vec{k}' - (\vec{k} + \vec{G})) \quad (245)$$

$$\therefore E(\vec{k}) = E^0(\vec{k}) + V_0 + \sum_{\vec{G} \neq 0} \frac{|V(\vec{G})|^2}{E_{\vec{k}}^0 - E_{\vec{k}+\vec{G}}^0} \quad (246)$$

$V(\vec{G}) \rightarrow$ Fourier component of the perturbation of wavevector \vec{G} .
degeneracy

This formula is only valid when $E_{\vec{k}}^0 \neq E_{\vec{k}+\vec{G}}^0$. This w'd happen at MB $|\vec{k}| = |\vec{k} + \vec{G}|$, i.e. when \vec{k} is at a BZ boundary.

at a zone boundary ($\text{at } \vec{k} = \vec{G}/2$) we assume only the waves of \vec{k} 's differing by a reciprocal lattice are mixed we have:

$$\psi_{\vec{k}} = \sum_{\vec{G}} \alpha_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}} \quad \vec{k} \rightarrow \text{reduced B.Z.}$$

$$\therefore \left[-\frac{\nabla^2}{2} + V(\vec{r}) \right] \psi_{\vec{k}} = \epsilon(\vec{k}) \psi_{\vec{k}} \quad \text{--- (248)}$$

projection on $e^{i(\vec{k}-\vec{G}') \cdot \vec{r}}$ yields:

$$\left[\epsilon_{\vec{k}-\vec{G}'}^{(0)} - \epsilon(\vec{k}) \right] \alpha_{\vec{k}-\vec{G}'} + \sum_{\vec{G} \neq \vec{G}'} V_{(\vec{G}-\vec{G}')} \alpha_{\vec{k}-\vec{G}} = 0 \quad \text{--- (248)}$$

$$\forall \vec{G}, \vec{G}'$$

At first order in the perturbation:

When \vec{k} is at a zone boundary formed by vector \vec{G} then $\epsilon_{\vec{k}}^{(0)} = \epsilon_{\vec{k}-\vec{G}}^{(0)}$. Considering only these 2 waves in (248) ($\vec{G}' = 0$ & $\vec{G}' = \vec{G}$)

we get

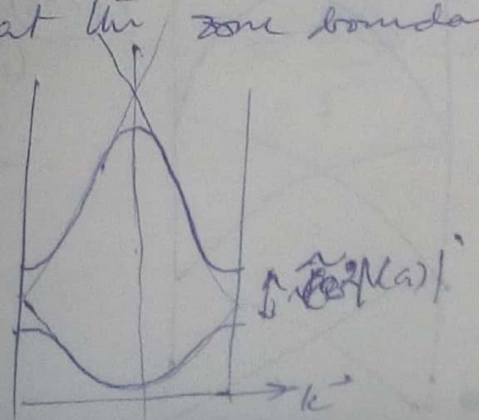
$$\left. \begin{aligned} (\epsilon_{\vec{k}}^{(0)} - \epsilon(\vec{k})) \alpha_{\vec{k}} + V_{\vec{G}} \alpha_{\vec{k}-\vec{G}} &= 0 \\ V_{-\vec{G}} \alpha_{\vec{k}} + (\epsilon_{\vec{k}-\vec{G}}^{(0)} - \epsilon(\vec{k})) \alpha_{\vec{k}-\vec{G}} &= 0 \end{aligned} \right\} \text{--- (249)}$$

These can be solved to get

$$\epsilon^{\pm}(\vec{k}) = \frac{1}{2} (\epsilon^{(0)}(\vec{k}) + \epsilon^{(0)}(\vec{k}-\vec{G})) \pm \frac{1}{2} \sqrt{(\epsilon^{(0)}(\vec{k}) - \epsilon^{(0)}(\vec{k}-\vec{G}))^2 + 4|V_{\vec{G}}|^2}$$

& $\psi^{\pm}(\vec{k})$ eigenfn.

Thus the degeneracy gets split at the zone boundaries.



Hartree-Fock Theory (Review)

many-electron wavefn: First let's consider the independent electron problem.

$$\hat{H} = \sum_i \hat{h}(i) \quad \text{--- (251)}$$

We can separate variables & look for solution of

$$\hat{h} \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) \quad \text{--- (252)}$$

Since, in the Fock basis, the many-electron wavefn is a product of one-electron wavefn's

$$\Psi(x_1, x_2, x_3, \dots, x_N) = \prod_{i=1}^N \psi_{\epsilon_i}(x_i) \quad \text{--- (253)}$$

where $x_i = (\vec{r}_i, \sigma_i) \rightarrow$ spin coordinates

$$\text{spin orbitals} \leftarrow \Psi(x) = \psi(\vec{r}) \chi(\sigma) \rightarrow$$

Let $\hat{P}_{ij} \rightarrow$ permutation operator of i & j e's.

$$\hat{P}_{ij} \Psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = \Psi(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad \text{--- (254)}$$

Note that $\hat{P}_{ij}^2 = \mathbb{1}$

Also note that $[\hat{P}_{ij}, \hat{H}] = 0 \quad \forall i \neq j$

$$\left. \begin{array}{l} \hat{P}_{ij}^2 = \mathbb{1} \\ [\hat{P}_{ij}, \hat{H}] = 0 \end{array} \right\} \quad \text{--- (255)}$$

\therefore eigenfn's s/d be common. But Ψ written above are not eigenfn's of \hat{P}_{ij} .

Let Φ be an eigenfn of \hat{P}_{ij} .

$$\Rightarrow \hat{P}_{ij} \Phi = \lambda \Phi$$

$$\& \hat{P}_{ij}^2 \Phi = \Phi = \lambda^2 \Phi \Rightarrow \lambda = \pm 1 \quad \text{--- (256)}$$

$$\Rightarrow \Phi(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N) = \pm \Phi(x_1, x_2, \dots, x_j, \dots, x_i, \dots, x_N) \quad \text{--- (257)}$$

Fundamental particles are divided into Bosons & fermions if λ is + & - respectively.

being fermions require $\hat{P}_{ij} \Phi = -\Phi$ — (258)

Note that the set of permutation $\{\hat{P}_{ij}, \hat{P}_{ij}, \hat{P}_{kl}, \dots\}$ form a group (Permutation group) and the eigenfn of \hat{P} form a 1-d representation for the group.

All even permutations have eigenvalue +1 (character)

while odd " " " " " -1

To construct Φ from Ψ we can consider the L.C.

$$\Phi = \sum_m c_m \hat{P}^{(m)} \Psi \quad \text{--- (259)}$$

where m runs over all $N!$ permutations of N electron

Turns out that $\Phi = \hat{A} \Psi(x_1, x_2, \dots, x_N)$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1}(x_1) & \psi_{n_2}(x_1) & \dots & \psi_{n_N}(x_1) \\ \psi_{n_1}(x_2) & \psi_{n_2}(x_2) & \dots & \psi_{n_N}(x_2) \\ \dots & \dots & \dots & \dots \\ \psi_{n_1}(x_N) & \psi_{n_2}(x_N) & \dots & \psi_{n_N}(x_N) \end{vmatrix}$$

$\Phi \rightarrow$ Slater Determinant

By construction follows P.E.P.

The choice of $\{n_i\}$ is called a configuration. — (260)

1/2018

Dec 15. Hartree-Fock Theory (ctd)

matrix elements w/ Slater determinants: (Slater-Condon Rules)

Let $\Phi_n \equiv \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P} \psi_{n_1}(x_1) \psi_{n_2}(x_2) \dots \psi_{n_N}(x_N)$ — (261)

The operators we will encounter can be classified into 1-body & 2-body operators:

$\hat{f}_1 \equiv \sum_{i=1}^N \hat{f}(\hat{x}_i)$ — (262)

$\hat{g}_{12} = \sum_{i < j} \hat{g}(\hat{x}_i, \hat{x}_j)$ — (263)

Pair permutation symmetric
i.e. $g(\hat{x}_i, \hat{x}_j) = g(\hat{x}_j, \hat{x}_i)$

We are interested in determining the matrix elements of such operators over Slater determinants. i.e. $\langle \Phi_m | \hat{F} | \Phi_n \rangle = ?$

Consider that \hat{F} is permutation symmetric operator. i.e. if \hat{P} is an arbitrary particle permutation then

$\hat{P} \hat{F} = \hat{F} \hat{P}$ — (264)

Now, $\langle \Phi_m | \hat{F} | \Phi_n \rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \langle \Phi_m | \hat{F} \hat{P} | \psi_{n_1}(x_1) \psi_{n_2}(x_2) \dots \psi_{n_N}(x_N) \rangle$
 $= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \langle \hat{P}^{-1} \Phi_m | \hat{F} | \psi_{n_1} \psi_{n_2} \dots \psi_{n_N} \rangle$ (∵ $\hat{P}^\dagger = \hat{P}^{-1}$)
 $= \frac{1}{\sqrt{N!}} \sum_P (-1)^{2P} \langle \Phi_m | \hat{F} | \psi_{n_1} \psi_{n_2} \dots \psi_{n_N} \rangle$ — (265)

$$= \frac{1}{\sqrt{N!}} \int dx_1 dx_2 \dots dx_N \Phi_m^* \hat{F}(\psi_{m_1} \psi_{m_2} \dots \psi_{m_N}) \quad (267)$$

This is a useful formula to obtain matrix elements.

It's assume that $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ — (268)

Then, Consider $\hat{F} = \hat{1}$

$$\Rightarrow \langle \Phi_m | \Phi_m \rangle = \frac{1}{\sqrt{N!}} \int dx_1 dx_2 \dots dx_N \Phi_m^* \times (\psi_{m_1} \psi_{m_2} \dots \psi_{m_N})$$

$$= \sum_P \frac{1}{P!} \int dx_1 dx_2 \dots dx_N \hat{P} \{ \psi_{m_1} \psi_{m_2} \dots \psi_{m_N} \} (\psi_{m_1} \psi_{m_2} \dots \psi_{m_N}) \quad (269)$$

~~$$\neq \frac{1}{N!} \int dx_1 dx_2 \dots dx_N \psi_{m_1} \psi_{m_2} \dots \psi_{m_N}$$~~

Now if $m_1 < m_2 < \dots < m_N$ is the convention then

$$\langle \Phi_m | \Phi_m \rangle = \frac{1}{N!} \langle \psi_{m_1} | \psi_{m_1} \rangle \dots \langle \psi_{m_N} | \psi_{m_N} \rangle = \frac{1}{N!} \delta_{m_1 n_1} \dots \delta_{m_N n_N} \quad (270)$$

∴ any other permutation w/d necessarily give 0 by (268)

Thus, the Slater determinants formed by various choices of $\psi(n_1, n_2, \dots, n_N)$ are ^{mutually} orthogonal.

~~$$\Rightarrow \langle \Phi_m | \Phi_n \rangle = \frac{1}{\sqrt{N!}} \int dx_1 \dots dx_N \Phi_m^* \hat{F}(\psi_{m_1} \psi_{m_2} \dots \psi_{m_N})$$~~

~~$$\frac{1}{N!} \int dx_1 \dots dx_N \hat{P} \{ \psi_{m_1} \psi_{m_2} \dots \psi_{m_N} \} \psi_{n_1} \psi_{n_2} \dots \psi_{n_N}$$~~

$$= \sum_{j=1}^N \sum_P (-1)^P \int dx_{1-N} \hat{P} \{ \psi_{m_1} \psi_{m_2} \dots \psi_{m_N} \} \times f(x_j) \psi_{m_j}$$

$$= \sum_{j=1}^N \langle \psi_{m_j} | \psi_{m_j} \rangle \delta_{m,n}$$

no other combination

$$= \sum_{j=1}^N \sum_{\mu \neq j} \lambda_p \left(\prod_{\mu \neq j} \langle \psi_{m_\mu} | \psi_{m_j} \rangle \right) \langle \psi_{m_j} | \psi_{m_j} \rangle$$

Use this to show that.

(1) $\langle \Phi_n | \hat{F}_2 | \Phi_n \rangle = \sum_{i=1}^N \langle \psi_{n_i} | \hat{F} | \psi_{n_i} \rangle$ — (271)

(2) Φ_n & Φ_m differ by switching $\psi_i \rightarrow \psi_j$ then

$$\langle \Phi_m | \hat{F}_2 | \Phi_n \rangle = \langle \psi_j | \hat{F} | \psi_i \rangle$$
 — (272)

(3) $\langle \Phi_n | \hat{F}_2 | \Phi_n \rangle = \frac{1}{2} \sum_i \sum_j \left[\langle \psi_i \psi_j | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \psi_j \psi_i \rangle \right]$

$$= \frac{1}{2} \sum_i \sum_j \langle \psi_i \psi_j | \psi_i \psi_j \rangle$$
 — (273)

(4) $\Phi_n \rightarrow \Phi_m$ involves $\psi_{\mu i} \rightarrow \psi_{\mu j}$

$$\langle \Phi_m | \hat{F}_2 | \Phi_n \rangle = \sum_j \langle \psi_{\mu i} \psi_{\mu j} | \psi_{\mu i} \psi_{\mu j} \rangle$$
 — (274)

③ If $\Phi_m \rightarrow \Phi_n$ involves $\psi_\mu \psi_\nu \rightarrow \psi_\nu \psi_\mu$ then

$$\langle \Phi_m | \hat{F}_2 | \Phi_n \rangle = \langle \psi_\mu \psi_\nu | | \psi_\nu \psi_\mu \rangle \quad \text{--- (275)}$$

8/2/2018

Lec 16. Hartree Fock Theory (ch 1)

We look for the best Slater determinant wavefn composed of spin orbitals $\{\psi_\mu\}$ that yields the lowest energy estimate

$$E = \frac{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \quad \text{--- (276)}$$

This is the Hartree-Fock problem.

Since the working space is that of spin orbitals $\{\psi_\mu\}$ we further restrict the choices to be mutually orthogonal & normalized

$$\langle \psi_\mu | \psi_\nu \rangle = \delta_{\mu\nu} \quad \text{--- (277)}$$

$\mu, \nu = 1, N$

We've seen that if (277) holds then $\langle \Phi_0 | \Phi_0 \rangle = 1$

where $\Phi_0 = \hat{A} \{\psi_1, \psi_2, \dots, \psi_N\}$. --- (278)

Therefore

Thus, $E \equiv E[\{\psi_\mu\}] = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$ --- (279)

$E \rightarrow$ functional of the spin orbitals

Knowing that $\hat{H} = \sum_{i=1}^N h(\hat{x}_i) + \sum_{i < j} \frac{1}{r_{ij}}$ — (280)

we use the Slater-Condon rules to evaluate (279) as:

$$E[\{\psi_\mu\}] = \sum_{\mu=1}^N \langle \psi_\mu | \hat{h} | \psi_\mu \rangle + \frac{1}{2} \sum_{\mu, \nu} \langle \psi_\mu \psi_\nu | | \psi_\mu \psi_\nu \rangle \quad \text{--- (280)}$$

To determine the choice $\{\psi_\mu\}$ that minimizes E subject to the constraints (277) we construct the following functional:

$$G[\{\psi_\mu\}] = E[\{\psi_\mu\}] - \sum_{\mu, \nu} \lambda_{\mu, \nu} (\langle \psi_\mu | \psi_\nu \rangle - \delta_{\mu, \nu}) \quad \text{--- (281)}$$

Unconstrained optimization of G is equivalent to the HF problem.

Functional derivatives:

Let $G \equiv G[\phi(x)]$. Then modifying the function ϕ by $\delta\phi(x)$ will yield: $G[\phi + \delta\phi] \approx G[\phi] + \delta G$ — (282)

The functional derivative is then defined through

$$\delta G \downarrow = \int \underbrace{\frac{\delta G}{\delta \phi}}_x \delta \phi(x) dx \quad \text{--- (283)}$$

↘ Functional derivative.

For eg. if $G[\phi] = \int f(\phi(x)) dx$, then

$$G[\phi + \delta\phi] = \int f(\phi + \delta\phi) dx \approx \int f(\phi) dx + \int \frac{\partial f}{\partial \phi} \delta\phi dx$$

$$\Rightarrow \delta G = \int f'(\phi(x)) \delta\phi(x) dx \quad \text{--- (284)}$$

Comparing w/ (283) we have $\frac{\delta G[\phi]}{\delta \phi(x)} = f'(\phi(x))$ — (285)

This can be extended to functionals of multiple functions

If $G \equiv G[\phi_1, \phi_2, \dots, \phi_k]$ ~~then~~ $= \int f(\phi_1, \phi_2, \dots, \phi_k) dx$

$$\frac{\delta G}{\delta \phi_j} \Big|_{\phi_1, \phi_2, \dots} = \int \frac{\partial f}{\partial \phi_j} \Big|_{\phi_1, \phi_2, \dots, \phi_k} \quad \text{--- (286)}$$

Such functionals are called local functionals. We will come across non-local functionals soon.

Note that G in (281) is actually a functional of complex orbitals ψ_μ . There are 2 parts of every ψ_μ we could vary independently - real & imaginary. Alternatively, we could treat ψ_μ & ψ_μ^* as the independent variables. Thus,

$$G \equiv G[\{\psi_\mu, \psi_\mu^*\}] \quad \text{--- (287)}$$

Let $G = f + g$ --- (288)
 \downarrow \rightarrow
 1-electron terms 2-electron term

$$\frac{\delta G}{\delta \psi_c^*} = \frac{\delta f}{\delta \psi_c^*} + \frac{\delta g}{\delta \psi_c^*} \quad \text{--- (289)}$$

$$\frac{\delta f}{\delta \psi_c^*} f[\psi_c^* + \delta \psi_c^*] = \sum_{\mu \neq c} \langle \psi_\mu | \hat{h} | \psi_\mu \rangle + \langle \psi_c + \delta \psi_c | \hat{h} | \psi_c \rangle$$

$$\approx f[\psi] + \langle \delta \psi_c | \hat{h} | \psi_c \rangle \quad \text{--- (290)}$$

$$\Rightarrow \delta f = \int dx \delta \psi_z^* (\hat{h} \psi_z(x)) \quad \text{--- (291)}$$

$$\text{or } \frac{\delta f}{\delta \psi_z^*} = \hat{h} \psi_z(x) \quad \text{--- (292)}$$

why

$$g[\psi_z^* + \delta \psi_z^*] = \frac{1}{2} \sum_{\mu \neq z} \sum_{\nu \neq z} \langle \psi_\mu \psi_\nu | | \psi_\mu \psi_\nu \rangle$$

$$+ \frac{1}{2} \sum_{\mu} \langle \psi_\mu \psi_z | | \psi_\mu \psi_z \rangle \langle \psi_\mu (\psi_z + \delta \psi_z) | | \psi_\mu \psi_z \rangle$$

$$+ \frac{1}{2} \sum_{\nu} \langle \psi_z \psi_\nu | | \psi_z \psi_\nu \rangle \langle (\psi_z + \delta \psi_z) \psi_\nu | | \psi_z \psi_\nu \rangle$$

$$\approx \frac{1}{2} \sum_{\mu} \sum_{\nu} \langle \psi_\mu \psi_\nu | | \psi_\mu \psi_\nu \rangle + \frac{1}{2} \sum_{\mu} \left[\langle \psi_\mu \delta \psi_z | | \psi_\mu \psi_z \rangle + \langle \delta \psi_z \psi_\mu | | \psi_z \psi_\mu \rangle \right] \quad \text{--- (293)}$$

$$\Rightarrow \delta g = \frac{1}{2} \sum_{\mu} \left[\langle \psi_\mu \delta \psi_z | | \psi_\mu \psi_z \rangle + \langle \delta \psi_z \psi_\mu | | \psi_z \psi_\mu \rangle \right] \quad \text{--- (294)}$$

Now,

$$\langle \psi_i \psi_j | | \psi_k \psi_l \rangle = \int dx_1 \int dx_2 \frac{\psi_i^*(x_1) \psi_j^*(x_2) \psi_k(x_1) \psi_l(x_2)}{r_{12}}$$

$$= \int dx_2 \int dx_1 \frac{\psi_i^*(x_2) \psi_j^*(x_1) \psi_k(x_2) \psi_l(x_1)}{r_{12}}$$

$$= \langle \psi_j \psi_i | | \psi_l \psi_k \rangle \quad \text{--- (295)}$$

b'cos of r_{12} being symmetric.

~~1/2~~

$$\therefore \delta g = \sum_{\mu} \langle \delta \psi_{\mu} \psi_{\mu} | \psi_{\mu} \psi_{\mu} \rangle$$

$$= \int dx_1 \delta \psi_{\mu}^*(x_1) \sum_{\mu} \left(\int dx_2 \frac{\psi_{\mu}^*(x_2) \psi_{\mu}(x_2)}{r_{12}} \right) \psi_{\mu}(x_1)$$

$$- \int dx_1 \delta \psi_{\mu}^*(x_1) \sum_{\mu} \left(\int dx_2 \frac{\psi_{\mu}^*(x_2) \psi_{\mu}(x_2)}{r_{12}} \right) \psi_{\mu}(x_1) \quad (296)$$

$$\Rightarrow \left. \frac{\delta g}{\delta \psi_{\mu}^*(x_1)} \right|_{\psi} = \left\{ \hat{V}_H(x_1) + \hat{V}_X(x_1) \right\} \psi_{\mu}(x_1) \quad (297)$$

$$\text{where } \hat{V}_H(x_1) \psi_{\mu}(x_1) = \left(\int dx_2 \frac{\sum_{\mu} |\psi_{\mu}(x_2)|^2}{r_{12}} \right) \psi_{\mu}(x_1) \quad (298)$$

$$\hat{V}_X \psi_{\mu}(x_1) = - \left(\int dx_2 \sum_{\mu} \frac{\psi_{\mu}^*(x_2) \hat{P}_{12} \psi_{\mu}(x_2)}{r_{12}} \right) \psi_{\mu}(x_1) \\ = - \sum_{\mu} \left(\int dx_2 \frac{\psi_{\mu}^*(x_2) \psi_{\mu}(x_2)}{r_{12}} \right) \psi_{\mu}(x_1) \quad (299)$$

$V_H \rightarrow$ Hartree potential

- electrostatic potential due to all the electrons averaged (classical)

$V_X \rightarrow$ Exchange potential (non classical)

The constraint term is easy to evaluate & yields a functional dv. $\rightarrow \sum_{\mu} \lambda_{\mu} \psi_{\mu}(x) \quad (300)$

Thus, we get

$$\left. \frac{\delta G}{\delta \psi_z^*} \right|_{\psi} = \left[\hat{h}(x) + \hat{v}_H(x) + \hat{v}_X(x) \right] \psi_z - \sum_{\nu} \lambda_{z\nu} \psi_{\nu}(x) \quad - (301)$$

For, the choice $\{\psi_{\mu}\}$ to be optimal we must have

$$\frac{\delta G}{\delta \psi_z^*} = 0 \quad \forall z = 1, N \quad - (302)$$

ψ_z must satisfy

$$\left[\hat{h}(x) + \hat{v}_H(x) + \hat{v}_X(x) \right] \psi_z(x) = \sum_{\nu} \lambda_{z\nu} \psi_{\nu}(x) \quad - (303)$$

This ~~looks~~ looks like an eigenvalue equation except for the RHS. This can be simplified by choosing a L.C. of ψ_{ν} that diagonalizes λ while preserving the orthonormality. The transformation does not affect \hat{H}_0 (why??)

Thus, we get, w/ such a choice of $\{\psi_z\}$

$$\left[\hat{h}(x) + \hat{v}_H(x) + \hat{v}_X(x) \right] \psi_z(x) = \epsilon_z \psi_z(x) \quad \tau = 1, N \quad - (304)$$

These N coupled differential eqns. are called the canonical HF eqns.

Note that $v_{HF} = v_H + v_X$ depends on the solutions $\{\psi_z\}$. Thus these equations are non-linear in nature. They can be solved iteratively by starting w/ a guess solution $\{\psi_z^{(0)}\}$ & successively improving it by ~~solving~~ solving (304).

$$\{\psi_z^{(0)}\} \rightarrow v_{HF}^{(0)} \rightarrow \{\psi_z^{(1)}\} \rightarrow v_{HF}^{(1)} \rightarrow \{\psi_z^{(2)}\} \rightarrow \dots$$

This process is repeated until the v_{HF} constructed using

a given set $\{\psi_r^{(n)}\}$ ~~is~~ results back in the same set when solving (304). Such a potential is said to be self-consistent and the approach is called as self consistent field (scf) approach. In practice, the iteration are carried out until ~~a threshold~~ the differences in V_{HF} from successive iterations is below a chosen threshold.

9/2/2017

lec 17. Hartree-Fock ~~method~~ (ctd)

Spatial version of the HF: Restricted HF.

Let's consider a non-magnetic / closed shell system where there are equal number of up & down spin electrons, i.e. $N_{\uparrow} = N_{\downarrow} = \frac{N}{2}$. In such system we can use the same spatial orbital for ~~2 spins~~ 2 electrons of opposite spins in constructing the Slater Determinant (S.D.). In particular, we assume that

$$\psi_{\mu}(\mathbf{r}, \sigma) = \begin{cases} \varphi_{\frac{\mu}{2}}(\mathbf{r}) \alpha(\sigma) & \text{if } \mu \text{ is odd} \\ \varphi_{\frac{\mu}{2}}(\mathbf{r}) \beta(\sigma) & \text{if } \mu \text{ is even.} \end{cases}$$

Thus we only need $\frac{N}{2}$ spatial orbitals $\{\varphi_{\nu}\}_{\nu=1, \dots, \frac{N}{2}}$ for the S.D. Making this substitution we get:

$$\sum_{\mu=1}^N \langle \psi_{\mu} | \hat{h} | \psi_{\mu} \rangle = 2 \sum_{\nu=1}^{\frac{N}{2}} \langle \varphi_{\nu} | \hat{h} | \varphi_{\nu} \rangle \quad \text{--- (305)}$$

$$\psi_{\mu}(\mathbf{x}) = \int d\sigma \psi_{\mu}(\mathbf{r}, \sigma) \delta(\mathbf{x} - \mathbf{r}) \delta(\sigma - \sigma')$$

$$n(\mathbf{x}) = \sum_{\mu} |\psi_{\mu}(\mathbf{x})|^2 = \sum_{\nu=1}^{\frac{N}{2}} |\varphi_{\nu}(\mathbf{r})|^2 \{ |\alpha(\sigma)|^2 + |\beta(\sigma)|^2 \} \quad \text{--- (306)}$$

density:

$$n(\mathbf{r}) \equiv \int d\sigma n(\mathbf{x}) = 2 \sum_{\nu=1}^{\frac{N}{2}} |\varphi_{\nu}(\mathbf{r})|^2 \quad \text{--- (307)}$$

$$V_H(x) = \int d^3r' \int d\sigma' \frac{\sum_{\mu=1}^N |\psi_{\mu}(x)|^2}{|\vec{r}-\vec{r}'|} = \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} \equiv V_H(\vec{r}) \quad (308)$$

$$V_x(x) = - \int d^3r' \int d\sigma' \frac{\sum_{\mu=1}^N \psi_{\mu}^*(x') \hat{p}_{12} \psi_{\mu}(x')}{|\vec{r}-\vec{r}'|}$$

$$= - \int d^3r' \int d\sigma' \left\{ \frac{\sum_{\nu=1}^{N/2} \psi_{\nu}^*(\vec{r}') \alpha(\sigma') \hat{p}_{12} \psi_{\nu}(\vec{r}') \alpha(\sigma')}{|\vec{r}-\vec{r}'|} + \frac{\psi_{\nu}^*(\vec{r}') \beta(\sigma') \hat{p}_{12} \psi_{\nu}(\vec{r}') \beta(\sigma')}{|\vec{r}-\vec{r}'|} \right\} \quad (309)$$

Now,

$$V_x(x) \psi_{\mu}(\vec{r}) \alpha(\sigma) = - \int d^3r' \left\{ \frac{\sum_{\nu=1}^{N/2} \psi_{\nu}^*(\vec{r}') \hat{p}_{12} \psi_{\nu}(\vec{r}')}{|\vec{r}-\vec{r}'|} \right\} \psi_{\mu}(\vec{r}) \alpha(\sigma) \quad (310)$$

$$\& V_x(x) \psi_{\mu}(\vec{r}) \beta(\sigma) = - \int d^3r' \left\{ \frac{\sum_{\nu=1}^{N/2} \psi_{\nu}^*(\vec{r}') \hat{p}_{12} \psi_{\nu}(\vec{r}')}{|\vec{r}-\vec{r}'|} \right\} \psi_{\mu}(\vec{r}) \beta(\sigma) \quad (311)$$

So only one of the terms in (309) contributes for a given spin

~~Now let us define~~

Take (304) and let $\psi_{\vec{r}}(x) = \psi_{\mu}(\vec{r}) \alpha(\sigma)$.

$$\left\{ \hat{h}(x) + \hat{v}_H(x) + \hat{v}_x(x) \right\} \psi_{\mu}(\vec{r}) \alpha(\sigma) = \epsilon_{\mu} \psi_{\mu}(\vec{r}) \alpha(\sigma) \quad (312)$$

Project onto $\alpha(\sigma)$. We get

$$\left\{ \hat{h}(\vec{r}) + \hat{v}_H(\vec{r}) - \int d^3r' \left(\frac{\sum_{\nu=1}^{N/2} \psi_{\nu}^*(\vec{r}') \hat{p}_{12} \psi_{\nu}(\vec{r}')}{|\vec{r}-\vec{r}'|} \right) \right\} \psi_{\mu}(\vec{r}) = \epsilon_{\mu} \psi_{\mu}(\vec{r}) \quad (313)$$

We get the same result if $\psi_{\vec{r}}(x) = \psi_{\mu}(\vec{r}) \beta(\sigma)$ & we project on $\beta(\sigma)$.

Let's take a closer look at what's happening. If an e^- sits in the spatial orbital $\psi_\mu(\vec{r})$, then its spatial density is $|\psi_\mu(\vec{r})|^2$ & the potential ~~given~~ due to this density at ~~the~~ \vec{r} is given by

$$J_\mu(\vec{r}) = \int d^3r' \frac{|\psi_\mu(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} \quad \text{--- (314)}$$

Thus, the potential due to e^- in $\text{all } \{\psi_\mu\}$ is given by

$$J(\vec{r}) = \sum_{\mu=1}^{N/2} J_\mu(\vec{r}) \quad \text{--- (315)}$$

Since each orbital has both an up spin & down spin electron the ~~total~~ giving the same spatial density, the total repulsive potential due the distribution $2 \sum_{\mu} |\psi_\mu(\vec{r})|^2$ is:

$$V_H(\vec{r}) = 2 \int J(\vec{r}) \quad \text{--- (316)}$$

But it's actually unfair to give the same weightage to contribution from both electrons in the orbitals to potential felt by an e^- of a given spin ^(say \uparrow). This is b/c other \uparrow spin e^- s will not approach the test electron as closely as the \downarrow spin ones due to Pauli exclusion principle. So the contribution from such PEP forbidden configuration needs to be removed. This job is achieved by the exchange term which appears w/ a negative sign & involves only $1/2$ the no. of terms as (316)

$$K(\vec{r}) = \sum_{\mu < \nu} K_{\mu\nu}(\vec{r}) \quad \text{--- (317)}$$

$$K_{\mu\nu}(\vec{r}) = \frac{\int d^3r' \psi_\nu^*(\vec{r}') \hat{P}_{12} \psi_\mu(\vec{r}')}{|\vec{r}-\vec{r}'|} \quad \text{--- (318)}$$

$$K_{\nu\mu}(\vec{r}) \psi_\mu(\vec{r}) = \int d^3r' \frac{\psi_\nu^*(\vec{r}') \psi_\mu(\vec{r}')}{|\vec{r}-\vec{r}'|} \psi_\nu(\vec{r}) \quad \text{--- (319)}$$

$$V_x(\vec{r}) \equiv - \sum_i K(\vec{r}_i) \quad \text{--- (320)}$$

The Fock operator is defined as $\hat{f} = \hat{h} + \hat{v}_H - \hat{v}_x$ --- (321)

The spatial version becomes $\hat{f}(\vec{r}) = \hat{h}(\vec{r}) + 2J(\vec{r}) - K(\vec{r})$ --- (322)

~~Total g.s. energy in HF is given by~~

~~$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$

$$= 2 \sum_m \langle \psi_m | \hat{h} | \psi_m \rangle +$$~~

~~$$\sum_{m \neq n} \langle \psi_m \psi_n | \hat{v}_x | \psi_m \psi_n \rangle - \sum_{m \neq n} \langle \psi_m \psi_n | \hat{v}_x | \psi_n \psi_m \rangle$$~~

Now,

$$\sum_{m=1}^N \sum_{n=1}^N \langle \psi_m \psi_n | \hat{v}_x | \psi_m \psi_n \rangle = \sum_{m=1}^{N/2} \sum_{n=1}^{N/2} \left\{ 4 \langle \psi_m \psi_n | \psi_m \psi_n \rangle - 2 \langle \psi_m \psi_n | \psi_n \psi_m \rangle \right\}$$

$\alpha \beta, \beta \alpha, \alpha \alpha, \beta \beta$
 $\alpha \beta, \beta \alpha$
 $\alpha \alpha, \beta \beta$
 $\alpha \alpha, \beta \beta$
 only $\alpha \alpha$ & $\beta \beta$
 terms survive

--- (323)

\therefore Total g.s. energy in HF is given by

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_{m=1}^N \langle \psi_m | \hat{h} | \psi_m \rangle + \frac{1}{2} \sum_{m \neq n} \langle \psi_m \psi_n | \hat{v}_x | \psi_m \psi_n \rangle$$

$$= 2 \sum_{m=1}^{N/2} \langle \psi_m | \hat{h} | \psi_m \rangle + \sum_{m \neq n} \sum_{v=1}^{N/2} \left\{ 2 \langle \psi_m \psi_v | \psi_m \psi_v \rangle - \langle \psi_m \psi_v | \psi_v \psi_m \rangle \right\}$$

$$= 2 \sum_{m=1}^{N/2} h_{mm} + \sum_{m=1}^{N/2} \sum_{v=1}^{N/2} \left\{ 2 J_{mv} - K_{mv} \right\} \quad \text{--- (324)}$$

Hartree-Fock orbital energies

$$\begin{aligned}
 \epsilon_{\mu} &= \langle \psi_{\mu} | \hat{F} | \psi_{\mu} \rangle \\
 &= \langle \psi_{\mu} | \hat{h} | \psi_{\mu} \rangle + \langle \psi_{\mu} | \hat{V}_H(x) + \hat{V}_X(x) | \psi_{\mu} \rangle \\
 &= h_{\mu\mu} +
 \end{aligned}$$

$$\epsilon_{\mu} = \langle \psi_{\mu} | \hat{F}(\vec{r}) | \psi_{\mu} \rangle$$

$$\begin{aligned}
 &= h_{\mu\mu} + 2 \int d^3r \psi_{\mu}^*(\vec{r}) \hat{J}(\vec{r}) \psi_{\mu}(\vec{r}) - \int d^3r \psi_{\mu}^*(\vec{r}) \hat{K}(\vec{r}) \psi_{\mu}(\vec{r}) \\
 &= h_{\mu\mu} + \sum_{\nu} \{ 2J_{\mu\nu} - K_{\mu\nu} \} \quad \text{--- (325)}
 \end{aligned}$$

$$\Rightarrow E_0 = 2 \sum_{\mu=1}^{N/2} \epsilon_{\mu} - \sum_{\nu} \{ 2J_{\mu\nu} - K_{\mu\nu} \} \quad \text{--- (326)}$$

in spin orbital version:

$$\epsilon_{\mu} = \langle \psi_{\mu} | \hat{h} | \psi_{\mu} \rangle + \sum_{\nu} \langle \psi_{\mu} \psi_{\nu} || \psi_{\mu} \psi_{\nu} \rangle \quad \text{--- (327)}$$

$$\Rightarrow E_0 = \sum_{\mu=1}^N \epsilon_{\mu} - \frac{1}{2} \sum_{\mu\nu} \langle \psi_{\mu} \psi_{\nu} || \psi_{\mu} \psi_{\nu} \rangle \quad \text{--- (328)}$$

