Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'

Prof. P.C. Deshmukh
Department of Physics
Indian Institute of Technology-Madras

Lecture 16
Electron Gas in Hatree Fock And Random Phase Approximation

Okay, greetings, and welcome to the unit 3 of this course on theory of atomic collisions and spectroscopy. We have done the Hartree Fock formalism; we have discussed it in a previous course on atomic physics on special topics and atomic physics. So, in today's class we will discuss, we will revisit some aspects of the Hartree Fock formalism but from a slightly different angle.

And this is specifically adapted toward developing what is known as the random phase approximation which is one of the very powerful techniques used to deal with electron correlations in many body systems. So, we are sort of essentially preparing ourselves to develop the random phase approximation in this class.

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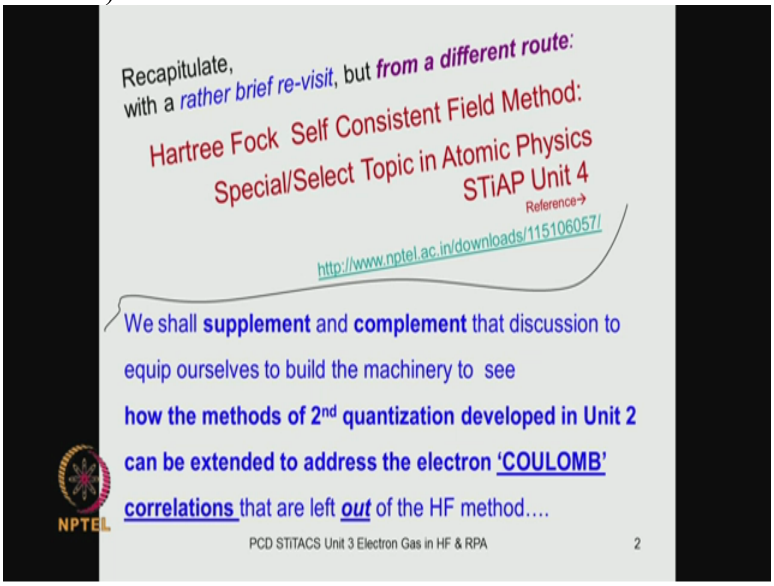

Recapitulate,
with a *rather brief re-visit*, but ***from a different route:***

Hartree Fock Self Consistent Field Method:
Special/Select Topic in Atomic Physics
STiAP Unit 4
Reference→
http://www.nptel.ac.in/downloads/115106057/

We shall **supplement** and **complement** that discussion to equip ourselves to build the machinery to see **how the methods of 2nd quantization developed in Unit 2 can be extended to address the electron 'COULOMB' correlations** that are left ***out*** of the HF method….

Now I will invite you to go through the contents of the lecture on the Hartree Fock or the set of lectures on the Hartree Fock in the previous course on special topics in atomic physics. These lectures are available on the internet already and what we will do is to use the methods of second quantization which we developed in the previous unit, in unit 2 of this course. And we will use the methods of second quantization.

And our intent of course is to deal with the Coulomb correlations which are left out of the Hartree Fock. The Hartree Fock as we know includes the exchange correlations or the statistical correlations, the Fermi Dirac correlations as we refer to them but not the Coulomb correlations which are the many-body effects. And our intent is to address these Coulomb correlations.

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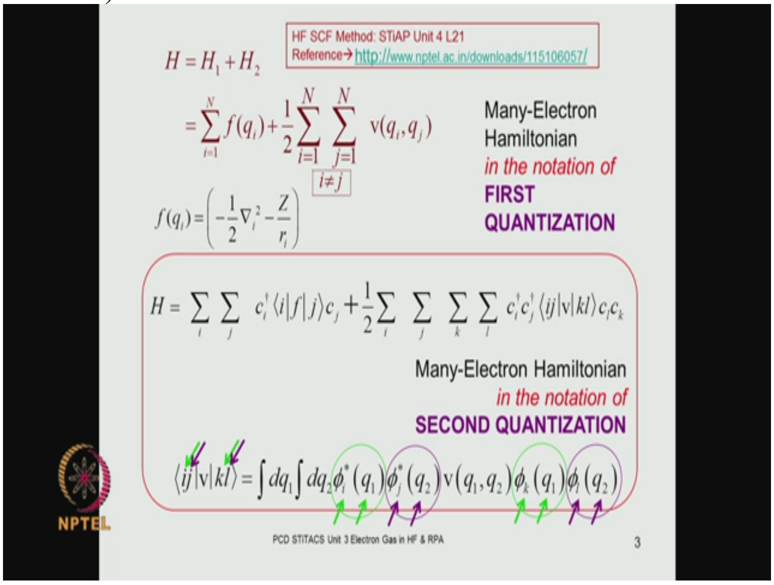

HF SCF Method: STiAP Unit 4 L21
Reference→ http://www.nptel.ac.in/downloads/115106057/

$$H = H_1 + H_2$$

$$= \sum_{i=1}^{N} f(q_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ \boxed{i \neq j}}}^{N} \mathrm{v}(q_i, q_j)$$

$$f(q_i) = \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right)$$

Many-Electron Hamiltonian
in the notation of
FIRST QUANTIZATION

$$H = \sum_i \sum_j c_i^\dagger \langle i|f|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}|kl\rangle c_l c_k$$

Many-Electron Hamiltonian
in the notation of
SECOND QUANTIZATION

$$\langle ij|\mathrm{v}|kl\rangle = \int dq_1 \int dq_2 \phi_i^*(q_1)\phi_j^*(q_2)\mathrm{v}(q_1, q_2)\phi_k(q_1)\phi_l(q_2)$$

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So, let me recall the basic Hamiltonian which we dealt with in the previous course on atomic physics and we developed the self-consistent field for the solutions of the Schrodinger equation for n number of electrons. For which the Hamiltonian was written as a set of one particle and two particle operators fqi are the one particle operators which consist of the kinetic energy part and the nuclear attractive potential as you can see.

And then you of course have the electron-electron repulsion term between every pair of electrons and you have to exclude i = j from this double summation which is over i and j going from 1 through n. This is the Hamiltonian as we worked with in the first quantized notation.

Now in the second quantization notation the same Hamiltonian is written in this form as we have discussed in the previous unit, in unit 2 of this course okay, so in the previous unit we developed methods of second quantization. We introduced the creation and destruction operators and in terms of these creation and destruction operators we wrote the N electron Hamiltonian in the second quantization notation.

And this is essentially just a matter of notation in atomic physics we are not dealing with such high energies that you really have to work with you know creation and destruction of particles. But transitions from one particle state to another particle state can be viewed as destruction of particle in one state and creation in another.

And that is how we use the very powerful methods of second quantization in atomic physics atomic and also molecular physics. Now mind you if you look at these arrows q1 and q2 are the integration variables and typically we always consider the integration variables to be dummy variables so it does not matter whether you write the integration variable as q1 or zeta 1 or x1 or y1 or, or whatever.

Nevertheless it is important to keep track of which variable is associated with which quantum state. So, q1 is the argument of the single particle function for the quantum state k and q2 is the one for the quantum state l because that is associated with the q1 variable being associated with the quantum state i and q2 being associated with the quantum state j okay.

So, one has to keep track of this that these dummy variables are dummies yes you can change them but then you have to do it in a consistent manner okay. So, ink will have the same dummy label, dummy variable whichever it is and j and l will have the same whatever it is and these two can be changed arbitrarily but in a consistent manner.

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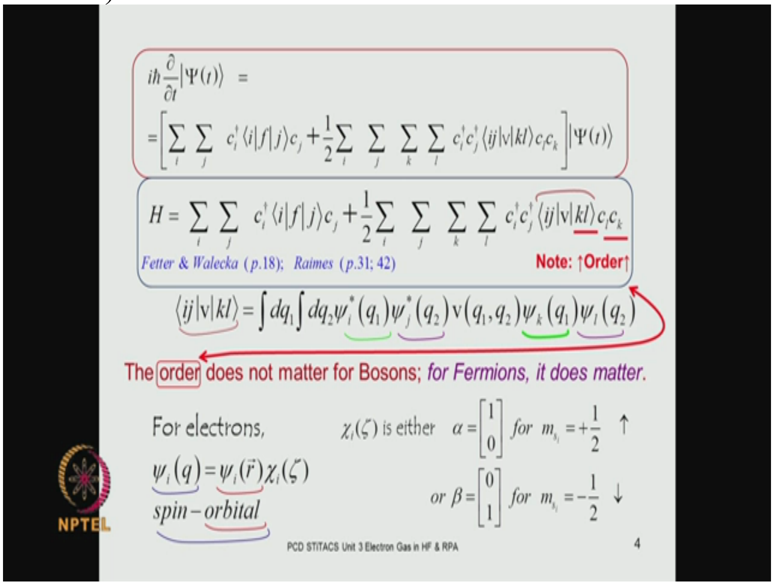

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle =$$
$$=\left[\sum_i\sum_j c_i^\dagger\langle i|f|j\rangle c_j+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger\langle ij|v|kl\rangle c_l c_k\right]|\Psi(t)\rangle$$

$$H=\sum_i\sum_j c_i^\dagger\langle i|f|j\rangle c_j+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger\overbrace{\langle ij|v|\underline{kl}\rangle}\underline{c_l c_k}$$

Fetter & Walecka (p.18); Raimes (p.31; 42)

Note: ↑Order↑

$$\underbrace{\langle ij|v|kl\rangle}=\int dq_1\int dq_2\underbrace{\psi_i^*(q_1)}\underbrace{\psi_j^*(q_2)}v(q_1,q_2)\underbrace{\psi_k(q_1)}\underbrace{\psi_l(q_2)}$$

The $\boxed{\text{order}}$ does not matter for Bosons; *for Fermions, it does matter.*

For electrons,

$$\underbrace{\psi_i(q)}=\underbrace{\psi_i(\vec{r})}\chi_i(\zeta)$$

$$\underbrace{spin-\underbrace{orbital}}$$

$\chi_i(\zeta)$ is either $\alpha=\begin{bmatrix}1\\0\end{bmatrix}$ *for* $m_{s_i}=+\frac{1}{2}$ ↑

or $\beta=\begin{bmatrix}0\\1\end{bmatrix}$ *for* $m_{s_i}=-\frac{1}{2}$ ↓

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So, this is the Hamiltonian in the second quantization formalism I will like to refer you to the very nice books by Fetter and Walecka and Raimes and you will find most of the discussion for today's class drawn from these two books. And you have the two center integral the i, j, v, k, l which is this double integration over q1 and q2.

Each variable is actually a set of you know four variables because there are three space coordinates and once one spin coordinates. So, integration over one variable is equivalent to integration over three continuous variables plus the summation over the corresponding spin index.

Now always remember that one has to keep track of the order of these operators cl, ck these are destruction operators for the lth and the kth state respectively. But this order is important for fermions it is not important for bosons because the commutation and anti commutation rules for the creation and destruction operators for fermions and bosons are different as you are well aware.

We certainly work with electrons and we will work with electron wave functions the spin orbital's as they are called. So, you write them as a product of the spin part Chi and orbital part Psi. And the spin part is either in alpha or beta which is corresponding to either a spin up state or a spin down state with the m quantum number being plus half or minus half.

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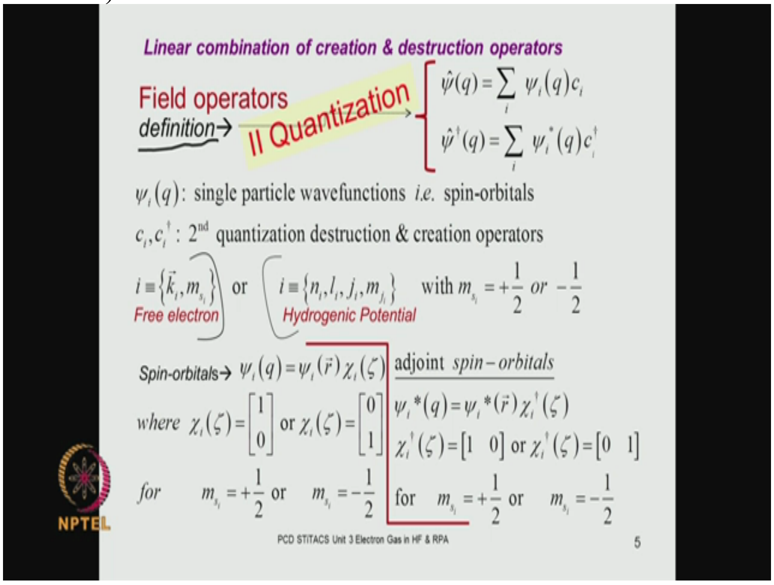

Linear combination of creation & destruction operators

Field operators definition→ II Quantization →

$$\begin{cases} \hat{\psi}(q) = \sum_i \psi_i(q) c_i \\ \hat{\psi}^{\dagger}(q) = \sum_i \psi_i^{*}(q) c_i^{\dagger} \end{cases}$$

$\psi_i(q)$: single particle wavefunctions *i.e.* spin-orbitals

$c_i, c_i^{\dagger}$: 2^{nd} quantization destruction & creation operators

$i \equiv \{\vec{k}_i, m_{s_i}\}$ or $i \equiv \{n_i, l_i, j_i, m_{j_i}\}$ with $m_{s_i} = +\frac{1}{2}$ *or* $-\frac{1}{2}$

Free electron Hydrogenic Potential

Spin-orbitals→ $\psi_i(q) = \psi_i(\vec{r})\chi_i(\zeta)$

where $\chi_i(\zeta) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ or $\chi_i(\zeta) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

for $m_{s_i} = +\frac{1}{2}$ or $m_{s_i} = -\frac{1}{2}$

adjoint *spin − orbitals*

$\psi_i{}^{*}(q) = \psi_i{}^{*}(\vec{r})\chi_i^{\dagger}(\zeta)$

$\chi_i^{\dagger}(\zeta) = [1 \quad 0]$ or $\chi_i^{\dagger}(\zeta) = [0 \quad 1]$

for $m_{s_i} = +\frac{1}{2}$ or $m_{s_i} = -\frac{1}{2}$

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Now we work with the field operators these are linear superposition of the creation and destruction operators. And this is part of the reason this methodology is called a second quantization because in first quantization you replace the classical dynamical variables by operators. And now instead of the wave function Psi you work with the Psi on the left hand side which is actually an operator rather than just a scalar function.

So, these are the field operators Psi and Psi dagger and the subscripts i are a set of quantum numbers. They come from the complete set of quantum numbers which are appropriate for describing the single electron states. If it is a free electron these are the momentum Eigen states. So you have got the three momentum Eigen values in units of h cross = 1.

These are k1, k2 and k3 and there is the spin quantum number which is ms. And if you have a Hydrogenic potential these are the n,l,j,m quantum numbers. So, these are the spin orbital's for the electrons you have the corresponding adjoint spin orbital's which you get simply by taking the transposition of the basic spin orbital's.

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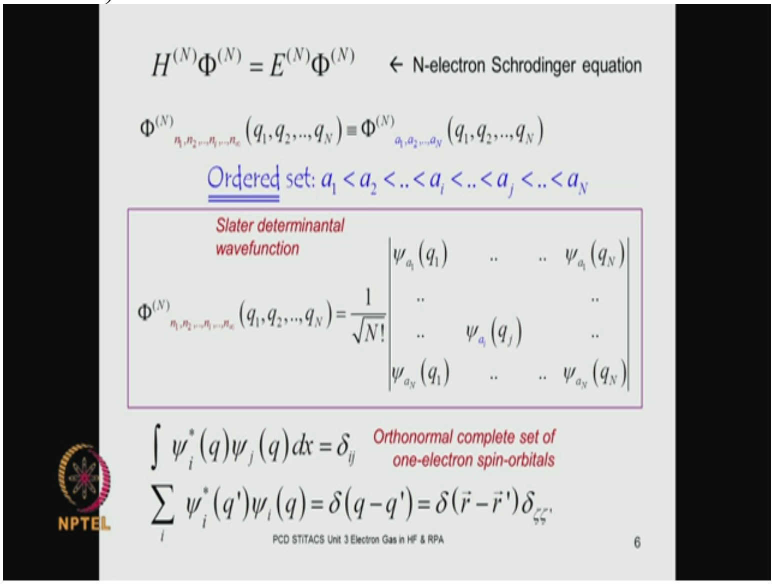

$$H^{(N)}\Phi^{(N)} = E^{(N)}\Phi^{(N)}$$ ← N-electron Schrodinger equation

$$\Phi^{(N)}{}_{n_1,n_2,\dots,n_i,\dots,n_\infty}(q_1,q_2,\dots,q_N) \equiv \Phi^{(N)}{}_{a_1,a_2,\dots,a_N}(q_1,q_2,\dots,q_N)$$

Ordered set: $a_1 < a_2 < .. < a_i < .. < a_j < .. < a_N$

Slater determinantal wavefunction

$$\Phi^{(N)}{}_{n_1,n_2,\dots,n_i,\dots,n_\infty}(q_1,q_2,\dots,q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{a_1}(q_1) & .. & .. & \psi_{a_1}(q_N) \\ .. & & & .. \\ .. & \psi_{a_i}(q_j) & & .. \\ \psi_{a_N}(q_1) & .. & .. & \psi_{a_N}(q_N) \end{vmatrix}$$

$$\int \psi_i^*(q)\psi_j(q)dx = \delta_{ij}$$ Orthonormal complete set of one-electron spin-orbitals

$$\sum_i \psi_i^*(q')\psi_i(q) = \delta(q-q') = \delta(\vec{r}-\vec{r}\,')\delta_{\zeta\zeta'}$$

So, what we have to do is to solve the Schrodinger equation for the N electron system. Now we work with determinantal functions in the Hartree Fock formalism in which you specify the number of electrons occupying each one electron quantum state. And that number for fermions is either 1 or 0.

So, the occupation numbers for all the infinite set of Eigen one electron Eigen states n1 through an infinity each can be either 1 or 0, the sum of all the ones will add up to the total number of electrons in the system. And the ones which are occupied are those which are labelled by the quantum states a1, a2 up to an. These are the N single particle quantum states which are occupied with occupation number one.

The occupation number of everything else being 0, so what we do is to line them up in a certain order and with reference to this order, we have got the first n which are occupied in the ground state of an N electron system. So, this is the Slater determinant wave function that we shall work with and these provide you with a set of one electron orthonormal complete set of basis okay.

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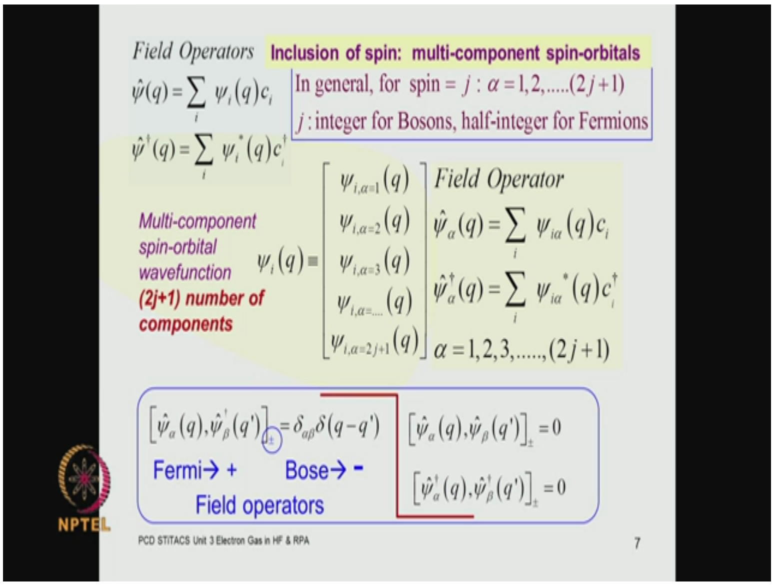

Field Operators **Inclusion of spin: multi-component spin-orbitals**

$\hat{\psi}(q)=\sum_i \psi_i(q)c_i$

$\hat{\psi}^\dagger(q)=\sum_i \psi_i^*(q)c_i^\dagger$

In general, for spin $= j : \alpha = 1,2,.....(2j+1)$

j : integer for Bosons, half-integer for Fermions

Multi-component spin-orbital wavefunction (2j+1) number of components

$$\psi_i(q)\equiv\begin{bmatrix}\psi_{i,\alpha=1}(q)\\ \psi_{i,\alpha=2}(q)\\ \psi_{i,\alpha=3}(q)\\ \psi_{i,\alpha=....}(q)\\ \psi_{i,\alpha=2j+1}(q)\end{bmatrix}$$

Field Operator

$\hat{\psi}_\alpha(q)=\sum_i \psi_{i\alpha}(q)c_i$

$\hat{\psi}_\alpha^\dagger(q)=\sum_i \psi_{i\alpha}^*(q)c_i^\dagger$

$\alpha = 1,2,3,.....,(2j+1)$

$\left[\hat{\psi}_\alpha(q),\hat{\psi}_\beta^\dagger(q')\right]_{\pm}=\delta_{\alpha\beta}\delta(q-q')$

Fermi→ + Bose→ -

Field operators

$\left[\hat{\psi}_\alpha(q),\hat{\psi}_\beta(q')\right]_{\pm}=0$

$\left[\hat{\psi}_\alpha^\dagger(q),\hat{\psi}_\beta^\dagger(q')\right]_{\pm}=0$

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So, this is the summary of what we have got, we have got the field operators in terms of this creation and destruction operators. You can now go ahead and write this more comprehensively and completely with explicit reference to the spin. Because when you have a spin j you have got 2j + 1 components okay.

So, depending on j being either integer or half integer you will have an appropriate number of 2j + 1 number of components, j is always an integer for bosons and half integer for fermions. So, you will have a multi-component spin-orbital away function okay. And Psi iq where you had written the quantum state i as a single index will now need to be specified with two indices one is i and the second is alpha which will go from 1 through 2j +1.

Because there are 2j+1 components, so the field operators Psi i will now be written explicitly in terms of these 2j +1 components corresponding to the spin. And this, these are the expressions for the field operators, so you do have a summation over i but this is how it is for each component alpha, alpha going from 1 through 2j+1.

So, you can write the commutation and anti commutation relations for the Fermi and Bose field operators inclusive of the spin index and they are obvious extensions of the corresponding expressions that you have seen before, except for the fact that spin has now been explicitly pointed out. Yes Ankur (Question time: 12:27- not audible) yeah it is just the fact that each quantum state corresponds to a spin which is j.

But the j will have 2j + 1 components, so all those 2j + 1 components are being written out explicitly as alpha going from 1 through 2j + 1. So, alpha is the index which keeps track of which particular component amongst the family of 2j + 1 component that you have because when you do space quantization you have 2j + 1 components of the spin index. So, alpha keeps track of that.

So, you have got these commutations and anti commutation relations for Fermi and Bose field operators, yes (Question time: 13:30 – not audible) which one is the operator field operative Psi q yeah written as summation Psi i q ci and Psi i is a matrix written like this then the ci then that multiplication ci can be written as matrix that is the standard that is the product.

Yes, because ci will also have the corresponding spin components so you have to handle them consistently because that will also have because i, will now have to keep track of all the quantum states and if there are different multiplicity of components coming from the spin that will be explicitly referred to in this.

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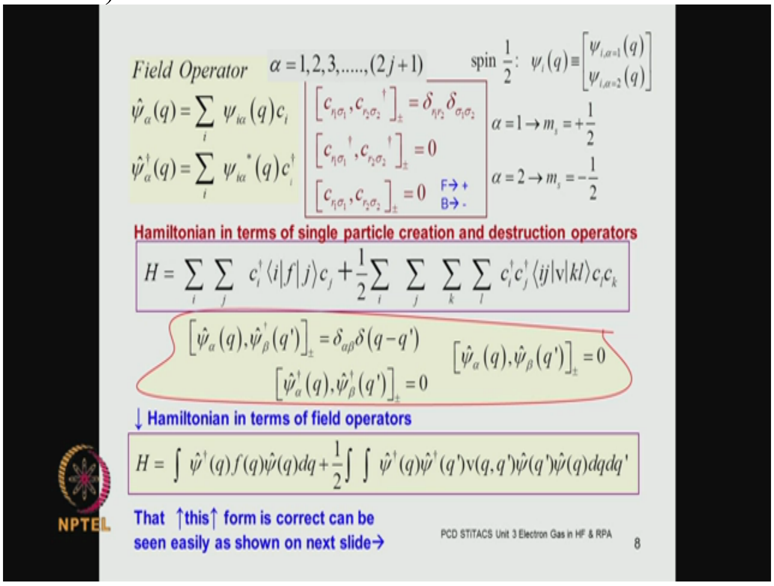

Field Operator $\alpha = 1,2,3,......,(2j+1)$

spin $\frac{1}{2}$: $\psi_i(q) \equiv \begin{bmatrix} \psi_{i,\alpha=1}(q) \\ \psi_{i,\alpha=2}(q) \end{bmatrix}$

$\hat{\psi}_\alpha(q) = \sum_i \psi_{i\alpha}(q) c_i$

$\hat{\psi}^\dagger_\alpha(q) = \sum_i \psi^*_{i\alpha}(q) c^\dagger_i$

$\left[c_{r_1\sigma_1}, c_{r_2\sigma_2}{}^\dagger\right]_\pm = \delta_{r_1 r_2}\delta_{\sigma_1\sigma_2}$

$\left[c_{r_1\sigma_1}{}^\dagger, c_{r_2\sigma_2}{}^\dagger\right]_\pm = 0$

$\left[c_{r_1\sigma_1}, c_{r_2\sigma_2}\right]_\pm = 0$ F→ + B→ -

$\alpha = 1 \rightarrow m_s = +\frac{1}{2}$

$\alpha = 2 \rightarrow m_s = -\frac{1}{2}$

Hamiltonian in terms of single particle creation and destruction operators

$$H = \sum_i \sum_j c_i^\dagger \langle i|f|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|v|kl\rangle c_l c_k$$

$$\left[\hat{\psi}_\alpha(q), \hat{\psi}^\dagger_\beta(q')\right]_\pm = \delta_{\alpha\beta}\delta(q-q') \qquad \left[\hat{\psi}_\alpha(q), \hat{\psi}_\beta(q')\right]_\pm = 0$$

$$\left[\hat{\psi}^\dagger_\alpha(q), \hat{\psi}^\dagger_\beta(q')\right]_\pm = 0$$

↓ Hamiltonian in terms of field operators

$$H = \int \hat{\psi}^\dagger(q) f(q) \hat{\psi}(q) dq + \frac{1}{2}\int\int \hat{\psi}^\dagger(q)\hat{\psi}^\dagger(q') v(q,q') \hat{\psi}(q')\hat{\psi}(q) dq dq'$$

That ↑this↑ form is correct can be seen easily as shown on next slide→

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So, it is just writing it more fully it is the same expression but written more explicitly taking into account all the components of the spin index. So these are the field operators, so now the commutation and anti commutation relations for the Fermi and Bose particles I have my interest over here is specifically for electrons which we of course know are fermions.

So, we have got two states ms = + half and ms = - half corresponding to which alpha is 1 and 2. So, these are the two indices that we will have to keep track off. And this single particle creation and destruction operators which we used in the expression for the Hamiltonian, we can now write the same Hamiltonian in terms of the field operators okay.

So, this is the expression of this Hamiltonian in terms of the creation and destruction operators, the single particle creation and destruction operators. This is the expression that we did arrive at fully in our previous unit okay. And in terms of the field operators for which the commutation relations are now we just discussed and they are what they are as you see on the screen.

And in terms of these field operators the same Hamiltonian is now written as the expression that you see at the bottom of this slide. So, you have got the integral Psi dagger f Psi corresponding to the one electron operators. And then you have got a double integration work q and q prime corresponding to the two particle interactions.

Now we can very easily show that these two forms are completely equivalent both our second quantization forms except that the first one is in terms of the creation and destruction single particle operators. And the one at the bottom is in terms of the field operators and these two are completely equivalent and that is more or less obvious but we can see it explicitly in the next slide.

Here again let me remind you that q and q prime are dummy labels. But it is important to keep track of which label is associated with which operator and they must be written in a consistent fashion for exactly the same reason that we discussed earlier because the field operators for bosons commute whereas those for fermions anti commute.

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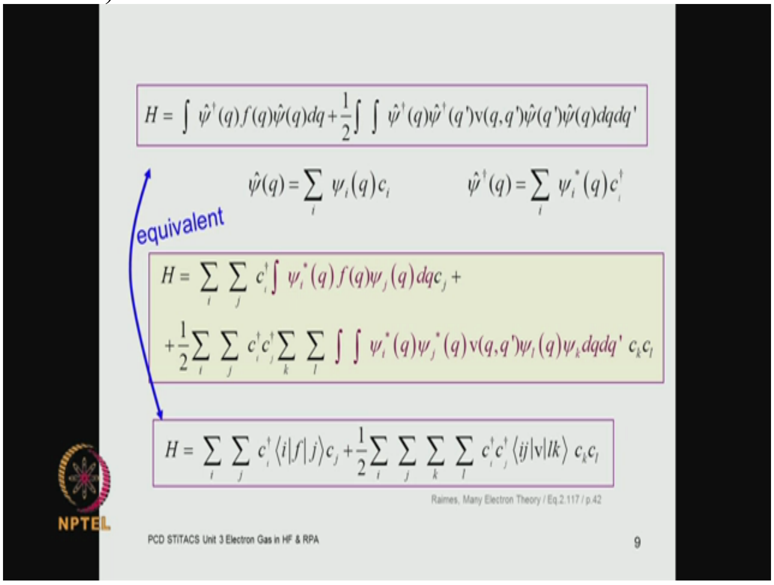

$$\boxed{H = \int \hat{\psi}^{\dagger}(q) f(q) \hat{\psi}(q) dq + \frac{1}{2}\int\int \hat{\psi}^{\dagger}(q)\hat{\psi}^{\dagger}(q') v(q,q') \hat{\psi}(q')\hat{\psi}(q) dq dq'}$$

$$\hat{\psi}(q) = \sum_i \psi_i(q) c_i \qquad \hat{\psi}^{\dagger}(q) = \sum_i \psi_i^*(q) c_i^{\dagger}$$

equivalent

$$\boxed{\begin{aligned} H = {} & \sum_i \sum_j c_i^{\dagger} \int \psi_i^*(q) f(q) \psi_j(q) dq\, c_j + \\ & + \frac{1}{2}\sum_i \sum_j c_i^{\dagger} c_j^{\dagger} \sum_k \sum_l \int\int \psi_i^*(q)\psi_j^*(q) v(q,q') \psi_l(q) \psi_k dq dq'\, c_k c_l \end{aligned}}$$

$$\boxed{H = \sum_i \sum_j c_i^{\dagger} \langle i|f|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^{\dagger} c_j^{\dagger} \langle ij|v|lk\rangle c_k c_l}$$

Raimes, Many Electron Theory / Eq.2.117 / p.42

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So, now this is the form that we have proposed and if you simply plug in the expansions of the field operators Psi and Psi dagger which we have with us and all you do is to plug in these explicit forms and rewrite the Hamiltonian you find that it is nothing but the same form the of the Hamiltonian which you had written in terms of the creation and destruction operators.

So, if we have just very it is almost trivial but it is important to convince ourselves that the expression in terms of the field operators is pretty much the same is exactly the same as that in terms of the creation and destruction operators. So, now we have got the Hamiltonian in terms of the field operators as well.

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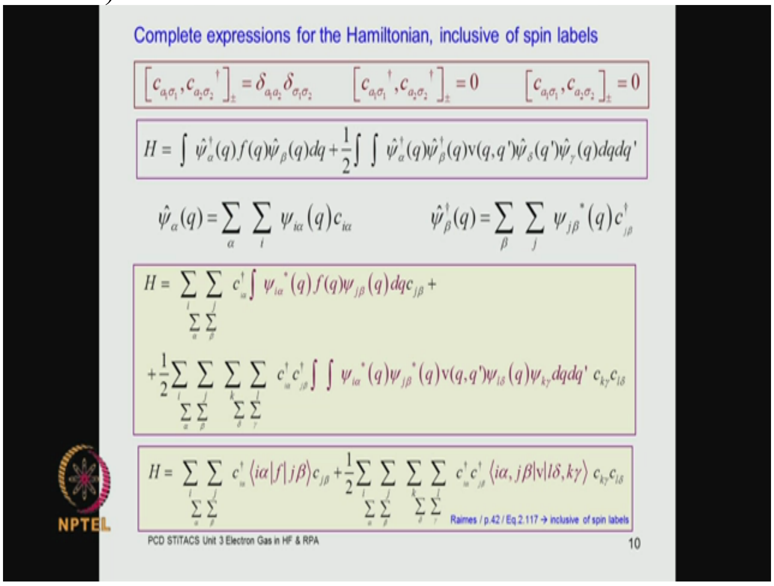

Complete expressions for the Hamiltonian, inclusive of spin labels

$$\left[c_{a_1\sigma_1}, c_{a_2\sigma_2}^{\dagger}\right]_{\pm} = \delta_{a_1a_2}\delta_{\sigma_1\sigma_2} \qquad \left[c_{a_1\sigma_1}^{\dagger}, c_{a_2\sigma_2}^{\dagger}\right]_{\pm} = 0 \qquad \left[c_{a_1\sigma_1}, c_{a_2\sigma_2}\right]_{\pm} = 0$$

$$H = \int \hat{\psi}_{\alpha}^{\dagger}(q) f(q) \hat{\psi}_{\beta}(q) dq + \frac{1}{2}\int\int \hat{\psi}_{\alpha}^{\dagger}(q)\hat{\psi}_{\beta}^{\dagger}(q) v(q,q')\hat{\psi}_{\delta}(q')\hat{\psi}_{\gamma}(q) dq dq'$$

$$\hat{\psi}_{\alpha}(q) = \sum_{\alpha}\sum_{i} \psi_{i\alpha}(q) c_{i\alpha} \qquad \hat{\psi}_{\beta}^{\dagger}(q) = \sum_{\beta}\sum_{j} \psi_{j\beta}^{*}(q) c_{j\beta}^{\dagger}$$

$$H = \underset{\sum_{\alpha}}{\sum_{i}}\ \underset{\sum_{\beta}}{\sum_{j}} c_{i\alpha}^{\dagger} \int \psi_{i\alpha}^{*}(q) f(q) \psi_{j\beta}(q) dq\, c_{j\beta} + \frac{1}{2}\underset{\sum_{\alpha}}{\sum_{i}}\ \underset{\sum_{\beta}}{\sum_{j}}\ \underset{\sum_{\delta}}{\sum_{k}}\ \underset{\sum_{\gamma}}{\sum_{l}} c_{i\alpha}^{\dagger} c_{j\beta}^{\dagger} \int\int \psi_{i\alpha}^{*}(q)\psi_{j\beta}^{*}(q) v(q,q')\psi_{l\delta}(q)\psi_{k\gamma} dq dq'\, c_{k\gamma} c_{l\delta}$$

$$H = \underset{\sum_{\alpha}}{\sum_{i}}\ \underset{\sum_{\beta}}{\sum_{j}} c_{i\alpha}^{\dagger} \langle i\alpha|f|j\beta\rangle c_{j\beta} + \frac{1}{2}\underset{\sum_{\alpha}}{\sum_{i}}\ \underset{\sum_{\beta}}{\sum_{j}}\ \underset{\sum_{\delta}}{\sum_{k}}\ \underset{\sum_{\gamma}}{\sum_{l}} c_{i\alpha}^{\dagger} c_{j\beta}^{\dagger} \langle i\alpha, j\beta|v|l\delta, k\gamma\rangle\, c_{k\gamma} c_{l\delta}$$

Raimes / p.42 / Eq.2.117 → inclusive of spin labels

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And we have we can write them explicitly in terms of the spin components. So, now we have taken it to the next level of detail so it is the same Hamiltonian for the field operators but now we point out the summation over alpha okay. And the summation over alpha will go from 1 through 2j + 1 and accordingly you have a number of summations specially in the two electron term.

So, the summations are doubled because there are two components of spin for half which is corresponding to alpha and beta or spin up and spin down okay. So, it is the same Hamiltonian now but written explicitly in terms of the components corresponding to the spin multiplicity.

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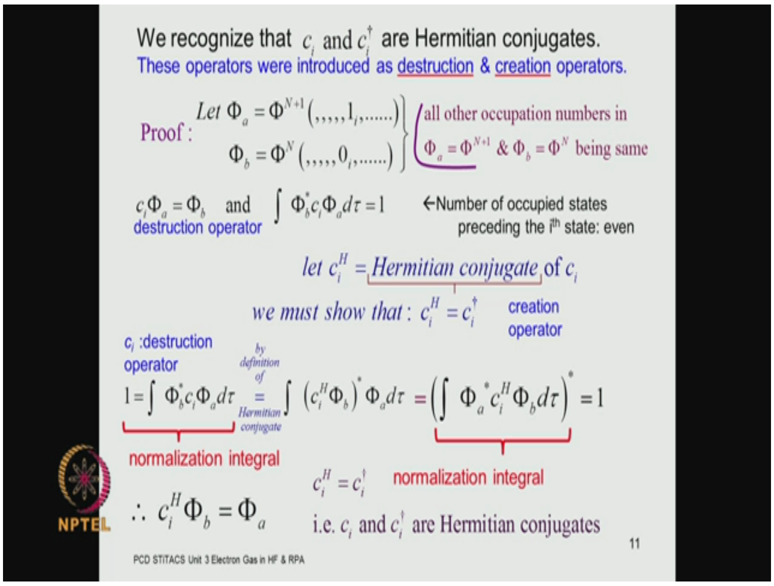

We recognize that c_i and $c_i^\dagger$ are Hermitian conjugates.

These operators were introduced as destruction & creation operators.

Proof : $\left.\begin{aligned} Let\ \Phi_a &= \Phi^{N+1}(,,,,,1_i,......) \\ \Phi_b &= \Phi^{N}(,,,,,0_i,......) \end{aligned}\right\}$ all other occupation numbers in $\Phi_a = \Phi^{N+1}$ & $\Phi_b = \Phi^N$ being same

$c_i\Phi_a = \Phi_b$ and $\int \Phi_b^* c_i \Phi_a d\tau = 1$ ←Number of occupied states preceding the i^{th} state: even

destruction operator

$$let\ c_i^H = \underbrace{Hermitian\ conjugate}\ of\ c_i$$

$$we\ must\ show\ that:\ c_i^H = c_i^\dagger$$ creation operator

c_i :destruction operator

$$\underbrace{1 = \int \Phi_b^* c_i \Phi_a d\tau}_{\text{normalization integral}} \overset{\text{by definition of}}{\underset{\text{Hermitian conjugate}}{=}} \int \left(c_i^H \Phi_b\right)^* \Phi_a d\tau = \underbrace{\left(\int \Phi_a^* c_i^H \Phi_b d\tau\right)^*}_{\text{normalization integral}} = 1$$

$$\therefore c_i^H \Phi_b = \Phi_a$$

$c_i^H = c_i^\dagger$

i.e. c_i and $c_i^\dagger$ are Hermitian conjugates

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Now just for completeness let me remind you that these operators which have been primarily introduced as destruction and creation operators are hermitian conjugates of each other okay. So, our first introduction was in terms of creation and destruction operators. So, if you have got an n + 1 particle state okay and which is Phi a. And another state which is an n particle state which is Phi b.

So, there is only one single electron state which is occupied in excess in the n + 1 state and let this be the single particle state with label i okay. So, the occupation number of i in Phi a, is one where as occupation number of the state i in Phi b is 0 and except for this all the other occupation numbers of all the single particle states and there are infinite of them. So, all the other occupation numbers are essentially the same.

So, you go from one to the other by adding or subtracting one electron and you can do this by way of creating and destructing the corresponding electron. So, you can use the creation and destruction operators to achieve this. So, these are the two states that we will work with you can use the destruction operator on Phi a, and you will get Phi b.

And naturally you can say, you will have the normalization integral because you can destroy a particle from Phi a, in the ith state and you will get Phi b. So, essentially you get the normalization integral for the quantum state Phi b okay, so this is the normalization integral. Now if you now have a Hermitian conjugate or operator for ci which we anticipate will be the same as ci dagger but till we demonstrate it I represented by the superscript H.

So, this is the Hermitian conjugate of ci which is cih. And we now work with the Hermitian conjugate because you have the normalization integral you take the Hermitian conjugate so you get ci h Phi b complex conjugate Phi a. And this integral is nothing but the complex conjugate of the integral of the corresponding complex conjugates.

So, you have the Phi a star and then the ci h Phi b okay and this is the corresponding normalization integral and this tells us that this cih operator must be nothing but ci dagger okay. So, we know that what were introduced as creation and destruction operators are actually Hermitian conjugates of each other.

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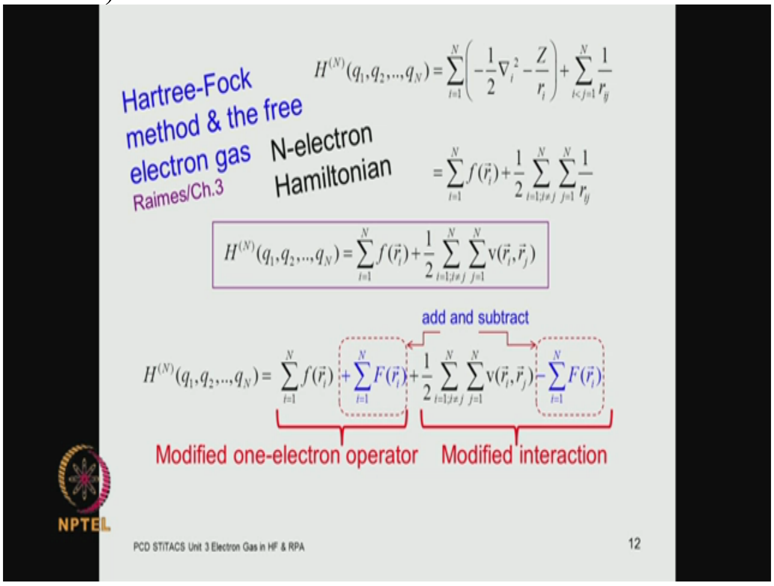

Hartree-Fock method & the free electron gas

Raimes/Ch.3

N-electron Hamiltonian

$$H^{(N)}(q_1,q_2,\ldots,q_N)=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

$$\boxed{H^{(N)}(q_1,q_2,\ldots,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)}$$

add and subtract

$$H^{(N)}(q_1,q_2,\ldots,q_N)=\underbrace{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified interaction}}$$

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So, we now proceed to discuss the Hartree Fock method for an N electron system but now we are going to work with the free electron gas. And this is what we will develop further we will use the free electron gas is the model system for which we will develop the random phase approximation and then develop it further will other applications.

So, most of this discussion again is from the book by Raimes called many electron theory from chapter 3 of this. So, you now have the atomic Hamiltonian but instead of the nuclear potential which was in the atomic case we will now work with free electrons okay. So, further we will now specialized for the free electron Hamiltonian.

You will nevertheless have the Hamiltonian, the N electron Hamiltonian written as a sum of two parts one is the one electron part which will of course have the kinetic energy of every electron and then you will have the two electron part which is coming from the electron-electron Coulomb interaction or what we are going to do to this is to add and subtract a single particle operator okay.

Now the choice of the single particle operator is going to be the main focus of discussion for today’s class. What you see from the relation in front of you is that you have added a certain term you have subtracted the same term so you are okay mathematically. What we are going to do is discuss the choice of f. Now f is to be so chosen that it will have most of the two electron term two electron interactions built into it.

It cannot have all of it but a certain approximation to it which will get as close as possible to the two electron term. So, that the difference between the term this term and this term becomes very small and the smaller it becomes the better is it because then the first two terms represent most of the Hamiltonian and they are both single particle operators okay.

What is left is the difference between the term v and the term F and if this difference is small we can hope to treat it perturbatively. So, that the requirements of perturbation theory will be satisfied, so that will be one criterion to choose F and the question is how do we choose F okay. So, you have a modified one electron operator modified because to the first term which is the actual kinetic energy term.

You have added a certain term which is yet to be found and you have subtracted the same term from the two electron term. So, it becomes a modified two electron term. So, you have got the modified interaction and the modified one electron operator. What we are now going to discuss is how to choose F.

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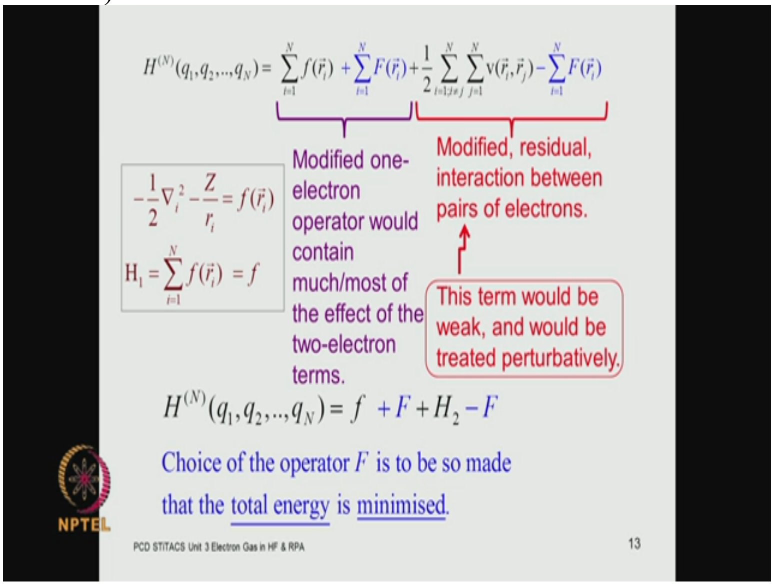

$$H^{(N)}(q_1,q_2,\ldots,q_N) = \underbrace{\sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i)}_{} + \underbrace{\frac{1}{2}\sum_{i=1; i\neq j}^{N}\sum_{j=1}^{N} v(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)}_{}$$

$$\boxed{\begin{array}{l} -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} = f(\vec{r}_i) \\ H_1 = \sum_{i=1}^{N} f(\vec{r}_i) = f \end{array}}$$

Modified one-electron operator would contain much/most of the effect of the two-electron terms.

Modified, residual, interaction between pairs of electrons.

This term would be weak, and would be treated perturbatively.

$$H^{(N)}(q_1,q_2,\ldots,q_N) = f + F + H_2 - F$$

Choice of the operator F is to be so made that the total energy is minimised.

Now quite obviously F is to be chosen, so that the difference, so that the modified residual interaction is very weak that we certainly know. And the one electron term includes the atomic potential in the atomic case in the free electron Hamiltonian the term Z over r will be missing okay. Because these are free electrons and the N electron Hamiltonian I am using a notation little f for the sum over F.

So no need to get confused about it I am just simply pointing out to the notation over here. So, you have F + h2 is your Hamiltonian and you have added and subtracted the term in F which is actually a sum over all the single particle operators which are yet to be chosen and we need to find what appropriate criterion we should use to select F.

Obviously F should be chosen so that the total energy is minimized okay. So, that is an obvious criterion that the total energy must be minimized because if F does anything which does not minimize the total energy then it will not be very helpful (Question time: 26:38 – not audible) where is the H1 defined H2 is the two particle interaction term right and where is the h1 defined separately what is the h1then; h1 is just a single particle operator.

It is just a single particle operator and explicitly it is the sum of all the single particle operator in the free electron case it is will be the sum of all the kinetic energy operators for each electron. For the atomic case it will include the nuclear attractive potential as well. So, F is to be chosen so that the total energy is minimized.

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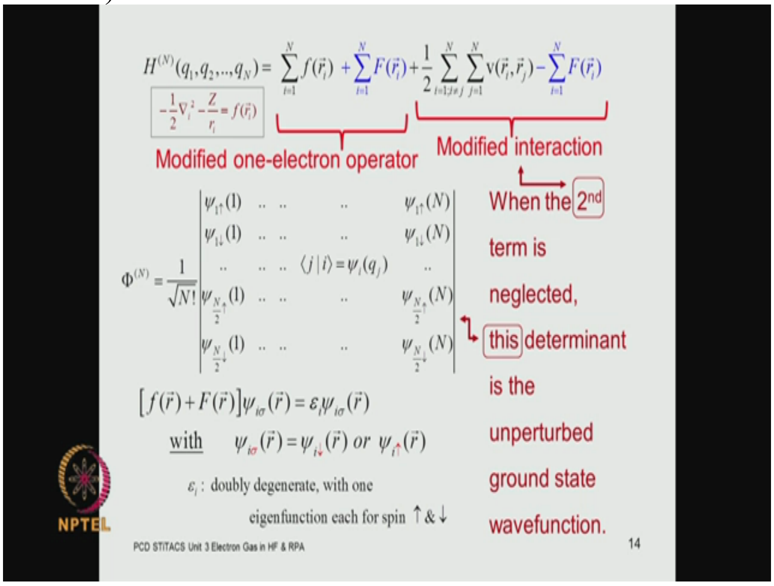

$$H^{(N)}(q_1,q_2,...,q_N)=\underbrace{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified interaction}}$$

$$\boxed{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}=f(\vec{r}_i)}$$

$$\Phi^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{1\uparrow}(1) & .. & .. & .. & \psi_{1\uparrow}(N)\\ \psi_{1\downarrow}(1) & .. & .. & .. & \psi_{1\downarrow}(N)\\ .. & .. & .. & \langle j|i\rangle=\psi_i(q_j) & ..\\ \psi_{\frac{N}{2}\uparrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\uparrow}(N)\\ \psi_{\frac{N}{2}\downarrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\downarrow}(N)\end{vmatrix}$$

When the $\boxed{2^{nd}}$ term is neglected, $\boxed{\text{this}}$ determinant is the unperturbed ground state wavefunction.

$$\left[f(\vec{r})+F(\vec{r})\right]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$$

with $\psi_{i\sigma}(\vec{r})=\psi_{i\downarrow}(\vec{r})$ or $\psi_{i\uparrow}(\vec{r})$

ε_i : doubly degenerate, with one eigenfunction each for spin ↑ & ↓

And what we will do is to work with a Slater determinantal wave function, so now we have a determinantal wave function which would be the correct unperturbed ground state if the second term which is the modified interaction were completely missing, if it were neglected okay. When it is to be introduced you will have a different Slater determinant. But when you do not include the modified interaction you will have a Slater determinant.

Which is a determinant of wave function for the N electron state, which is coming from the solution from the self-consistent field solution for the N electron Hamiltonian which is made up of the little f + the capital F which is the modified single particle interaction. So we are still working with the Hartree Fock.

But as you can already see this approach is slightly different from what we did in the previous course. So, the size which I have used in this Slater determinant these are Eigen functions of the modified one electron operator f little f + the capital F. And these are Eigen functions of the single particle operator’s f + capital F.

And please keep a track of this relationship. I am going to come back and refer to this equation as the discussion progresses today further and spin orbital’s are either Psi i up or Psi i down okay. Depending on the state being up or down and if you have an N electron system each single particle state is doubly degenerate.

With reference to the two spin states of the electron. So, you have got n by 2 states each being the being doubly degenerates. So, Psi 1 up and Psi 1 down would correspond to the degenerate Eigen functions okay. So, that is the notation I have used over here.
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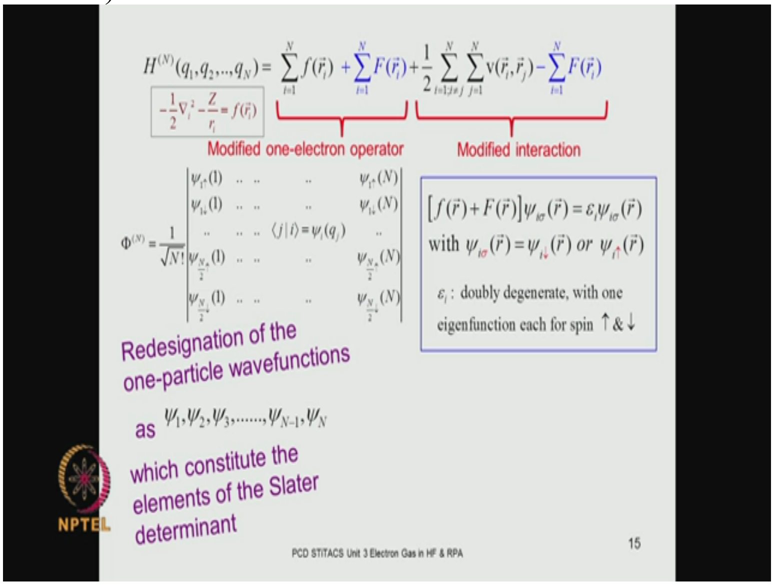

$$H^{(N)}(q_1,q_2,\dots,q_N)=\underbrace{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified interaction}}$$

$$\boxed{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}=f(\vec{r}_i)}$$

$$\Phi^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{1\uparrow}(1) & \cdots & \cdots & \psi_{1\uparrow}(N)\\ \psi_{1\downarrow}(1) & \cdots & \cdots & \psi_{1\downarrow}(N)\\ \cdots & \cdots & \langle j|i\rangle=\psi_i(q_j) & \cdots\\ \psi_{\frac{N}{2}\uparrow}(1) & \cdots & \cdots & \psi_{\frac{N}{2}\uparrow}(N)\\ \psi_{\frac{N}{2}\downarrow}(1) & \cdots & \cdots & \psi_{\frac{N}{2}\downarrow}(N)\end{vmatrix}$$

$$[f(\vec{r})+F(\vec{r})]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$$

with $\psi_{i\sigma}(\vec{r})=\psi_{i\downarrow}(\vec{r})$ or $\psi_{i\uparrow}(\vec{r})$

ε_i : doubly degenerate, with one eigenfunction each for spin ↑ & ↓

Redesignation of the one-particle wavefunctions as $\psi_1,\psi_2,\psi_3,\dots\dots,\psi_{N-1},\psi_N$ which constitute the elements of the Slater determinant

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So, now you have the Slater determinant but before we proceed what I will do is I will re-designate these one particle wave functions which I had designated as Psi up and Psi1 down. So, Psi1 down I will give a different number I will call it 2 okay. So, I will simply re-designate them. So, you will have n labels and the Slater determinant will be written in terms of Psi1 through Psi n okay.
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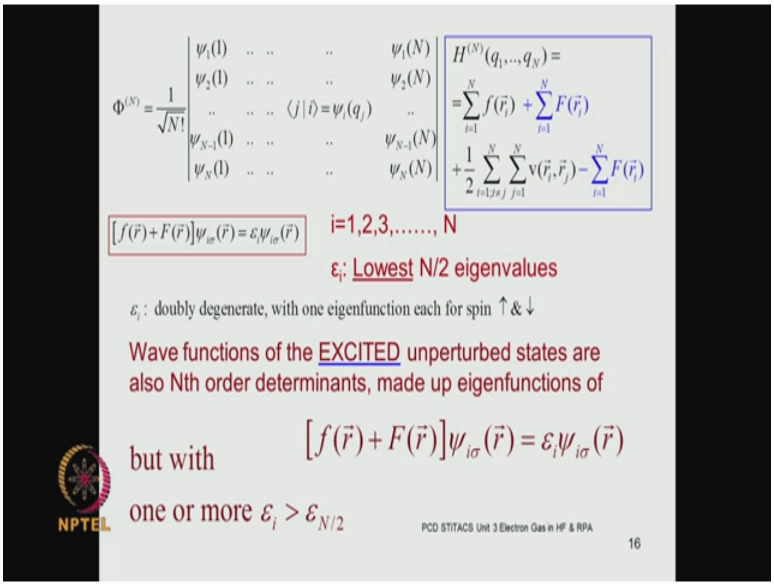

$$\Phi^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ \psi_2(1) & .. & .. & .. & \psi_2(N)\\ .. & .. & .. & \langle j|i\rangle=\psi_i(q_j) & ..\\ \psi_{N-1}(1) & .. & .. & .. & \psi_{N-1}(N)\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

$$\boxed{\begin{aligned}&H^{(N)}(q_1,\dots,q_N)=\\ &=\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)\\ &+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)\end{aligned}}$$

$$\boxed{[f(\vec{r})+F(\vec{r})]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})}$$

i=1,2,3,……, N

ε_i: Lowest N/2 eigenvalues

ε_i : doubly degenerate, with one eigenfunction each for spin ↑ & ↓

Wave functions of the EXCITED unperturbed states are also Nth order determinants, made up eigenfunctions of

$$[f(\vec{r})+F(\vec{r})]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$$

but with

one or more $\varepsilon_i>\varepsilon_{N/2}$

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So, these are the lowest n by 2 Eigen values which we are referring to as occupied states so far as this n particle system is concerned each single particle state being occupied by a spin up electron and a spin down electron. Now what about the excited state now an excited state will also be an Eigen function of the same equation which is a single particle equation however at least one Eigen value epsilon i will be greater than epsilon for n by 2 okay.

These are you have an ordered set, so I have stack them with the lowest one first and in this ordered set the uppermost which is n by 2 has been occupied by the N electron on system in doubly degenerate single particle states and if you now have an excited state of the N particle system.

In the excited state you will have at least one possibly more Eigen values epsilon i which are greater than n by 2. But we consider at least one and what our discussion which will apply for at least one can be very easily extended if you have more than one. So, we will have the excited states with at least one epsilon i which is greater than epsilon n by 2.
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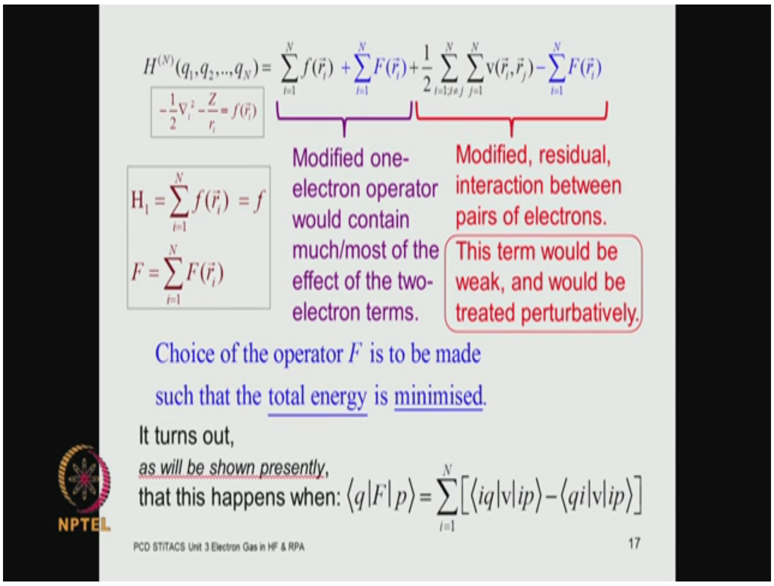

$$H^{(N)}(q_1,q_2,...,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)\underbrace{+\sum_{i=1}^{N}F(\vec{r}_i)}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\text{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}$$

$$\boxed{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}=f(\vec{r}_i)}$$

$$\boxed{\begin{aligned}H_1&=\sum_{i=1}^{N}f(\vec{r}_i)=f\\ F&=\sum_{i=1}^{N}F(\vec{r}_i)\end{aligned}}$$

Modified one-electron operator would contain much/most of the effect of the two-electron terms.

Modified, residual, interaction between pairs of electrons.

This term would be weak, and would be treated perturbatively.

Choice of the operator F is to be made such that the total energy is minimised.

It turns out,

as will be shown presently,

that this happens when: $\langle q|F|p\rangle=\sum_{i=1}^{N}\left[\langle iq|\text{v}|ip\rangle-\langle qi|\text{v}|ip\rangle\right]$

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And what we are going to do is to choose the operator F such that the total energy is minimized. Now it turns out and that is what we are going to show shortly in this class that the operator which will minimize this. Concurrently will be such that the matrix element of F in the Slater determinants q and p. In which q has got one state different from the previous one this matrix element is given by the expression that is on the right hand side.

So, let me show you that particular determinant yeah, so this state this operator, the criterion being that it is to be chosen such that the total energy is minimized which is the same principle that we invoked. In the same variational principle which we invoked in the Hartree Fock self-consistent field method, what we did was to find with the wave functions then N electron wave functions.

Such that the expectation value of the Hamiltonian was the minimum and this variational principle is what led us to the self consistent field equations right. So, this is going to happen as we will see shortly that the matrix element of F between q and p and q and p differ by only one electron okay it could elect very different one electron but minimally it has to differ by at least one electron.

So, that p refer to the ground state and q refers to an excited state with at least one electron which is missing in the previous set of occupied states up to the Fermi level and above it there is at least one electron which is occupied in what was the earlier awakened state okay. So, that is the matrix element of the operator F.

And this particular matrix element will turn out to be the sum over i. And the difference between these two to center integrals which we have been using all along

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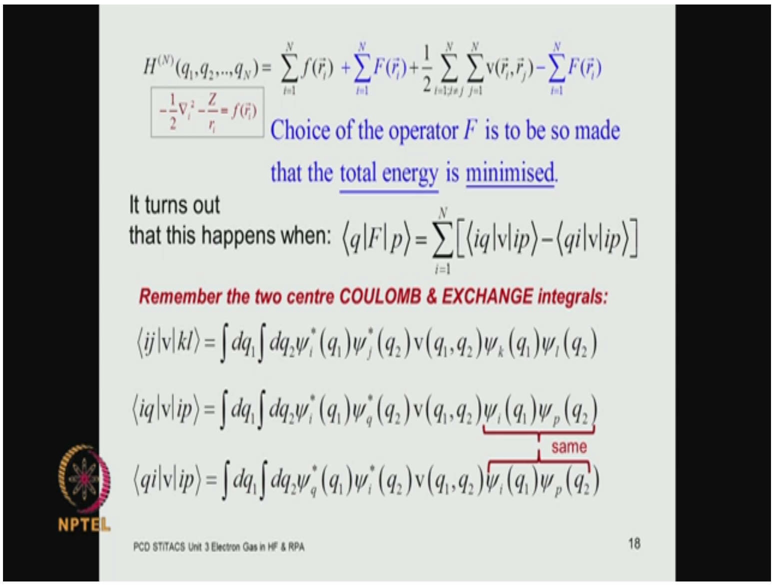

$$H^{(N)}(q_1,q_2,\dots,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$

$$\boxed{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}=f(\vec{r}_i)}$$

Choice of the operator F is to be so made that the total energy is minimised.

It turns out that this happens when: $\langle q|F|p\rangle=\sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle-\langle qi|\mathrm{v}|ip\rangle\right]$

Remember the two centre COULOMB & EXCHANGE integrals:

$$\langle ij|\mathrm{v}|kl\rangle=\int dq_1\int dq_2\psi_i^*(q_1)\psi_j^*(q_2)\mathrm{v}(q_1,q_2)\psi_k(q_1)\psi_l(q_2)$$

$$\langle iq|\mathrm{v}|ip\rangle=\int dq_1\int dq_2\psi_i^*(q_1)\psi_q^*(q_2)\mathrm{v}(q_1,q_2)\underbrace{\psi_i(q_1)\psi_p(q_2)}_{\text{same}}$$

$$\langle qi|\mathrm{v}|ip\rangle=\int dq_1\int dq_2\psi_q^*(q_1)\psi_i^*(q_2)\mathrm{v}(q_1,q_2)\overbrace{\psi_i(q_1)\psi_p(q_2)}$$

So, these are the Coulomb and the exchange integrals and I am writing them out explicitly over here for our reference. So, keep track of the same that you have got these two integrals i q,v, ip and q, i, v,ip. So, ip side is the same but the difference is over here, so these are the Coulomb and exchange integrals.

So, they are completely the same that we have discussed in the Hartree Fock formalism earlier okay. And this is what we have to show that the minimization of the total energy is concurrent with this particular expression for the matrix element between F the matrix element of the operator F in the states q and p okay. So, these are the coulomb and the exchange integrals.

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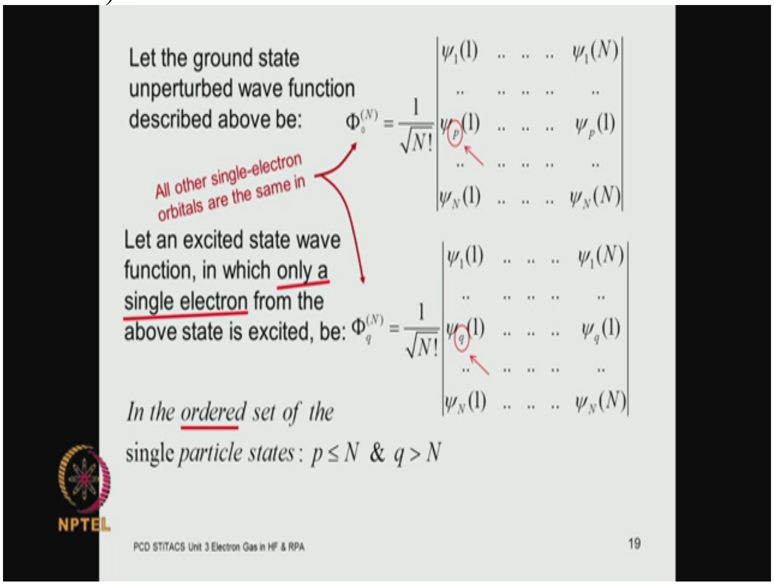

Let the ground state unperturbed wave function described above be:

$$\Phi_0^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_{\bigcirc p}(1) & .. & .. & .. & \psi_p(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

All other single-electron orbitals are the same in

Let an excited state wave function, in which only a single electron from the above state is excited, be:

$$\Phi_q^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_{\bigcirc q}(1) & .. & .. & .. & \psi_q(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

In the ordered set of the single particle states: $p\leq N$ & $q>N$

And this is these are the explicit expressions for Phi p and Phi q. So, Phi p is the ground state which is Phi 0 and in this the pth state was occupied whereas in the excited state Phi q the pth state is not occupied but instead the qth state is occupied. So, only one occupation number is different so it is the same n electron system but in a different configuration.

So, these are the Phi 0 and Phi q. Phi 0 is what I sometimes refer to as Phi p and Phi q is labelled with the index q. Because it is the qth which is occupied in the excited state whereas it was the pth state which was occupied in the ground state all the other occupation number is being essentially the same okay.

So, that is what we have got, of course we are referring to the ordered set without reference to the ordered set this discussion will not have any significance. And in this ordered set q is greater than N and p is less than or equal to N okay.

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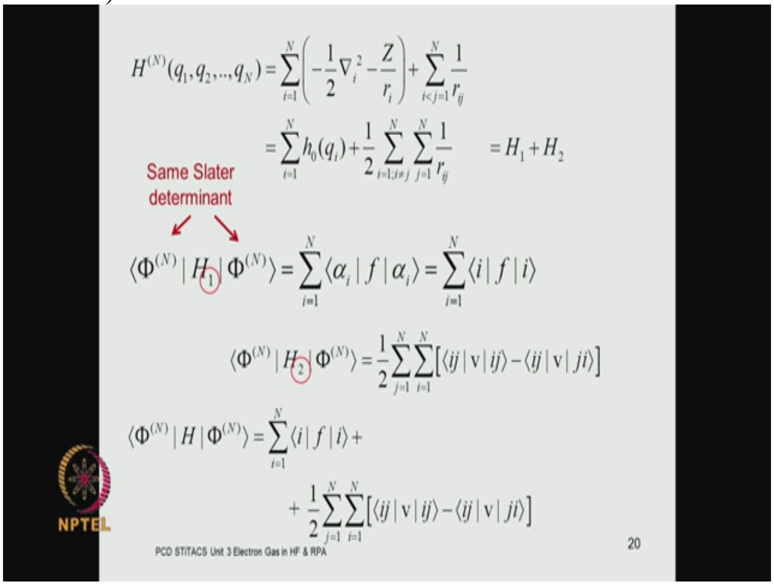

$$H^{(N)}(q_1,q_2,\dots,q_N)=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$=\sum_{i=1}^{N}h_0(q_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \qquad =H_1+H_2$$

Same Slater determinant

$$\langle\Phi^{(N)}|H_{\textcircled{1}}|\Phi^{(N)}\rangle=\sum_{i=1}^{N}\langle\alpha_i|f|\alpha_i\rangle=\sum_{i=1}^{N}\langle i|f|i\rangle$$

$$\langle\Phi^{(N)}|H_{\textcircled{2}}|\Phi^{(N)}\rangle=\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}[\langle ij|\mathrm{v}|ij\rangle-\langle ij|\mathrm{v}|ji\rangle]$$

$$\langle\Phi^{(N)}|H|\Phi^{(N)}\rangle=\sum_{i=1}^{N}\langle i|f|i\rangle+$$

$$+\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}[\langle ij|\mathrm{v}|ij\rangle-\langle ij|\mathrm{v}|ji\rangle]$$

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All right now let us have a look at the matrix element of the single particle operators the single particle operator is H1 and we have dealt with this in the previous course quite extensively, so I will not spend any time on getting these expressions. And we know that this is a sum of the matrix element which is the integral Psi i star F Psi i dq okay which I have written in the Dirac notation.

Likewise the matrix element for the two electron operators is this you do not have to worry about ruling out j = i because the Coulomb at the exchange integrals cancel each other for j =i, so I am not bothered about explicitly pointing out that j should not be equal to i but we know that j should not be equal to i right.

So, that is the term that we are working with and if you now combined the two terms you now have the expectation value of the Hamiltonian which will give you the corresponding energy in that particular Slater determinant wave function which is the sum of the one particle terms and the two particle terms.

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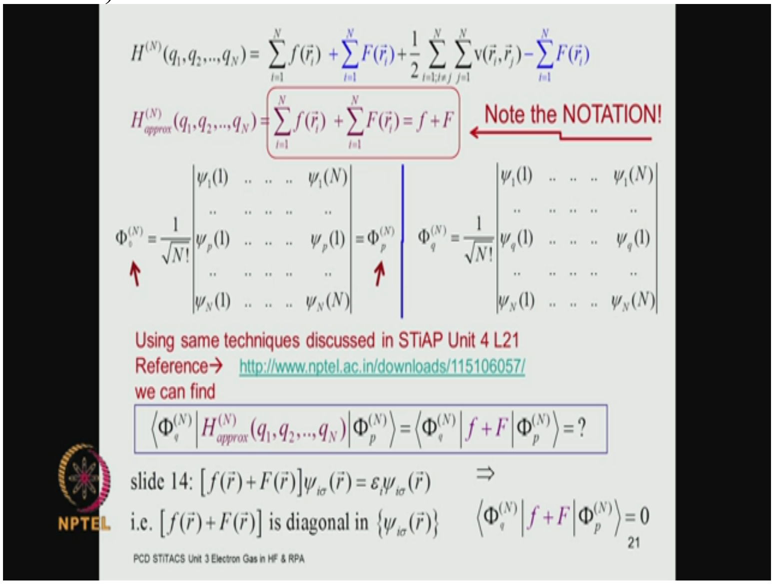

$$H^{(N)}(q_1,q_2,\ldots,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$

$$H_{approx}^{(N)}(q_1,q_2,\ldots,q_N)=\boxed{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)=f+F}\leftarrow \text{Note the NOTATION!}$$

$$\underset{\uparrow}{\Phi_0^{(N)}}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_p(1) & .. & .. & .. & \psi_p(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}=\underset{\uparrow}{\Phi_p^{(N)}}\quad\Bigg|\quad \Phi_q^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_q(1) & .. & .. & .. & \psi_q(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

Using same techniques discussed in STiAP Unit 4 L21

Reference→ http://www.nptel.ac.in/downloads/115106057/

we can find

$$\boxed{\left\langle\Phi_q^{(N)}\middle|H_{approx}^{(N)}(q_1,q_2,\ldots,q_N)\middle|\Phi_p^{(N)}\right\rangle=\left\langle\Phi_q^{(N)}\middle|f+F\middle|\Phi_p^{(N)}\right\rangle=?}$$

slide 14: $[f(\vec{r})+F(\vec{r})]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$ $\Rightarrow$

i.e. $[f(\vec{r})+F(\vec{r})]$ is diagonal in $\{\psi_{i\sigma}(\vec{r})\}$ $\left\langle\Phi_q^{(N)}\middle|f+F\middle|\Phi_p^{(N)}\right\rangle=0$

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Now you have to remember that what I write as little f is actually a sum of all these F, so I am not used a different symbol for that. So, this is just a matter of notation and you also have to remember that I have used Phi 0 and Phi p equivalently because I am focusing my attention on the fact that in the ground state other than the remaining n - 1 electron states it is a pth state which was occupied.

And it is this one which would be vacant in the excited state but replaced by the occupation number 1 for the qth state okay. So, Phi 0 and Phi p refer to the same and Phi q is the excited state. Now using techniques which we have discussed quite extensively in the previous course which again I will not discuss at all, I will refer to the discussion in the twenty first lectures of unit 4 in this course.

Using these techniques you can then show that this approximate N electron Hamiltonian which is the sum of the first two terms. You now have the first term, the second term, the third term and the fourth term. So, the third and the fourth term if you include, if you exclude the third and the fourth term and you can do so because when you subtract the fourth term from the third term you get a difference which is very weak okay.

So, what is left is the sum of the first two terms and that becomes a fairly good approximation to the N electron Hamiltonian okay. So, the matrix element if you now try to determine what is the matrix element of this approximate Hamiltonian which thus just the sum of the little f and the capital F. What is this matrix element? So, let us ask that question okay. What is the matrix element of the proximity Hamiltonian which is the sum of the first two terms?

The matrix element in the state in the Slater determinant Phi p and Phi q so that is the question that we have raised and just to remind you in slide 14 earlier we have shown that we are working with Eigen states of the single particle operator which is the modified single particle interaction which is sum of F little f and the upper case F. So, this operator f + F is obviously diagonal in this okay.

So, this one is diagonal and as a result of this it follows using the techniques that we have discussed earlier that this particular approximate Hamiltonian will have a matrix element which will vanish between two different Slater determinants which have different occupation numbers okay. So, this will automatically vanish, so I will not show this in any detail but refer you to the discussion in unit 4 of the previous course.

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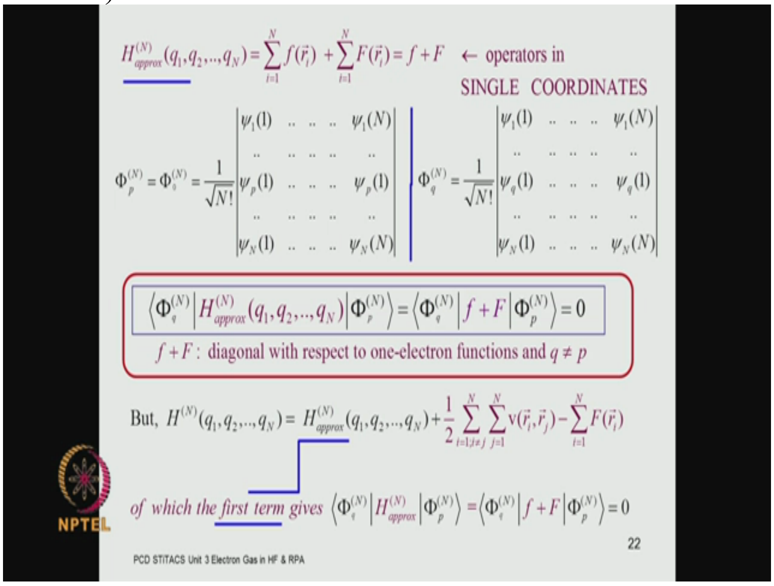

$$H_{approx}^{(N)}(q_1,q_2,...,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)=f+F \leftarrow \text{operators in}$$

SINGLE COORDINATES

$$\Phi_p^{(N)}=\Phi_0^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_p(1) & .. & .. & .. & \psi_p(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix} \qquad \Phi_q^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_q(1) & .. & .. & .. & \psi_q(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

$$\boxed{\left\langle\Phi_q^{(N)}\middle|H_{approx}^{(N)}(q_1,q_2,..,q_N)\middle|\Phi_p^{(N)}\right\rangle=\left\langle\Phi_q^{(N)}\middle|f+F\middle|\Phi_p^{(N)}\right\rangle=0}$$

$f+F$: diagonal with respect to one-electron functions and $q \neq p$

But, $H^{(N)}(q_1,q_2,..,q_N)=H_{approx}^{(N)}(q_1,q_2,...,q_N)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$

of which the first term gives $\left\langle\Phi_q^{(N)}\middle|H_{approx}^{(N)}\middle|\Phi_p^{(N)}\right\rangle=\left\langle\Phi_q^{(N)}\middle|f+F\middle|\Phi_p^{(N)}\right\rangle=0$

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So, what we now have is the following that f + F is diagonal with respect to the one electron functions. We know that q is not equal to p because we are referring to q as the excited state. So, we know that the first term which is the approximation Hamiltonian this term vanishes. So, now the question is what do we get from the remaining two terms which is the third and the fourth star okay.

What are we going to get from that the first term gives you a zero what about the second and the third okay.

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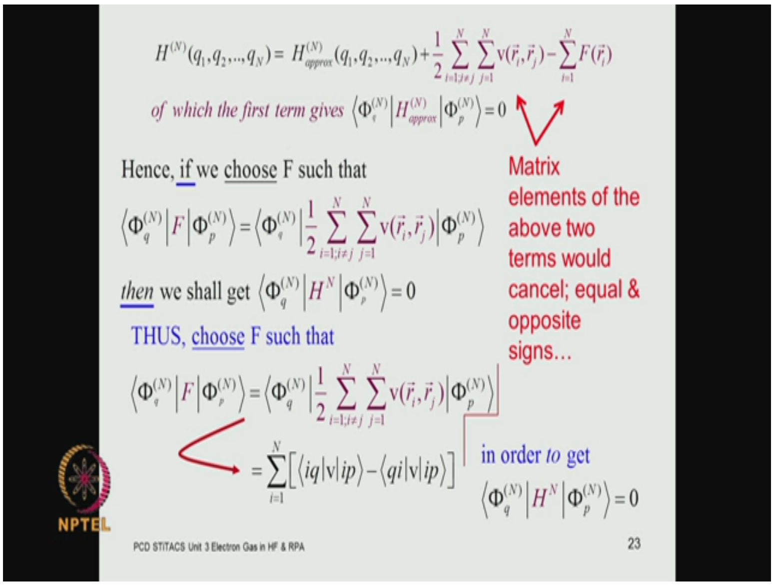

$$H^{(N)}(q_1,q_2,...,q_N) = H^{(N)}_{approx}(q_1,q_2,...,q_N) + \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} v(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)$$

of which the first term gives $\langle \Phi_q^{(N)} | H^{(N)}_{approx} | \Phi_p^{(N)} \rangle = 0$

Matrix elements of the above two terms would cancel; equal & opposite signs…

Hence, if we choose F such that

$$\langle \Phi_q^{(N)} | F | \Phi_p^{(N)} \rangle = \langle \Phi_q^{(N)} | \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} v(\vec{r}_i,\vec{r}_j) | \Phi_p^{(N)} \rangle$$

then we shall get $\langle \Phi_q^{(N)} | H^N | \Phi_p^{(N)} \rangle = 0$

THUS, choose F such that

$$\langle \Phi_q^{(N)} | F | \Phi_p^{(N)} \rangle = \langle \Phi_q^{(N)} | \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} v(\vec{r}_i,\vec{r}_j) | \Phi_p^{(N)} \rangle$$

$$= \sum_{i=1}^{N}\left[\langle iq|v|ip\rangle - \langle qi|v|ip\rangle\right]$$

in order *to* get

$$\langle \Phi_q^{(N)} | H^N | \Phi_p^{(N)} \rangle = 0$$

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So, the first term which is approximate Hamiltonian it gives you zero for this matrix element. We now ask what are we going to get from the second and the third term but what we can see very clearly is that if we choose F and this is the main question that we decided to discuss in today’s class, how do we choose F?

Here is this suggestion that if F is so chosen that the matrix element of the third term is exactly equal to the matrix element of the fourth term given the fact that the third term comes with a plus sign and the fourth term comes with a minus sign. Then these two will cancel each other and you will get the matrix element of the N electron Hamiltonian in the qth and the pth state to vanish.

Because the first term which is the approximate Hamiltonian that we have already seen gives you a vanishing matrix element okay, so if F is so chosen that the matrix element of the two electron term v is exactly equal to this new single particle interaction f and this is telling us how f should be chosen okay.

So, this the two matrix elements will cancel each other because they come with opposite signs. And this would give us the matrix element of the N electron Hamiltonian to vanish between this Slater determinant Phi q and Phi p okay.

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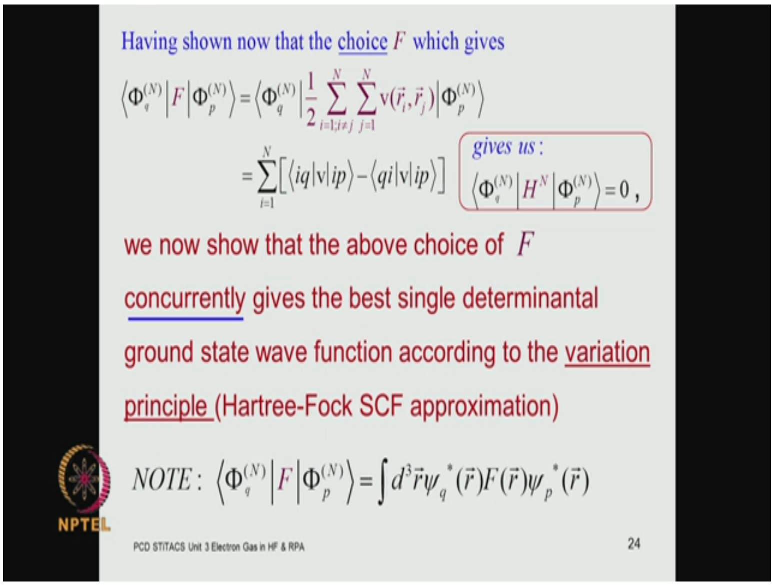

Having shown now that the choice F which gives

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| \frac{1}{2} \sum_{i=1;i\neq j}^{N} \sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) \middle| \Phi_p^{(N)} \right\rangle$$

$$= \sum_{i=1}^{N} \left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle \right]$$

gives us:

$$\left\langle \Phi_q^{(N)} \middle| H^N \middle| \Phi_p^{(N)} \right\rangle = 0 ,$$

we now show that the above choice of F concurrently gives the best single determinantal ground state wave function according to the variation principle (Hartree-Fock SCF approximation)

$$NOTE: \left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \int d^3\vec{r}\, \psi_q^*(\vec{r}) F(\vec{r}) \psi_p^*(\vec{r})$$

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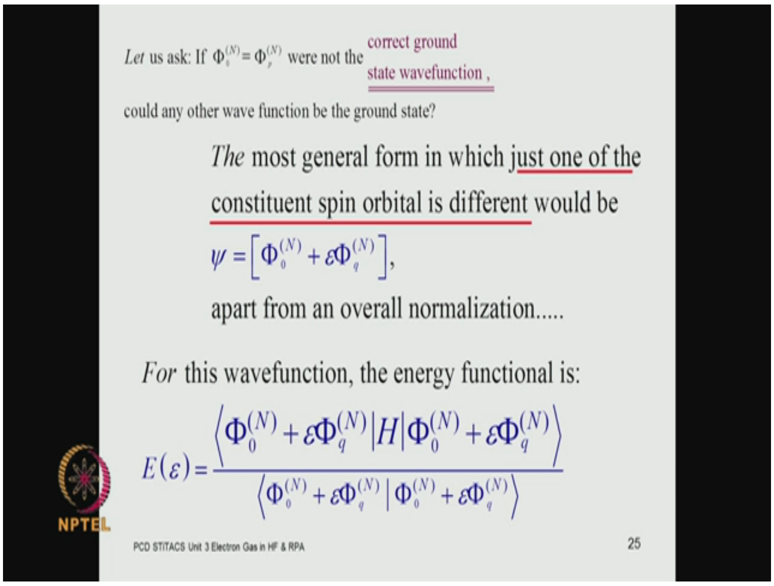
So, we have come this far and what we will now show is that this is completely consistent with our formalism of the Hartree Fock theory because this particular choice that we have suggested how is f to be suggested. So, that it will have the matrix elements of F to be equal to the matrix element of the two electron term v.

That this particular choice will give you the best single particle determinant of a function according to the principle of variation in the Hartree Fock formalism, excuse me. And what was the criterion there that in the frozen orbital approximation you must get a minimum of the expectation value of the n electron Hamiltonian right in the framework of the frozen orbital approximation.

Frozen orbital approximation which is where the Coulomb correlations get neglected right. So, now we ask how we are going to show this because we have suggested how F should be chosen but we now want to demonstrate that this particular choice will give you the best variational, best determinatal wave function within the framework of the frame frozen orbital approximation for the Hartree Fock theory okay.

(Refer Slide Time: 45:15)



Let us ask: If $\Phi_0^{(N)} = \Phi_p^{(N)}$ were not the correct ground state wavefunction ,

could any other wave function be the ground state?

The most general form in which just one of the constituent spin orbital is different would be

$$\psi = \left[\Phi_0^{(N)} + \varepsilon\Phi_q^{(N)}\right],$$

apart from an overall normalization.....

For this wavefunction, the energy functional is:

$$E(\varepsilon) = \frac{\left\langle \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \right\rangle}{\left\langle \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \middle| \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \right\rangle}$$

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So, let us ask this question that if ip was not the correct ground state, we have begun with the stipulation that it is in fact the correct ground state. In case it will not, which other wave function would be the correct ground state; it would be a mix of ip plus maybe something else right.

It would be a superposition of various terms and the most general form in which at least once determinative wave function is different is a superposition of Phi p which is Phi 0, it is just a matter of notation I have been denoting Phi 0 and Phi p equivalently okay. So, it will be a superposition of Phi 0 and 1 state which is different in at least one occupation number and the representative prototype of this state is Phi q okay.

So, you make a linear superposition of Phi 0 + Phi q the coefficient being epsilon and we certainly expect epsilon to vanish if Phi 0 is the correct ground state, not to vanish if it is not the correct round state and we must show that in the limit that epsilon goes to zero we get the correct variational minimum of the expectation value of the Hamiltonian in the N electrons state right.

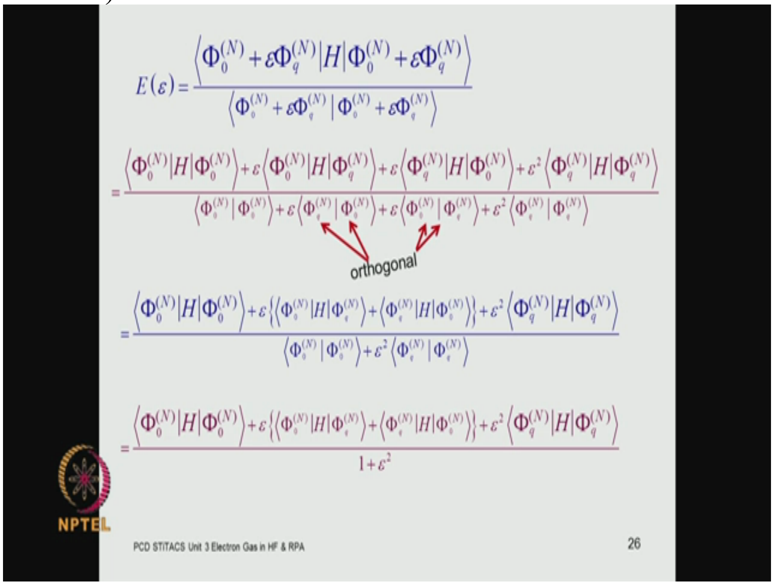
That is what we must show (Question time: 46:47- not audible) some other wave function it is it is Phi q is any state, any state in which at least one occupation number is different. So, q does not have any specific significance except for the fact that it represents an N electron determinate or wave function in which the occupation number of one of the N electron states is different.

So, it is a prototype of that it is not a particular choice but it is a prototype of that sure enough an excited state may have more than one but that will only make this stronger okay. This whole analysis will become only stronger if you have more than one electron excited but the minimum difference will be in the occupation of one of the N electron states.

So, if the determinatal wave function is now a superposition of Phi p and Phi q or Phi 0 and Phi q and this superposition is what I have written as Phi 0 n + epsilon Phi q okay. Then the corresponding energy functional is just the expectation value of the Hamiltonian in this state and you should make sure that it is divided by the norm of this new state.

Because if epsilon is not equal to 0 then it is the sum of the squares of the coefficients of Phi 0 and Phi q which will add up to unity okay. So, you have to divide it by the norm, so this is the energy functional for this new state all right.

(Refer Slide Time: 48:32)



$$E(\varepsilon)=\frac{\left\langle \Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\middle|\Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\right\rangle}$$

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\varepsilon\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_q^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_0^{(N)}\middle|\Phi_q^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|\Phi_q^{(N)}\right\rangle}$$

orthogonal

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|\Phi_q^{(N)}\right\rangle}$$

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{1+\varepsilon^2}$$

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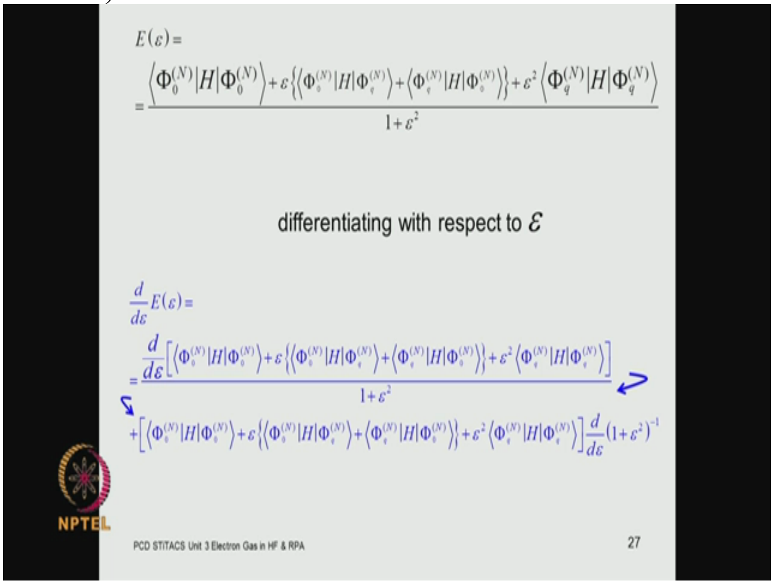
So, let us write this energy functional explicitly there are several terms okay. So, this is just an explicit expansion of this the numerator and the denominator. There are four terms in the numerator. The last term will be quadratic in epsilons there will be two terms which are linear in epsilon and the first term does not have epsilon at all which is just the expectation value of the Hamiltonian in the previous N electron state which is Phi p okay.

Likewise in the denominator there are for terms, now the denominator is easy to see because Phi 0 and Phi q are orthogonal to each other, so those two terms in the denominator already vanish, so now that simplifies the denominator okay. The four terms in the numerator have been retained explicitly.

And I have written it a little differently in the last expression here in which i have taken epsilon to be common okay. And you have a term in epsilon square in the denominator you

have Phi 0, Phi 0 norm which is equal to 1 and the second term will have the norm of Phi q which is also normalized. So, you will have 1 + epsilon square in the denominator okay.
(Refer Slide Time: 50:01)



$$E(\varepsilon)=$$

$$=\frac{\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{1+\varepsilon^2}$$

differentiating with respect to ε

$$\frac{d}{d\varepsilon}E(\varepsilon)=$$

$$=\frac{\frac{d}{d\varepsilon}\left[\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle\right]}{1+\varepsilon^2}$$

$$+\left[\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle\Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle\Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle\right]\frac{d}{d\varepsilon}(1+\varepsilon^2)^{-1}$$

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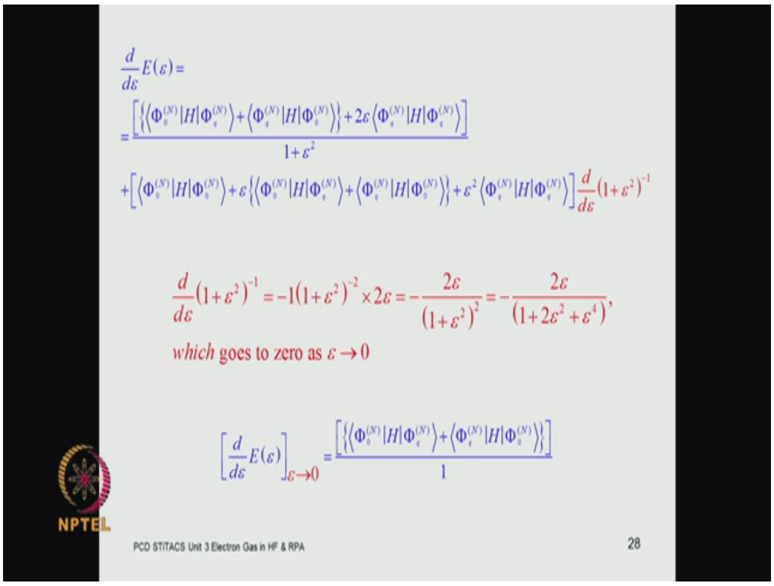
So, this is what we have got, now let us ask how will this energy functional change if you differentiate it with respect to epsilon. Because epsilon is the additional mix we expect this additional mix to go to 0 okay. So, that let us treat it parametrically as a variable and let us ask; what is the differential of the energy functional with respect to epsilon.

So, all I have done here is to differentiate the energy functional with respect to epsilon. So, it is the differential of the numerator divided by the denominator plus the numerator times the differential of the denominator okay. So, it is this differential that we are examining. So, the first term is the differential of the numerator.

Numerator has got no epsilon in the first term and this term is linear in epsilon. So, when differentiated with epsilon you will only have this combination of these two terms in this beautiful bracket. And then here you will have this coefficient times twice epsilon which is the differential of epsilon square with respect to epsilon okay.
(Refer Slide Time: 51:27)



$$\frac{d}{d\varepsilon}E(\varepsilon) =$$

$$= \frac{\left[\left\{\langle\Phi_0^{(N)}|H|\Phi_q^{(N)}\rangle + \langle\Phi_q^{(N)}|H|\Phi_0^{(N)}\rangle\right\} + 2\varepsilon\langle\Phi_q^{(N)}|H|\Phi_q^{(N)}\rangle\right]}{1+\varepsilon^2}$$

$$+\left[\langle\Phi_0^{(N)}|H|\Phi_0^{(N)}\rangle + \varepsilon\left\{\langle\Phi_0^{(N)}|H|\Phi_q^{(N)}\rangle + \langle\Phi_q^{(N)}|H|\Phi_0^{(N)}\rangle\right\} + \varepsilon^2\langle\Phi_q^{(N)}|H|\Phi_q^{(N)}\rangle\right]\frac{d}{d\varepsilon}(1+\varepsilon^2)^{-1}$$

$$\frac{d}{d\varepsilon}(1+\varepsilon^2)^{-1} = -1(1+\varepsilon^2)^{-2}\times 2\varepsilon = -\frac{2\varepsilon}{(1+\varepsilon^2)^2} = -\frac{2\varepsilon}{(1+2\varepsilon^2+\varepsilon^4)},$$

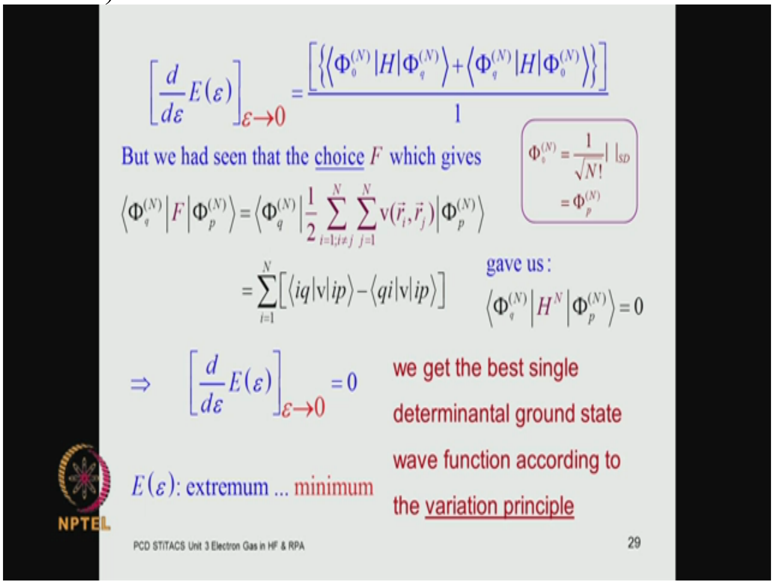
which goes to zero as $\varepsilon \to 0$

$$\left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\to 0} = \frac{\left[\left\{\langle\Phi_0^{(N)}|H|\Phi_q^{(N)}\rangle + \langle\Phi_q^{(N)}|H|\Phi_0^{(N)}\rangle\right\}\right]}{1}$$

So, that is what you have got in the next term that you have the differential of the numerator divided by the denominator which is 1 + epsilon square + the numerator times the differential of the denominator which is - 2 epsilon divided by 1 + 2 epsilon square + epsilon to the 4 okay.

That is the differential of the denominator. So, let us plug it in and you can see that after you insert all the terms and take the limit epsilon going to 0 you get just these two terms. But we already know what this result is? What is it?

(Refer Slide Time: 52:17)



$$\left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\to 0} = \frac{\left[\left\{\langle\Phi_0^{(N)}|H|\Phi_q^{(N)}\rangle + \langle\Phi_q^{(N)}|H|\Phi_0^{(N)}\rangle\right\}\right]}{1}$$

But we had seen that the choice F which gives

$$\langle\Phi_q^{(N)}|F|\Phi_p^{(N)}\rangle = \langle\Phi_q^{(N)}|\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j)|\Phi_p^{(N)}\rangle$$

$$= \sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle\right]$$

$$\boxed{\begin{aligned}\Phi_0^{(N)} &= \frac{1}{\sqrt{N!}}|\;|_{SD}\\ &= \Phi_p^{(N)}\end{aligned}}$$

gave us :

$$\langle\Phi_q^{(N)}|H^N|\Phi_p^{(N)}\rangle = 0$$

$$\Rightarrow \left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\to 0} = 0$$

we get the best single determinantal ground state wave function according to the variation principle

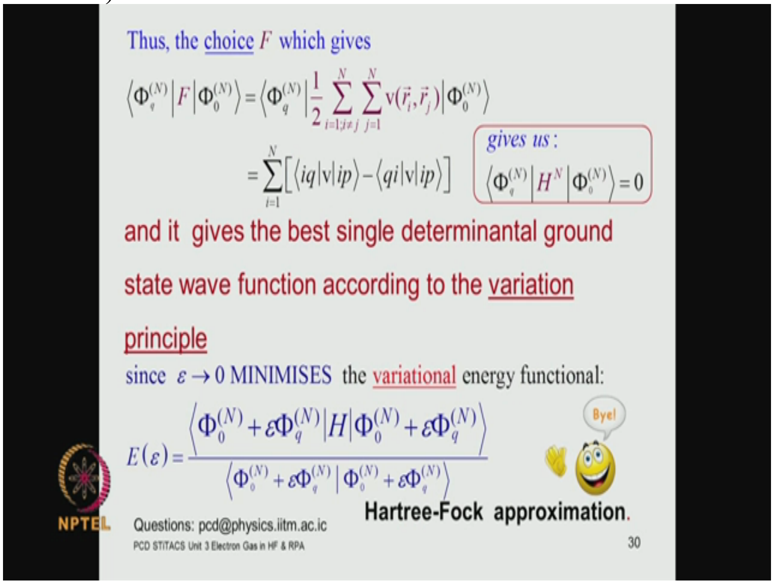
$E(\varepsilon)$: extremum ... minimum

This Phi 0 is the same state as Phi p and this is the matrix of the Hamiltonian in two Slater determinant of wave functions one of which is Phi p and the other is Phi q okay. So, we had chosen F such that the matrix element of F was equal to the matrix element of the two electron operator with this particular expansion in terms of the Coulomb and exchange integrals.

And this had given us that this matrix element of the N electron Hamiltonian in the state q and p this had vanished okay. So, this result we already have and what essentially we get is that the energy functional has a minimum okay. It must have a minimum because of the differential its variation with respect to epsilon vanishes in the limit epsilon going to 0. So, that is what gives you the best wave function.

Which is essentially the heart of the principle of the self consistent field why because we have invoked the frozen orbital approximation, we agreed that the difference between Psi q or Phi q and Phi p was only in one electron state everything else remaining the same all the occupation numbers of everything else all the other n - 1 electron states remain untouched.

So, within the framework of the frozen orbital approximation you get the best single determine until ground state okay written as a Slater determinant according to the variational principle in, now we have demonstrated that the variation with respect to epsilon gives you a minimum in the limit epsilon going to 0. So, the limit epsilon going to 0 is important.
(Refer Slide Time: 54:18)



Thus, the choice F which gives

$$\langle \Phi_q^{(N)} | F | \Phi_0^{(N)} \rangle = \langle \Phi_q^{(N)} | \frac{1}{2} \sum_{i=1; i \neq j}^{N} \sum_{j=1}^{N} \mathrm{v}(\vec{r}_i, \vec{r}_j) | \Phi_0^{(N)} \rangle$$

$$= \sum_{i=1}^{N} \left[\langle iq | \mathrm{v} | ip \rangle - \langle qi | \mathrm{v} | ip \rangle \right]$$

gives us:

$$\langle \Phi_q^{(N)} | H^N | \Phi_0^{(N)} \rangle = 0$$

and it gives the best single determinantal ground state wave function according to the variation principle

since $\varepsilon \to 0$ MINIMISES the variational energy functional:

$$E(\varepsilon) = \frac{\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} | H | \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \rangle}{\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} | \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \rangle}$$

Hartree-Fock approximation.

Questions: pcd@physics.iitm.ac.ic

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And the frozen orbital approximation is also explicitly referred to over here. And what we have now done is to begin to use methods of second quantization the properties of the creation and destruction operators integrate them in the framework of the Hartree Fock formalism. And we will now use this discussion to develop the many electron theory or for a free electron gas.

But then our interest will now be not just to deal with the Coulomb interactions as was done in the Hartree Fock in picture in the Hartree Fock approximation in which we certainly included the statistical correlations but we had excluded the Coulomb correlations. So, now what we are going to do is to make an attempt to address the Coulomb correlations that is where the RPA will come in.

So, in our next class we will begin to discuss that it will take us a few classes to deal with the random phase approximation I believe we have eight classes in this unit and as we go through all of these eight classes we will go through the method of Bohm and Pines which is the method of transformation of the Hamiltonian to address the electron correlations.

So, that will be the subject for this unit there are any questions today I will be happy to take. (Question time: 55:46 not audible) yes Jobine yes we have introduced capital F function yeah after adding that we have fort names and why would two electron integral will be you know minimal or close to zero sorry.

What we have done Jobin we have added and subtracted an F term the capital F what the capital F term when it adds to the first single particle operator is to give you a modified one electron operator okay. When you subtract it from the two electron term v which is the sum over i and j of v or ri,rj.

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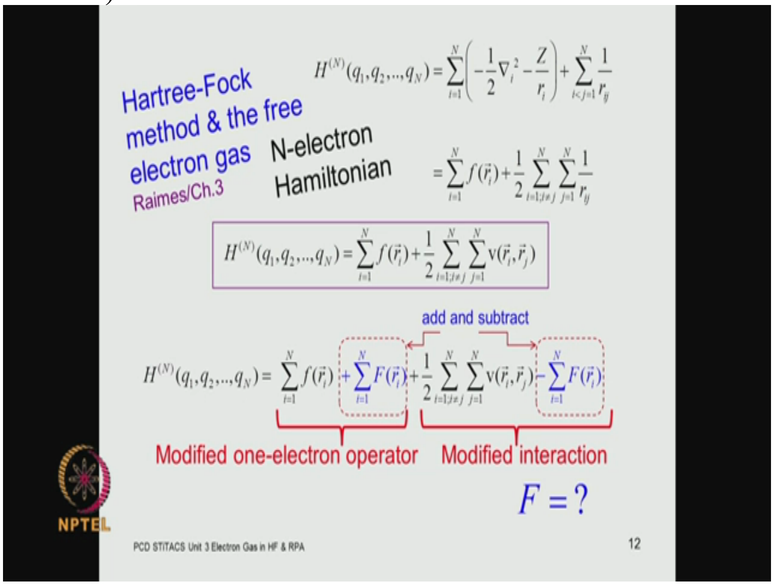

Hartree-Fock method & the free electron gas
Raimes/Ch.3

N-electron Hamiltonian

$$H^{(N)}(q_1,q_2,\ldots,q_N)=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

$$\boxed{H^{(N)}(q_1,q_2,\ldots,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)}$$

add and subtract

$$H^{(N)}(q_1,q_2,\ldots,q_N)=\underbrace{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}v(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified interaction}}$$

$F=?$

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You get a modified you get a modified interaction term okay. We are asking a question how should F be chosen. Now we want, we are going to choose F such that the expectation value of the Hamiltonian in the N electron determinative wave function is a minimum which is the heart of the variational principle okay.

So F is to be chosen according to that criterion and what we do is to develop a mechanism to show this how F is to be so chosen. The criterion to choose F is the following which comes I believe in not in this slide but in the next one that let me get to that quickly.

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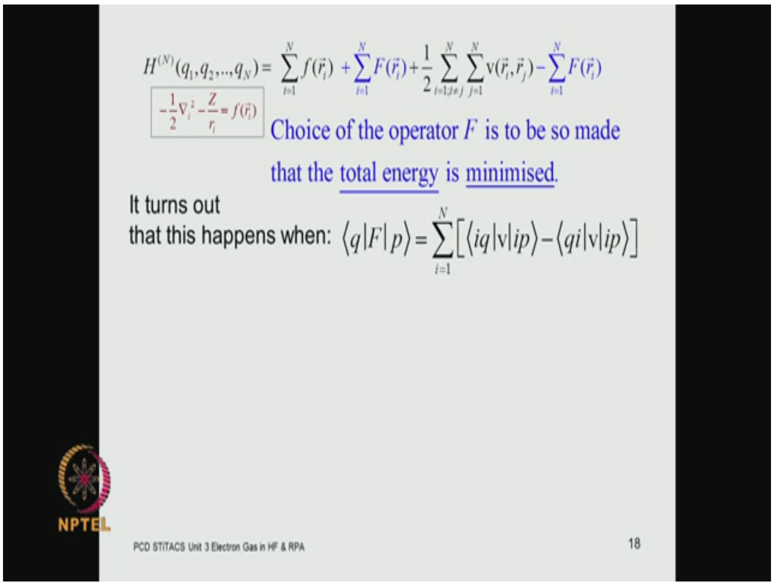

$$H^{(N)}(q_1,q_2,...,q_N) = \sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i) + \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)$$

$$\boxed{-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} = f(\vec{r}_i)}$$

Choice of the operator F is to be so made that the total energy is minimised.

It turns out that this happens when: $\langle q|F|p\rangle = \sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle\right]$

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It comes here. That the operator F which is to be chosen to minimize the total energy is such that the matrix element of F in two determinental wave functions q and p, q and p being different in only one electron state that this matrix element is given by the right hand side of this equation this is the criterion. And what this criterion does is to give you a minimum of the N electron Hamiltonian.

How because if this was not the case then the N electron Hamiltonian would not be just Phi p but it will be Phi p + epsilon times Phi q okay. So, if you now have an N electron determinant of wave function which is a superposition of Phi p and Phi q. So, this is the superposition which I wrote as Phi p + epsilon times Phi q or I might have written it as Phi 0 + epsilon times Phi q because I am using Phi 0 and Phi p equivalently okay.

Now this particular prescription of choosing F okay that the matrix element of F in q and p is given by this difference of Coulomb and exchange integrals sum over i going from 1 through n this is completely equivalent because what it does is concurrently it gives you the best wave function. How do you know it is the best wave function because if Phi p was not the best wave function.

Then the best wave function would need to be written as a superposition of Phi p with something else, that something else has to have at least one electron state which is occupied differently that is the one which I wrote as Phi as the qth state.
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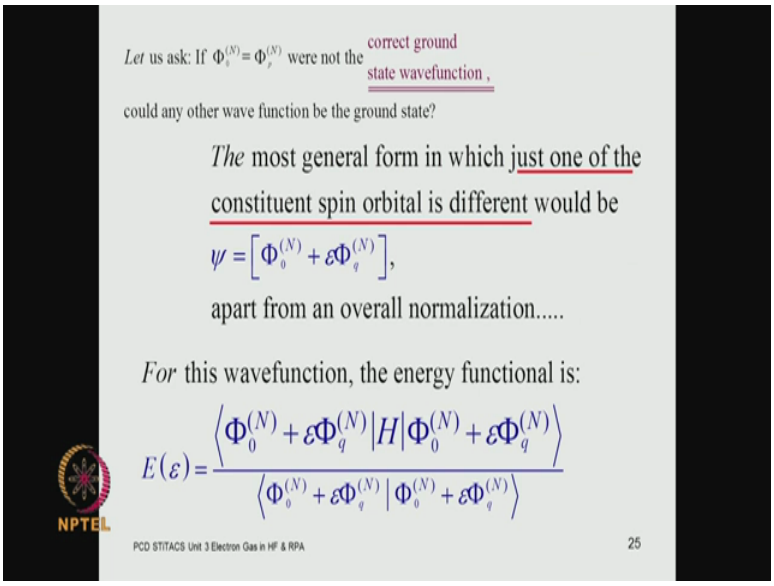

Let us ask: If $\Phi_0^{(N)} = \Phi_p^{(N)}$ were not the correct ground state wavefunction ,

could any other wave function be the ground state?

The most general form in which just one of the constituent spin orbital is different would be

$$\psi = \left[\Phi_0^{(N)} + \varepsilon \Phi_q^{(N)}\right],$$

apart from an overall normalization.....

For this wavefunction, the energy functional is:

$$E(\varepsilon) = \frac{\left\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \right\rangle}{\left\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \middle| \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \right\rangle}$$

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So, that state becomes the Phi 0 to your wave function if Phi 0 is not the best wave function which minimizes the expectation value of the Hamiltonian then the best wave function would be Phi 0 plus some mix of Phi q that mixing coefficient I propose this epsilon. Now what we find is that what minimizes the energy functional is the limit epsilon going to 0. Unless epsilon goes to 0, you do not get a minimum okay because the energy functional is capital E.

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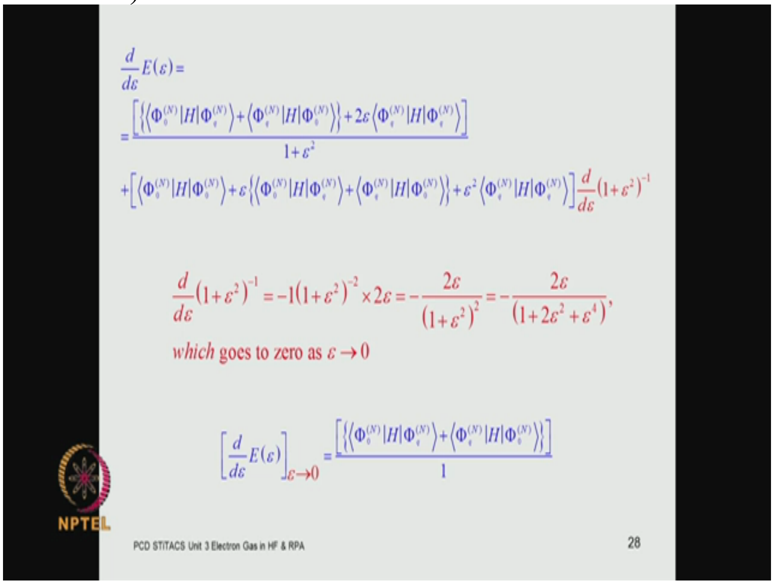

$$\frac{d}{d\varepsilon}E(\varepsilon) =$$

$$= \frac{\left[\left\{\left\langle \Phi_0^{(N)} | H | \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} | H | \Phi_0^{(N)} \right\rangle\right\} + 2\varepsilon \left\langle \Phi_q^{(N)} | H | \Phi_q^{(N)} \right\rangle\right]}{1+\varepsilon^2}$$

$$+\left[\left\langle \Phi_0^{(N)} | H | \Phi_0^{(N)} \right\rangle + \varepsilon\left\{\left\langle \Phi_0^{(N)} | H | \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} | H | \Phi_0^{(N)} \right\rangle\right\} + \varepsilon^2 \left\langle \Phi_q^{(N)} | H | \Phi_q^{(N)} \right\rangle\right] \frac{d}{d\varepsilon}\left(1+\varepsilon^2\right)^{-1}$$

$$\frac{d}{d\varepsilon}\left(1+\varepsilon^2\right)^{-1} = -1\left(1+\varepsilon^2\right)^{-2} \times 2\varepsilon = -\frac{2\varepsilon}{\left(1+\varepsilon^2\right)^2} = -\frac{2\varepsilon}{\left(1+2\varepsilon^2+\varepsilon^4\right)},$$

which goes to zero as $\varepsilon \to 0$

$$\left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon \to 0} = \frac{\left[\left\{\left\langle \Phi_0^{(N)} | H | \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} | H | \Phi_0^{(N)} \right\rangle\right\}\right]}{1}$$

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And what we see over here is that the variation of this energy functional in the limit epsilon going to 0 this is what we see over here, that in the limit epsilon going to 0 this energy functional is a minimum. The reason being the sum of the two terms in fact each of the two terms vanishes when that particular choice of F was made okay.

So, that is completely concurrent with the fact that the energy functional has got a minimum and that confirms to us that our stipulation that Phi 0 is the N electron ground state is appropriate. So, essentially this is the Hartree Fock theory because what we do in the Hartree

Fock is to find what is the criterion which will minimize the expectation value of the an electron Hamiltonian that is the question that we ask okay.

And then we conclude that yes the expectation value of the Hamiltonian in the N electron determinants wave function will in fact be a minimum. Of course the variation is subject to certain constraints which is where the Lagrange's variation multipliers walked into the Hartree Fock formalism that the constraints were that the single particle states must be normalized and orthogonal to each other.

So, with reference to those constraints the variation of the energy functional is a minimum and that led us to the self-consistent field equations. Which is the Hartree Fock self consistent field formalism right. So, the whole business of Hartree Fock is inspired by the motivation to get the energy functional to become a minimum subject to certain constraints of course.

But the governing approximation in this is the fact that we are working within the frozen orbital approximation okay. And that is the reason it was important to emphasize that the difference between Psi q and Psi p is only in the occupancy of one particle state all the remaining n - 1 electron states were essentially the same okay.

That is the essense of the frozen orbital approximation that is exactly what is left out of the Hartree Fock. So, there are two kinds of correlations in an N electron system one are the statistical correlations which come from the Fermi-Dirac statistics it comes because of the fact that the product wave function must be anti symmetrised. So, that is one correlation that is certainly included in the Hartree Fock.

But what is excluded in the Hartree Fock are the Coulomb correlations and it is the exclusion of the Coulomb correlations which is equivalent to the frozen orbital approximation. Because the variation in each orbital is being done in such a manner that all the other n - 1 electron remain untouched but that is not going to happen when you include the Coulomb correlations.

Because when you include the Coulomb correlations the occupations of the other electrons will also change and then that is what leads you to a multi configurational Hartree Fock state. You will need to include the configuration interaction okay. So, those are the correlations that we now want to address so that we completely we had left out those correlations in our previous discussion on the Hartree Fock.

And now what we want to do is to develop a many body formalism and there are means we have already stated earlier that a many body problem does not have exact solutions. So, we are going to have to make certain approximations one of the most powerful approximations is what is known as the random phase approximation which is what I will be discussing in this unit.

Any other question yes (Question time: 1:05:12) sir, we are adding that total Hamiltonian that one particular Hamiltonian and this interaction yeah a plus if and a minus if adding and subtracting then we are telling that f should be chosen like that the energy should be minimum yes but how can we choose f, which we are adding and subtracting to get a minimum of their total, why not.

Because you are adding and subtracting know, yeah so you are adding the same thing and subtracting the correct, correct you can change any, any anything like that if or you can you can always do that but there is no interest in adding and subtracting an arbitrary operator. But that will be zero know you are absolutely, absolutely necessary yeah so this is not just a question of showing that the previous Hamiltonian is equal to the new Hamiltonian.

What we are doing is we can do it with any arbitrary f that arithmetic sum will remain valid but the way we want to do it, is such that the energy functional will be a minimum and the second term will be weak. So, that it can be treated perturbatively most of the two-electron properties will go into the modified one electron operator.

So, modified one electron operator right and the Phi p and the Phi q are made up of Slater determinantal wave functions which are Eigen functions of the modified one electron operator okay. So these are not Eigen functions of an arbitrary operator these are Eigen functions of the modified one electron operator that is what gave us the approximate Hamiltonian okay.

Then we showed that the matrix element of the modified one electron operator in Phi p and Phi q vanishes that is because of the usual techniques of the single particle operators. But then we showed that if the matrix element of F is equal to the matrix element of v then the third and the fourth term also do not contribute and that is what gives you zero for that matrix element of the Hamiltonian in Phi p and Phi q that is what we have used.

Any other question well; Thank you very much and we will continue from here at the next class.