Select/ Special Topics in Atomic Physics
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Lecture - 20
Many-Electron Atoms: Hartree-Fock Self-Consistent Field Formalism II

Greetings, we will continue our discussion on the Hartree-Fock Self Consistent Field method.

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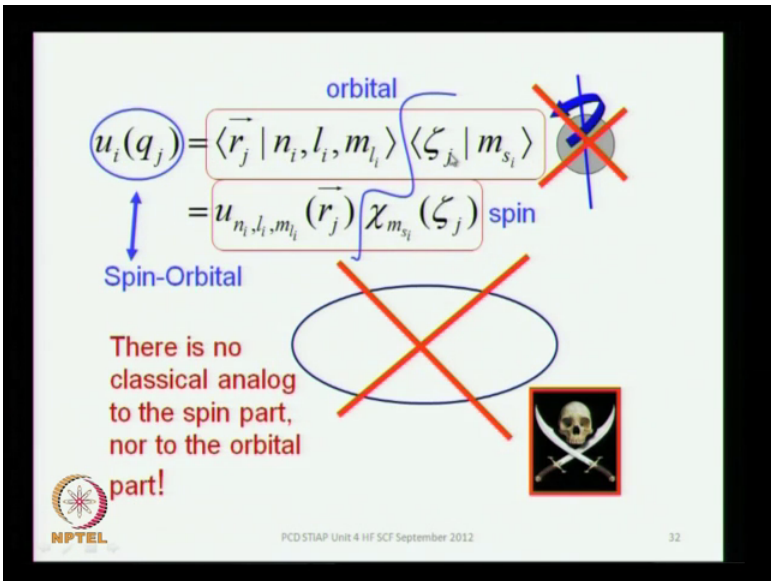

orbital

$$u_i(q_j) = \langle \vec{r}_j \,|\, n_i, l_i, m_{l_i} \rangle \langle \zeta_j \,|\, m_{s_i} \rangle$$

$$= u_{n_i,l_i,m_{l_i}}(\vec{r}_j)\, \chi_{m_{s_i}}(\zeta_j)$$ spin

Spin-Orbital

There is no classical analog to the spin part, nor to the orbital part!

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And the elements of the slitter determinant are the spin orbital's, another way always lying to remind that there is a no classical analog to the spin part also to the orbital part. And essentially, the spin orbital is made up of the these wave functions, you have got the an orbital part which is coordinator representation of the quantum state vector and this is the representation of the spin state vector in the spin space. So, you have got to spin part and the orbital part, and together they constitute the spin orbital, the subscript here I represents the quantum state, so it is represents set of 4 quantum numbers, and the argument q represents the space as well as spin coordinator.

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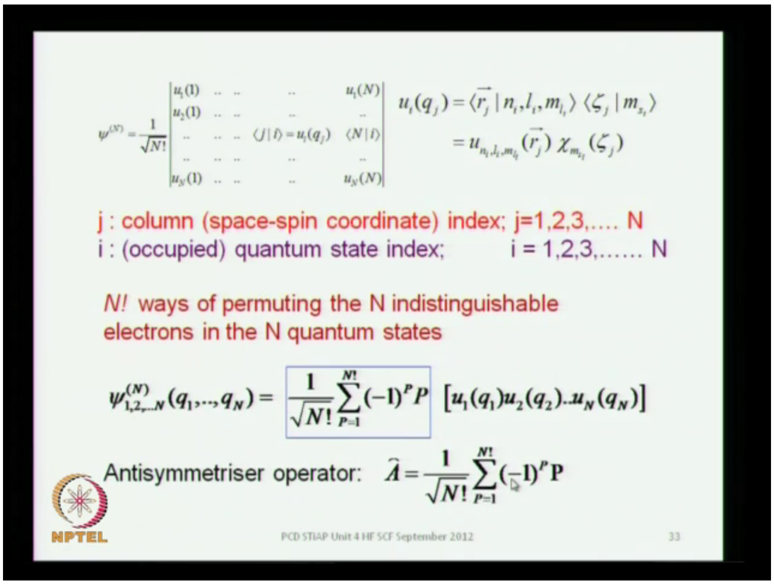

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & .. & .. & .. & u_1(N) \\ u_2(1) & .. & .. & .. & .. \\ .. & .. & .. & \langle j \mid i \rangle = u_i(q_j) & \langle N \mid i \rangle \\ .. & .. & .. & .. & .. \\ u_N(1) & .. & .. & .. & u_N(N) \end{vmatrix} \quad \begin{aligned} u_i(q_j) &= \langle \vec{r_j} \mid n_i, l_i, m_{l_i} \rangle \langle \zeta_j \mid m_{s_i} \rangle \\ &= u_{n_i,l_i,m_{l_i}}(\vec{r_j})\, \chi_{m_{s_i}}(\zeta_j) \end{aligned}$$

j : column (space-spin coordinate) index; j=1,2,3,.... N

i : (occupied) quantum state index; i = 1,2,3,...... N

N! ways of permuting the N indistinguishable electrons in the N quantum states

$$\psi^{(N)}_{1,2,...N}(q_1,..,q_N) = \boxed{\frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P P} \; [u_1(q_1) u_2(q_2) .. u_N(q_N)]$$

Antisymmetriser operator: $\hat{A} = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \mathrm{P}$

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Now, that is the notation we have and you have the columns, which sought of keep track of the coordinates and the rows, which have keep track of the quantum states which are occupied. And it is a matter of choice you know you choose that these are the states which are occupied, I gave the example of helium matter or you take a any atom sodium atom if you like. And you can say that 1 s 2 s 2 p 3 s states are occupied in one configuration, but in the excite side of sodium you have the low electron in the 3 s, but it is excited to 3 p.

So, the occupation of 3 s would be 0, and the occupation number of 3 p would be 1, so there will be no row corresponding to the 3 s, in the 11 electron system corresponding to the sodium atom in the excited state. So, that row will be missing, but it will be substituted by the row corresponding to 3 p, so considerations the choice of configuration, and the occupations, and choice of the rows is these are all connected to each other they are interrelated.

Now, there are factorial n ways of permitting, these n electrons in n quantum states, and that is what determinant represents and you can write this as a permutation operator, operating on this direct product of the this n particle states and single particle states. These are the elements which appear along the diagonal, and you permute and every time you permute, you pick a sign minus 1 every time there is a 180 change each interchange will contribute one change of sign.

And depending on the number of interchange is in a permutation, the parity would be either plus 1 or minus 1 for the permutation. At there are pictorial n permutation and assuming each of these single particle states belongs to an artho-normal basis, which is what we will seek. Eventually, the single particle states that will go into the slitter determinant, will require to belong to an artho-normal set, and in anticipation of that we can see that the normalization will be 1 over factorial, root factorial n.

You can easily see this 2 electron system, extended for 3 electron system or maybe if you do not want to try it out over here you will do it in the exam. So, this is the any electron wave function, this operator which generates and anti-symmetric wave function, is what is called as an anti-symmetries, because it that precisely what it does it describes operator very well.

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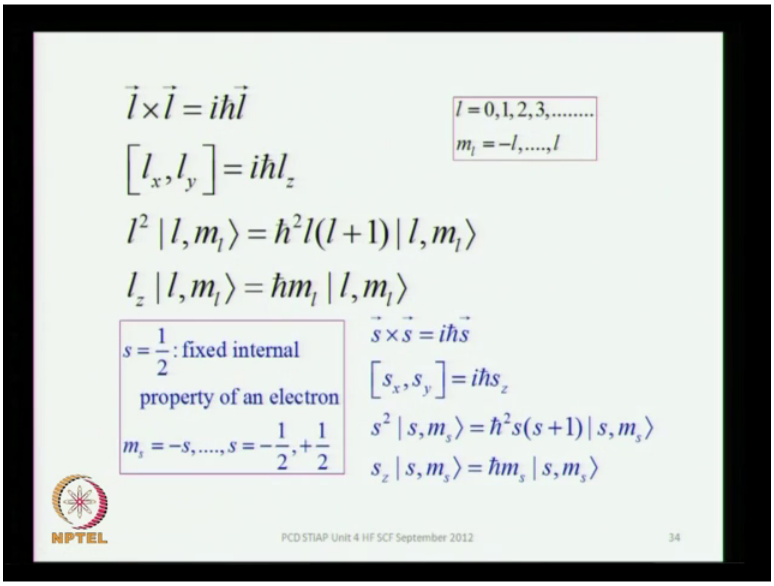

$$\vec{l}\times\vec{l} = i\hbar\vec{l}$$

$$[l_x, l_y] = i\hbar l_z$$

$$l^2\,|l,m_l\rangle = \hbar^2 l(l+1)\,|l,m_l\rangle$$

$$l_z\,|l,m_l\rangle = \hbar m_l\,|l,m_l\rangle$$

$l = 0,1,2,3,\ldots\ldots$

$m_l = -l,\ldots,l$

$s = \frac{1}{2}$: fixed internal property of an electron

$m_s = -s,\ldots,s = -\frac{1}{2},+\frac{1}{2}$

$$\vec{s}\times\vec{s} = i\hbar\vec{s}$$

$$[s_x, s_y] = i\hbar s_z$$

$$s^2\,|s,m_s\rangle = \hbar^2 s(s+1)\,|s,m_s\rangle$$

$$s_z\,|s,m_s\rangle = \hbar m_s\,|s,m_s\rangle$$

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And the spin and orbital angular momentum are defined by the accommodation relations as we have learnt in unit 2, and these are the ones which go into the description of the single particle states.

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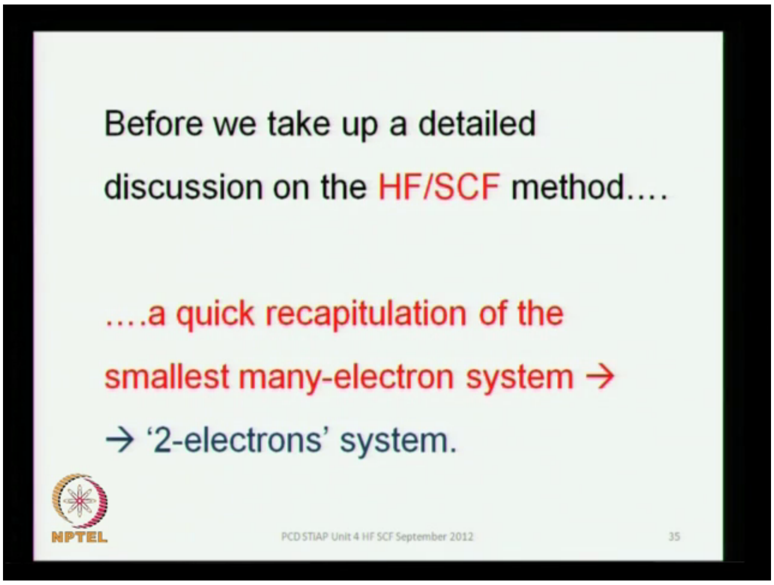

Before we take up a detailed discussion on the HF/SCF method….

….a quick recapitulation of the smallest many-electron system →

→ '2-electrons' system.

Now, before we have very extraction discussion on the entire self consistent field method, I will spend some time talking about smallest many electron system, which is the 2 electron system. So, let us consider 2 electron system, nothing else our entire system and the consideration is just a pair of electrons, these are identical particles the there will be decided by germinal, because they are completely indistinguishable. So, let us see what kind of quantum states we get, which describe this 2 electron system.

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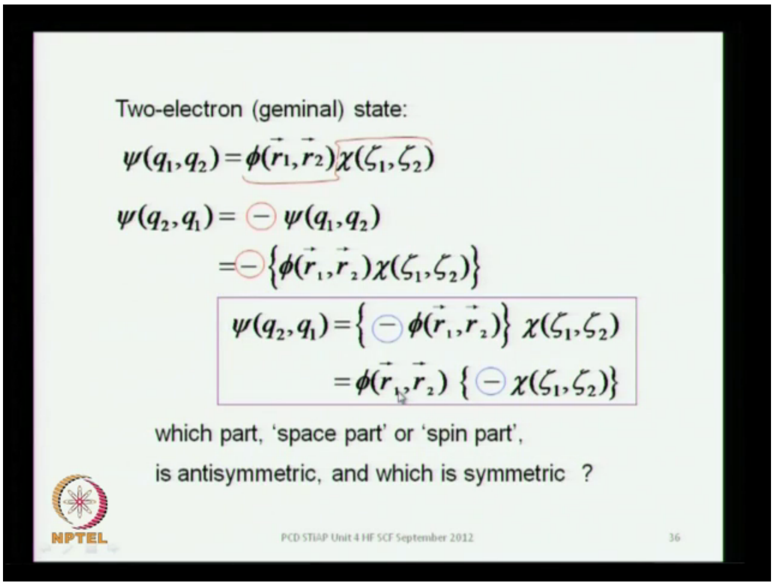

Two-electron (geminal) state:

$$\psi(q_1,q_2)=\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)$$

$$\psi(q_2,q_1)=-\psi(q_1,q_2)$$

$$=-\left\{\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)\right\}$$

$$\boxed{\begin{aligned}\psi(q_2,q_1)&=\left\{-\phi(\vec{r}_1,\vec{r}_2)\right\}\chi(\zeta_1,\zeta_2)\\&=\phi(\vec{r}_1,\vec{r}_2)\left\{-\chi(\zeta_1,\zeta_2)\right\}\end{aligned}}$$

which part, 'space part' or 'spin part', is antisymmetric, and which is symmetric ?

So, now this is the 2 electron system was argument are q 1 and q 2, q 1 is the set of 4 coordinates, q 2 is also set of 4 coordinates, so actually there are 8 variables setting in that. And this is written as spin orbital, this the orbital part, this space part and this is the spin part, chi zeta 1 zeta 2 is the spin part and phi r 1 r 2 is the orbital part. Now, if interchange q 1 and q 2, so in place of q 1 you have q 2 and in place of q 2 you have q 1, this is the original wave function subjected to one interchange. The wave function must change it is sign, because these are electron wave functions, this is the fermions system.

So, this becomes minus of psi q 1 and q 2, but this minus sign can be associate with by phi or with chi, you can have minus chi times plus chi or plus phi times minus chi. There are 2 possibilities, and both the possibilities are consistent with the at the symmetrical of the wave function, either of that. So, the question is which part space part or spin part which is anti-symmetric, and which is symmetric, because if you have the minus sign over here.

It is the space part which is anti-symmetric and the spin part, which is symmetric, over here it is the spin part which is anti-symmetric and the space part, which is symmetric. So, the properties of symmetry and the anti-symmetry can go either with the space part or with the spin part, but not with bock.

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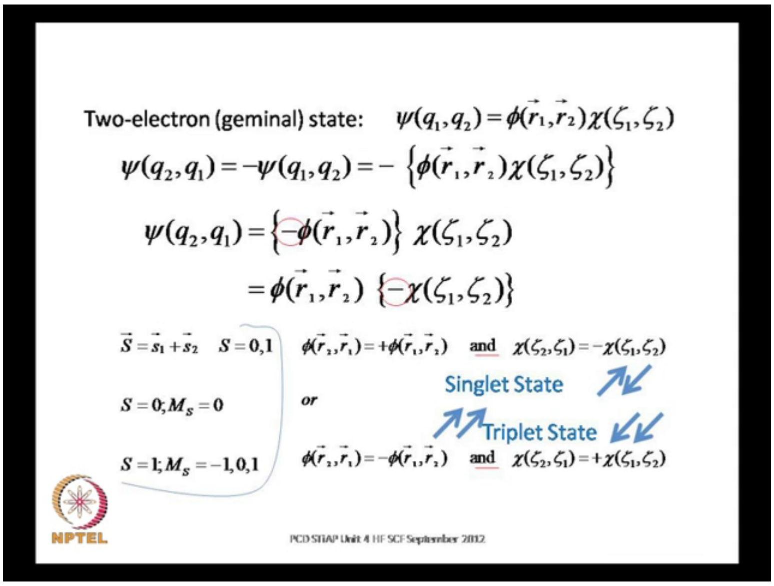

Two-electron (geminal) state: $\psi(q_1,q_2)=\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)$

$$\psi(q_2,q_1)=-\psi(q_1,q_2)=-\left\{\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)\right\}$$

$$\psi(q_2,q_1)=\left\{-\phi(\vec{r}_1,\vec{r}_2)\right\}\chi(\zeta_1,\zeta_2)$$

$$=\phi(\vec{r}_1,\vec{r}_2)\left\{-\chi(\zeta_1,\zeta_2)\right\}$$

$\vec{S}=\vec{s}_1+\vec{s}_2 \quad S=0,1$

$S=0; M_S=0$

$S=1; M_S=-1,0,1$

$\phi(\vec{r}_2,\vec{r}_1)=+\phi(\vec{r}_1,\vec{r}_2)$ and $\chi(\zeta_2,\zeta_1)=-\chi(\zeta_1,\zeta_2)$

Singlet State ↗↙

or

↗↗ Triplet State ↙↙

$\phi(\vec{r}_2,\vec{r}_1)=-\phi(\vec{r}_1,\vec{r}_2)$ and $\chi(\zeta_2,\zeta_1)=+\chi(\zeta_1,\zeta_2)$

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Now, this has very important consequences, so this is what we have got, and you have the anti-symmetric contain in this minus sign associated either with the orbital part or with the spin part. And these are the 2 possibilities that phi r 2 r 1 is equals to plus phi r 1 r 2, so phi r

2 r 1 should be equal to plus phi r 1 r 2, and chi zeta 2 zeta 1 must be equal to minus of chi zeta 1 zeta 2 or you should have phi r 2 r 1 to be equal to minus of phi r 1 r 2. So, either the orbital part is symmetric all the spin part is symmetric, but not bock, so what do these two possibilities correspond to.

They correspond to the spin being either 0 or 1, because the next spin-off 2 electron system is given by this summation of s 1 and s 2. So, this is the coupling of 2 angle of momentum both the, which are off, so the net spin will go from half minus half modeless which is 0, 2 half plus half with his 1. So, the 2 possibilities has been either 0 or 1, and if s 0 the corresponding m quantum number can be only 0 whereas, if s is 1 the corresponding m quantum number will be either minus 1 0 or 1, because m quantum number goes from minus j to plus j and j itself goes from modulus of j 1 minus j 2 to j 1 plus j 2, so that is all we have used here.

So, accordingly you have either strip less state with s equal to 1 or a sing lest state corresponding to s equal to 0. That means, singlet and triplet are self-explanatory, because you have got a single state corresponding to this there is only 1 m quantum number that you get over here, whereas over here you have 3 possibilities of m quantum numbers. So, this is the trip, so you have either the singlet triplet and the singlet state will have 0 spin, and the triplets state will have either 1 minus 1, so triplet state will have parallels spins, and singlet will have anti parallel spins.

Now, this is quite nicely it described that singlet states, because chi zeta 2 zeta 1 is equals to minus chi zeta 1 beta 2, and then if you have 0's on both sides, then 0 equal to minus 0 even in a atomic physics. So, that works well enough for us, the other state is the triplet state, you have got the singlet state and the triplet state, these are the 2 possibilities you get for the germinal wave function.

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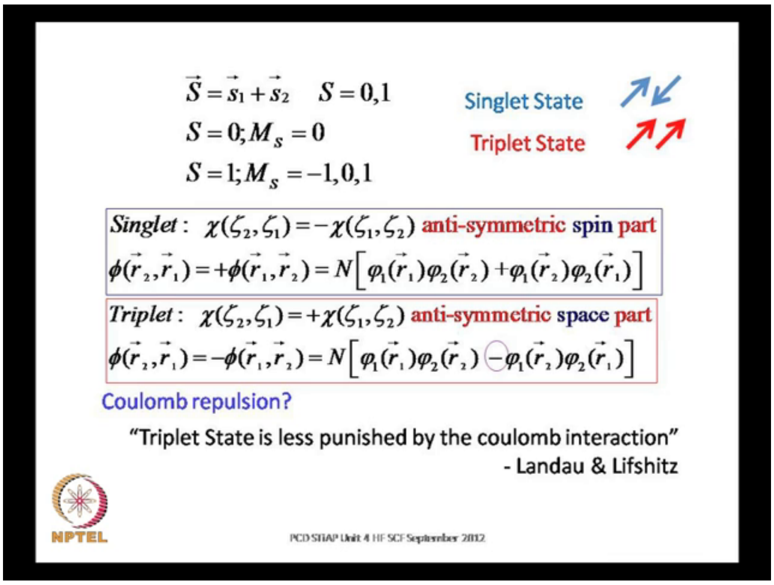

$\vec{S} = \vec{s}_1 + \vec{s}_2 \quad S = 0,1$

$S = 0; M_s = 0$

$S = 1; M_s = -1,0,1$

Singlet State ↗↙

Triplet State ↗↗

Singlet: $\chi(\zeta_2,\zeta_1) = -\chi(\zeta_1,\zeta_2)$ anti-symmetric spin part

$\phi(\vec{r}_2,\vec{r}_1) = +\phi(\vec{r}_1,\vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$

Triplet: $\chi(\zeta_2,\zeta_1) = +\chi(\zeta_1,\zeta_2)$ anti-symmetric space part

$\phi(\vec{r}_2,\vec{r}_1) = -\phi(\vec{r}_1,\vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$

Coulomb repulsion?

"Triplet State is less punished by the coulomb interaction"
- Landau & Lifshitz

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So, now that we have got this, let us ask the question which will have lower energy, do they have same energy, do they have different energy and if it is different, which state will have a lower energy. Now, the energy determined by the coulomb repulsion between the two, so you have to examine coulomb repulsion, so these are the singlet and triplet says the singlet has got and anti symmetric spin part and triplet as got an anti symmetric space part, this we know.

So, now, we examine the coulomb interaction, now can you guess, what with state would have lower energy, actually the form of the way function which is written on the slide would suggest you would have lower energy. If we examine it closely, notice that there is a plus here the orbital part, and this is got a minus sign over here. What it means is that in the limit r 2 going r 1, what will happen then r 2 goes to r 1 the 2 particles the 2 electrons get closer and closer, so as r 2 goes to r 1 what happens to the triplet state phi 1 r 1 phi 2 r 2 minus phi 1 r 2 phi 2 r 1 that would go to 0.

As, r 2 goes r 1, the space part would varnish and for the triplet state to exist r 2 would not be too close to r 1, it would be further way from each other than what is a required for the singlet state. So, the 2 particles, the 2 electrons would tends to be further way from each other in the triplet state, than in the singlet state, and what happens to the coulomb repulsion energy it goes 1 over distance.

So, now, you have larger distancing the triplet state compared to the singlet state, but this is the reparation, so the triplet will have lower energy compared to the singlet. So, this is very nicely stated in Landau and Lifshitz book in which they say that the triplet state is less punished by the coulomb interaction is nice way of saying it.

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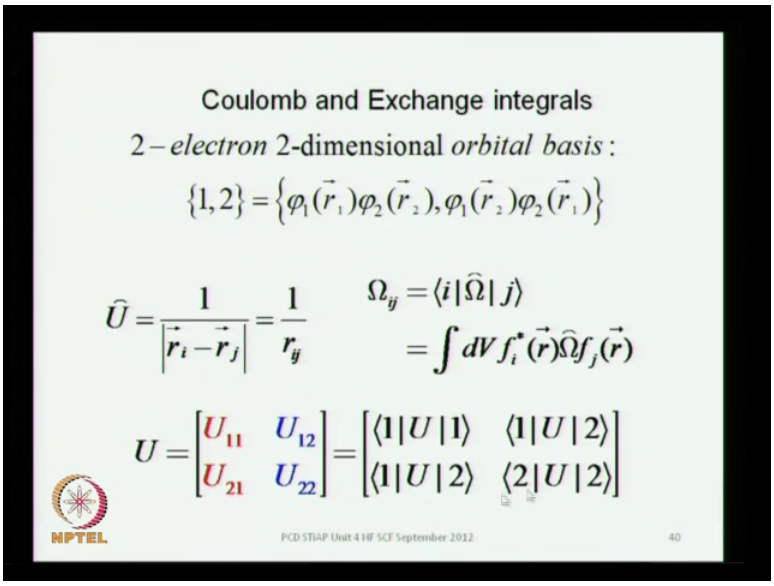

Coulomb and Exchange integrals

2 − *electron* 2-dimensional *orbital basis*:

$$\{1,2\} = \left\{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2), \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right\}$$

$$\hat{U} = \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} = \frac{1}{r_{ij}} \qquad \Omega_{ij} = \langle i|\hat{\Omega}|j\rangle = \int dV f_i^*(\vec{r})\hat{\Omega} f_j(\vec{r})$$

$$U = \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} = \begin{bmatrix} \langle 1|U|1\rangle & \langle 1|U|2\rangle \\ \langle 1|U|2\rangle & \langle 2|U|2\rangle \end{bmatrix}$$

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So, now, the next thing we will discuss is the representation of coulomb interaction in the germinal basis set, and you have got a two-dimensional basis, this is the basis for what this is the basis for pair of electrons, about the electron system is a pair of electrons. So, this is the 2 electron two-dimensional basis set, one corresponds to phi 1 r 1 phi 2 r 2 the other corresponds to the interchange of these 2 particles. So, that the electron, so this is major of the probabilities amplitude of the electron at coordinate r 2 to be in the contrive state phi 1, likewise this is probability amplitude that in the electron it coordinate r 1 is in the quantum state 2.

So, these are based functions, this is the first function, this is the second function and this is the interaction, you will looking at this is coulomb interaction, but 1 over the distance 1 over r i j. And you can look for matrix representation of the coulomb interaction in the basis set, and the typical matrix representation is simple given by this interval. So, this is what you have to do for the coulomb interaction, and accordingly you will have a matrix representation of the coulomb interaction, which will consist which consist of 2 by 2 matrix u 1 1 u 1 2 u 2 1 and u 2 2, so these are the integrate that we have to determine.

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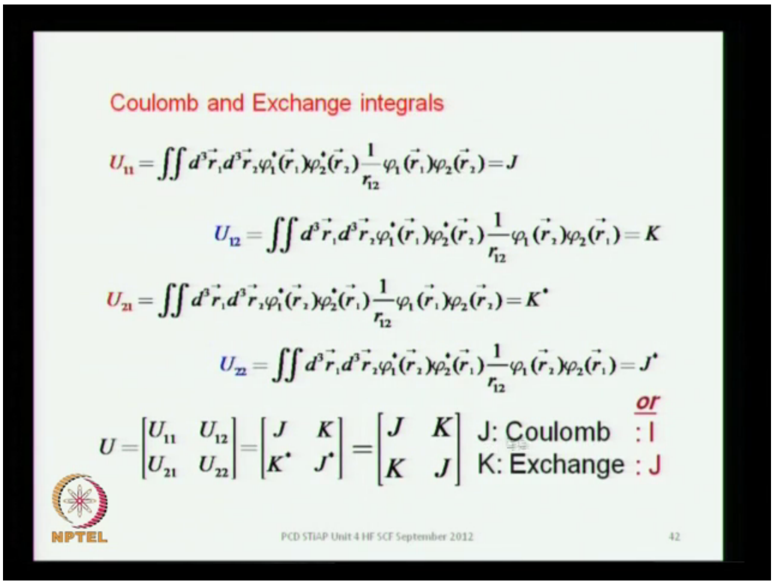

Coulomb and Exchange integrals

$$U_{11}=\iint d^3\vec{r}_1 d^3\vec{r}_2 \varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2)\frac{1}{r_{12}}\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)=J$$

$$U_{12}=\iint d^3\vec{r}_1 d^3\vec{r}_2 \varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2)\frac{1}{r_{12}}\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)=K$$

$$U_{21}=\iint d^3\vec{r}_1 d^3\vec{r}_2 \varphi_1^*(\vec{r}_2)\varphi_2^*(\vec{r}_1)\frac{1}{r_{12}}\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)=K^*$$

$$U_{22}=\iint d^3\vec{r}_1 d^3\vec{r}_2 \varphi_1^*(\vec{r}_2)\varphi_2^*(\vec{r}_1)\frac{1}{r_{12}}\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)=J^*$$

$$U=\begin{bmatrix}U_{11} & U_{12}\\ U_{21} & U_{22}\end{bmatrix}=\begin{bmatrix}J & K\\ K^* & J^*\end{bmatrix}=\begin{bmatrix}J & K\\ K & J\end{bmatrix}$$

or

J: Coulomb : I

K: Exchange : J

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So, let us look at the these integrals, now let us look at u 1 1, u 1 1 is this integral which is the integral of coulomb interaction, which 1 over r 1 and 2 in this phi 1 r 1, phi 2 r 2 both complex originated. And of this side you got phi 1 r 1 phi 2 r 2, and you may cent great over r 1 and r 2 r 1 consist of 3 space coordinate, so this is actually tripal integration. Likewise, r 2 is also set of 3 coordinates they could be x 2, y 2, z 2, or r 2 theta 2 phi 2, if you are using the spiracle polar coordinates, no matter what, but you must integrate to over all the variables over the entire space.

So, this integral is u 1 1 and this is often written as the coulomb integral written as j, this is the coulomb integral. What about u 1 2, u 1 2 is the integral in which you must savage coulomb operator, which is the 1 over distance operator between these 2 states between the first and the second. So, this is phi and star r 1 phi 2 star r 2, but here we have got phi 1 are 2 that is the interchange, and this is fight 2 r 1. And this is again a double integration, but each integration is the integration over 3 variables, so this is actually integration over 6 space variables.

So, when it refers to this is the double integration, you have to remember that each is over the set of 3 coordinates, so this is the matrix element u 1 2, which you write as k and this usually refer to as the exchange integral. So, these are our definitions of coulomb integral and exchange integral, and they will appear in mainly electron for mariner throughout. What about u 2 1, they will have expression u 2 1, so u 2 1 is this element, this is phi 1 star r 2 phi 2 star r 1, and then you have got phi 1 r 1 phi 2 r 2 on this side, so what is it k star.

So, this is the complex conjugate of k, now what is going to happen, if you take the complex conjugate of k star, take the complex conjugation of every term over here. So, let phi 1 star r 2 become phi 1 r 2 the phi 1 r 2 comes here, and if we just do it term by term, you find the k star is actually equal to k. K star the complex conjugate is same thing as k, because integration is over dummy variables r 2 and r 1 can be interchange, those levels can be interchange there is nothing big about it, whether you carry out integration over r 1 or r 2 is the same.

So, essentially you have got this matrix form of coulomb exchange integrals, which is j k k star j star, which is the same thing is j k k and j, because k star is equal to k, j star is equal to j, both are real. And this is the usual terminology, although some books refer to these as i and j, so instead of j and k some books refer to these as i and j, and then this j corresponds to exchange whereas, this j corresponds to coulomb.

Depending on you know what you are reading you have too little careful, but this is just a matter of terminology, one is coulomb interaction, and other is exchange interaction. Whether, you label it as j and k or i and j just a matter of you know some convention some choice of you know different authors, but it is good to alert that, because j may represent either the exchange or the coulomb depending on who you are reading.

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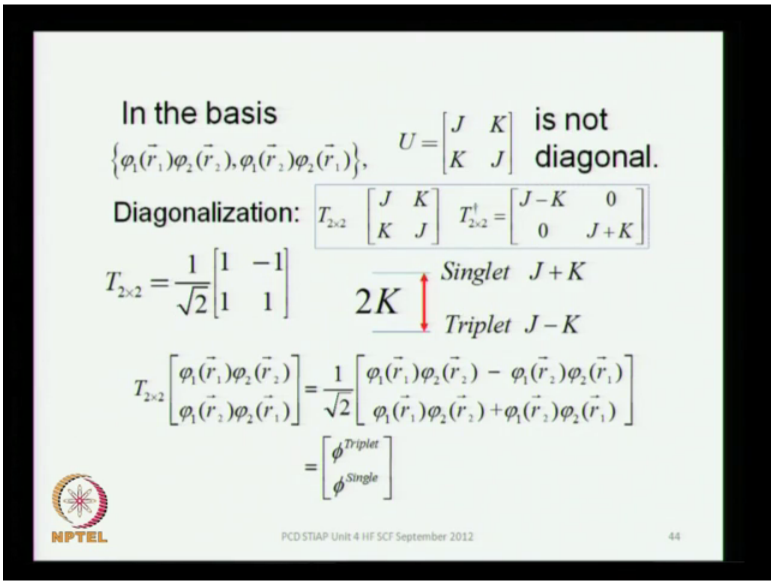

In the basis $\{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2), \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\}$, $U = \begin{bmatrix} J & K \\ K & J \end{bmatrix}$ is not diagonal.

Diagonalization: $\boxed{T_{2\times2} \begin{bmatrix} J & K \\ K & J \end{bmatrix} T^{\dagger}_{2\times2} = \begin{bmatrix} J-K & 0 \\ 0 & J+K \end{bmatrix}}$

$$T_{2\times2} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$$

$$T_{2\times2}\begin{bmatrix} \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \\ \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) \\ \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) \end{bmatrix}$$

$$= \begin{bmatrix} \phi^{Triplet} \\ \phi^{Single} \end{bmatrix}$$

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So, in this basis the coulomb interaction is; obviously, not diagonal, but you can diagonalized, so let us do that go ahead diagonallization. So, fine symmetric t, which will diagonalizen, so T U T diagonal will give you diagonal 2 by 2 matrix, at this is a simple problem in which the diagonallization, which you can 2 into 2 matrix. So, find the matrix, which will diagonalzed the symmetric of J K K J, and some of you perhaps already have the answer, and the diagonal elements will be respectively half of j minus k minus k plus j, which is j minus k and j plus k.

So, these are the diagonal elements and this will give the corresponding, you know like Eigen values of the problem, and the matrix which diagonalizes the matrix J K K J is the 1 over route 2 1 minus 1 1 1. So, this is the matrix which diagonalizes the 2 by 2 coulomb exchange matrix, notice that these two differ J minus K J plus K, the difference in the energy would be twice K.

And this matrix which diagonalizes this, will also transform this basis to your new basis and what you expect what this new basis would be, you have already have the answer, because this new basis when you operate or the this matrix operate on the basis that. So, phi 1 r 1 phi 2 r 2 and phi 2 r 1 phi 2 r 1 is basis that, and if you operate on this by this matrix t, which is the one t diagonals is the coulomb interaction. You get the singlet and triplet states, as you would expect, so these are the coulomb and the exchange integral and we will have we will be using them extensively in our discussion.

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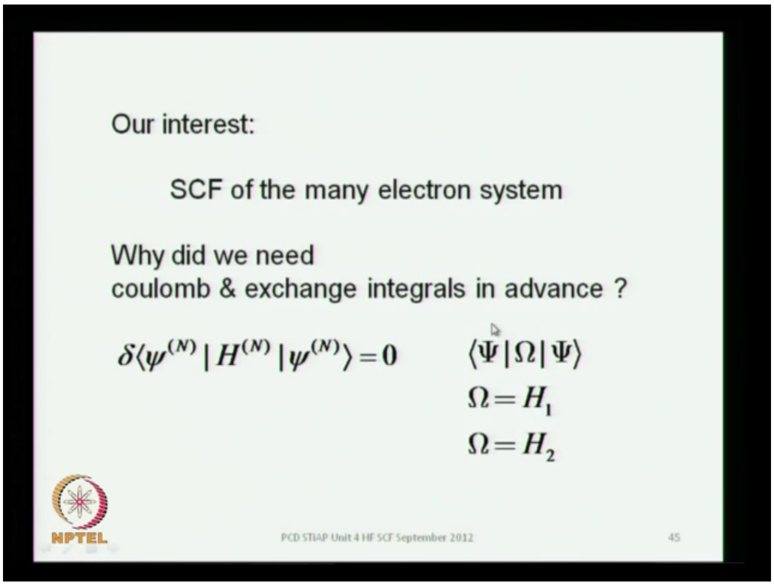

Our interest:

SCF of the many electron system

Why did we need
coulomb & exchange integrals in advance ?

$$\delta\langle\psi^{(N)}|H^{(N)}|\psi^{(N)}\rangle=0$$

$$\langle\Psi|\Omega|\Psi\rangle$$

$$\Omega=H_1$$

$$\Omega=H_2$$

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So, the main reason to spends some time on just 2 electron system and develop this expression for the coulomb and exchange integrals, is because our objective in the self consistent field method is to find the variation in the expectation of the value electron hamiltonian in the n electron wave function. Variant and c can extreme out with definitely look for a minimum, but I will explain, why you do not how you can take into account.

The second derivative and determined by the weather, it is a maximum are a minimum are saddle points, ((Refer Time: 24:07)) points these other settle ((Refer Time: 24:09)) of the variation technique, that we can discuss separately we will do that. But, for the time being we know that we are looking for a extremism, in the expectation value of n electron hamiltonian in the n electron wave function.

And this hamiltonian is made up of either the single particle operators, or the two particle operators, and these two particles operator is the coulomb interaction, the 1 over r 1 J or r i J. And we therefore, will need the coulomb and the exchange integrals, in the analysis of this expression, so it is for this reason, then I setup the missionary to handle the coulomb and the exchange integrals at the outset.

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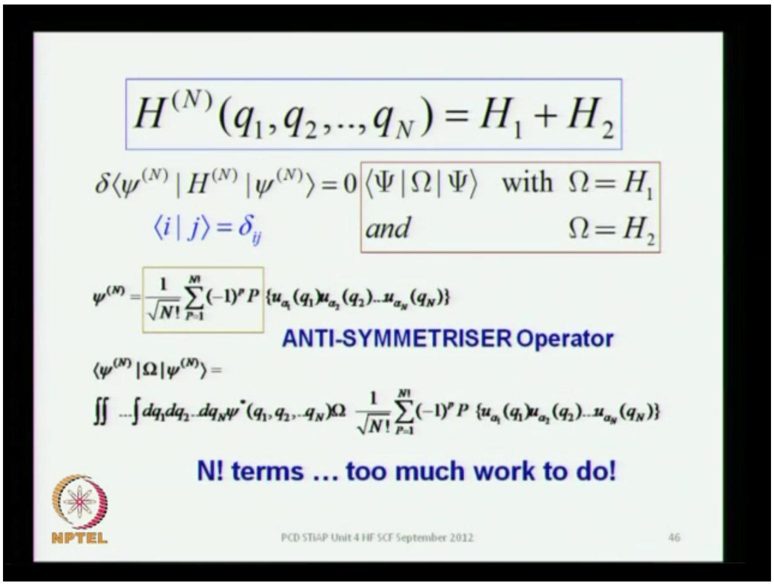

$$\boxed{H^{(N)}(q_1,q_2,..,q_N) = H_1 + H_2}$$

$$\delta\langle\psi^{(N)}|H^{(N)}|\psi^{(N)}\rangle = 0 \quad \boxed{\begin{array}{ll}\langle\Psi|\Omega|\Psi\rangle \text{ with} & \Omega = H_1 \\ \textit{and} & \Omega = H_2\end{array}}$$

$$\langle i|j\rangle = \delta_{ij}$$

$$\psi^{(N)} = \boxed{\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P}\,\{u_{\alpha_1}(q_1)u_{\alpha_2}(q_2)..u_{\alpha_N}(q_N)\}$$

ANTI-SYMMETRISER Operator

$$\langle\psi^{(N)}|\Omega|\psi^{(N)}\rangle =$$

$$\iint ...\int dq_1dq_2..dq_N\psi^*(q_1,q_2,..q_N)\Omega\ \frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P\ \{u_{\alpha_1}(q_1)u_{\alpha_2}(q_2)..u_{\alpha_N}(q_N)\}$$

N! terms … too much work to do!

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And now, we look for getting an extreme of this, so that variation of this would varnish subject to the constraints that the individuals spin orbital's, remain orthogonal to each other and normalized, so in a product i j is expressed as the chronicles delta. So, when j equal to i, it will be equal to 1 that will be normalization, when j is not equal to y it would vanish. Now, what are i and j these are sets of 4 quantum numbers represented by a single label single symbol, that it is set of 4 quantum numbers, and the wave functions of over here are the slated determinacy you can represented using the anti-symmetry riser operator.

So, the matrix element then consist of psi star omega psi, this psi star this is omega and this is psi and you have got factorial n terms on this psi and another factorial n term on this psi, it is a lot of work. And you will not going to be doing this just for helium atom, you will do it for neon, you will do it for calcium, iron, sliver, mercury got a periodic table, there are like 100 electrons. And you got n factorial n terms it is a lot of work, you do not have enough into write all this things you do not have enough storage space, so you need some really good tricks to handle this.

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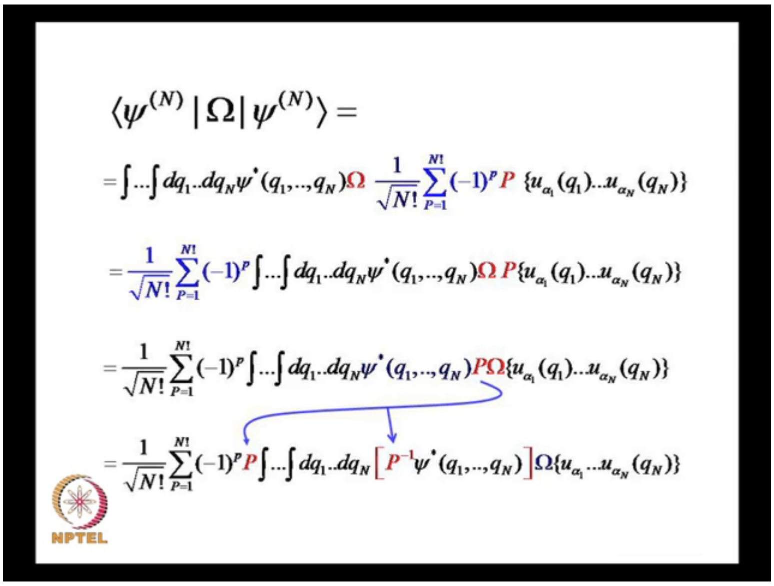

$$\langle\psi^{(N)}|\Omega|\psi^{(N)}\rangle =$$

$$=\int\ldots\int dq_1..dq_N\psi^*(q_1,..,q_N)\Omega\;\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P\;\{u_{\alpha_1}(q_1)\ldots u_{\alpha_N}(q_N)\}$$

$$=\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p\int\ldots\int dq_1..dq_N\psi^*(q_1,..,q_N)\Omega\,P\{u_{\alpha_1}(q_1)\ldots u_{\alpha_N}(q_N)\}$$

$$=\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p\int\ldots\int dq_1..dq_N\psi^*(q_1,..,q_N)P\Omega\{u_{\alpha_1}(q_1)\ldots u_{\alpha_N}(q_N)\}$$

$$=\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P\int\ldots\int dq_1..dq_N\left[P^{-1}\psi^*(q_1,..,q_N)\right]\Omega\{u_{\alpha_1}\ldots u_{\alpha_N}(q_N)\}$$

So, it is too much of work, we are lazy fellows, so we will finger out how to minimize our work, so let us look at this expression, now you got factorial n terms on the side and another factorial n terms of this side. I write the sizes are just as it is as an interregnal, this one I write expressively as the anti symmetries operator, operating on the product of the diagonal elements in the slated determine, which is u alpha 1 q 1, u alpha 2 q 2, u alpha 3 q 3, all the way of to u alpha n q n.

So, this the wave function, psi this the complex conjugate, which I write as it is psi star, but only on this side I write it as a slitter determinant, but not as slitter determinant in the form in which we use the anti symmetry operator, and we know that those two are completely equivalent to each other. So, now, let us tack this expression and see if we can simplify this little bit, under whole lot of implication is possible, in fact amazing amount of simplification.

Now, the summation and the constants and so on, can be written over here, these are the two operators, which stay over here omega p. What is omega, omega in our context is going to be either the single particle operator h 1 or the two particle operator h 2, at both of these operator do not care, whether you are calling this is one electro this is electron 2 or a vise a versa. In other words omega computed with the permutation operator, so you can write omega p, as p omega no problem, then it is because the interaction does not put name or a number on the electrons, you can permute them any which way and the interaction remains same.

So, omega p becomes p omega, and now let us see if we can move this operator p we are moved it from right to the left, and I want to tack all the way to the left outside the integrations sign. Then I must worry about what it would be due to psi star, because I finding to put permutation operator behind psi star. I must compensate for it, because the permutation operator, when it operates on the wave function or even the complex continuator of wave function. It will give you minus 1 times p times that wave function, which could be plus 1 or minus 1 depending on the interchange, which are involve in that permutation.

So, you can move it behind this, but you compensate for it by having p inverse and restrict the effect of the inverse to this bracket, so you can take this permutation operator p write it over here. And you find that this matrix element of omega is now given by this 1 over root factorial n, the permutation operator operating on this summation minus 1 to the power p is coming already over here, integration all of these n variables. Each variable is a set 4 variables mind you, and you have p inverse psi star omega and what you have over here is not slated determinant, but just since the direct product of the diagonal elements in the slitter determinant.

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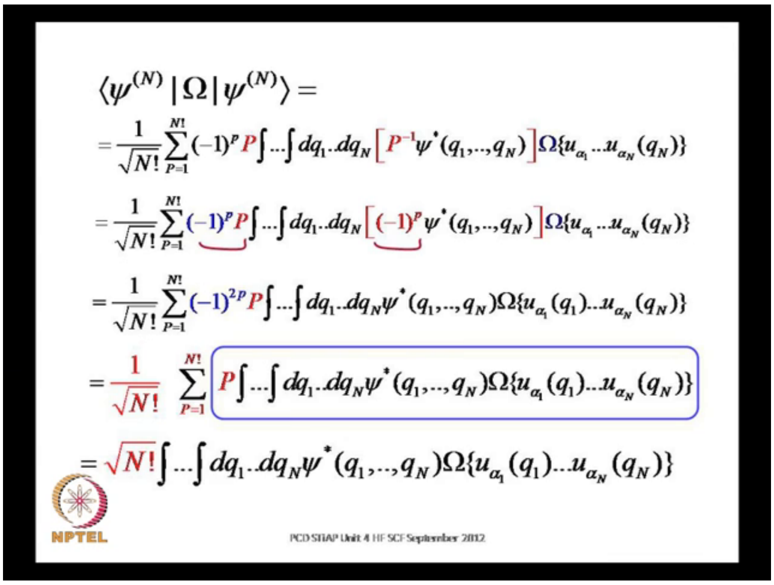

$$\langle \psi^{(N)} | \Omega | \psi^{(N)} \rangle =$$

$$= \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^p P \int \ldots \int dq_1 .. dq_N \left[P^{-1} \psi^*(q_1, .., q_N) \right] \Omega \{ u_{\alpha_1} \ldots u_{\alpha_N}(q_N) \}$$

$$= \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} \underbrace{(-1)^p P} \int \ldots \int dq_1 .. dq_N \left[\underbrace{(-1)^p} \psi^*(q_1, .., q_N) \right] \Omega \{ u_{\alpha_1} \ldots u_{\alpha_N}(q_N) \}$$

$$= \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^{2p} P \int \ldots \int dq_1 .. dq_N \psi^*(q_1, .., q_N) \Omega \{ u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N) \}$$

$$= \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} \boxed{P \int \ldots \int dq_1 .. dq_N \psi^*(q_1, .., q_N) \Omega \{ u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N) \}}$$

$$= \sqrt{N!} \int \ldots \int dq_1 .. dq_N \psi^*(q_1, .., q_N) \Omega \{ u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N) \}$$

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So, let me carry this result on the top of the next slide which is here with the same regression, so you got a p here and p inverse over here, and the omega over here, and a product of the diagonal elements in the slitter determinant here. And what is p inverse do the psi star, it will give you minus 1 to the power p, and this minus 1 to the power p together with this minus 1 to the power p will give you minus 1 to the 2 p and that will always be plus 1 it does not matter what permutations.

So, this minus 1 to the power 2 p will always be plus 1, so you can take it out from your expression, and now we have got this factor 1 over root factorial n. Then you must permute the result of whatever is in store over here, and that is an integration over all of these n variables psi star omega and here, you no longer have factorial n terms you have got only one term in place of that factorial n.

You began with factorial n terms in the apparent density, you have only one term that is a good big simplification over here, in fact it gets even better let us see how. So, now, you have got this expression here, now look at this result what is in this blue box is what is going to permute, and the result you will add factorial n times. You are integrating over all of these n variables, and then you permute indies, how does it matter, they are dummy labels q 1 q 2 everything is a dummy label I can call q 1 as x, q 2 as y.

So, I can call q 1 as q 2, and q 2 as q 1, so even after you do the interchange the result of that integral the multiple integral, you will remain in variant, and have got a quantity which remains variant and a permutation, and you keep adding to itself how many times factorial n times exactly. So, the result of the summation is factorial n times n integral, and that factorial n comes in the numerator, you have got root factorial n in the denominator, so you left with a root factorial n in the numerator times, this multiple n.

So, we have got a lot of simplification now look at this integral, this is an integrate, which is being integrated over the integration variables, what the integration variable, q 1 thorough q n what is this permutation operator doing it is going to permute the states. So, it is like evaluating the result which does not depend on this permutation, get a result permute the labels, and then add it to itself, because you must carry out a summation over all the permutation from 1 to factorial n. So, he have got a result that you keep adding itself factorial n times, so it is factorial n times the result of that integration, so this is what we got over here.

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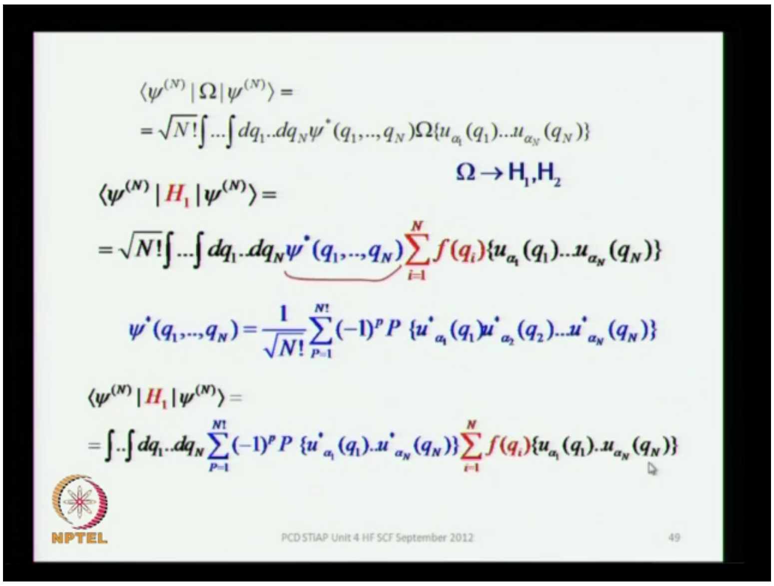

$$\langle \psi^{(N)} | \Omega | \psi^{(N)} \rangle =$$

$$= \sqrt{N!}\int \dots \int dq_1 .. dq_N \psi^*(q_1, \dots, q_N) \Omega \{u_{\alpha_1}(q_1) \dots u_{\alpha_N}(q_N)\}$$

$$\Omega \rightarrow \mathrm{H}_1, \mathrm{H}_2$$

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \sqrt{N!}\int \dots \int dq_1 .. dq_N \underbrace{\psi^*(q_1, \dots, q_N)} \sum_{i=1}^{N} f(q_i) \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

$$\psi^*(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^p P \, \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) \dots u^*_{\alpha_N}(q_N)\}$$

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \int .. \int dq_1 .. dq_N \sum_{P=1}^{N!} (-1)^p P \, \{u^*_{\alpha_1}(q_1) . u^*_{\alpha_N}(q_N)\} \sum_{i=1}^{N} f(q_i) \{u_{\alpha_1}(q_1) . u_{\alpha_N}(q_N)\}$$

And this is now our net result, that matrix element of the 1 electron operators, the 2 electron operators, we will have we are have to do this h for both h 1 and h 2 or f and j as some author calling. And you can determined this integral separately for h 1 and h 2 and oh omega would be either of these two operators, and we will have to work out this expression for both. So, let us do it for h 1, and what is h 1, h 1 is the sum of kinetic energy part of each electron plus the potential energy of that electron in the field of nucleus, the z over r or x a squire r, that is the h 1.

So, this depends on single coordinate, which is why it is a single particle operators, so f of q 1 is that single operator, which is the some of the kinetic energy part for the i th electron plus the potential energy of that electron in the field of nucleus that is the f. So, f of q 1 q i, i summed over from 1 to n is your operator h 1, and you must take it symmetric element. On this side on the opposite side, you have got just the direct product of the diagonal elements in the slated determinant here, he have got the entire factorial n terms in the slitter determinant.

So, this is your matrix element of h 1, here you have the entire factorial n terms, how do you get those factorial n terms by allowing the anti-symmetries operate on the diagonal elements product, but these are complex quantitative. This is how you get the psi star so; that means, that this matrix element of h 1 in the n electrons slated determinant is now given by this wave function psi star over here, this is the operator h 1, which is over here and this is the product of the diagonal elements in the slated determinant.

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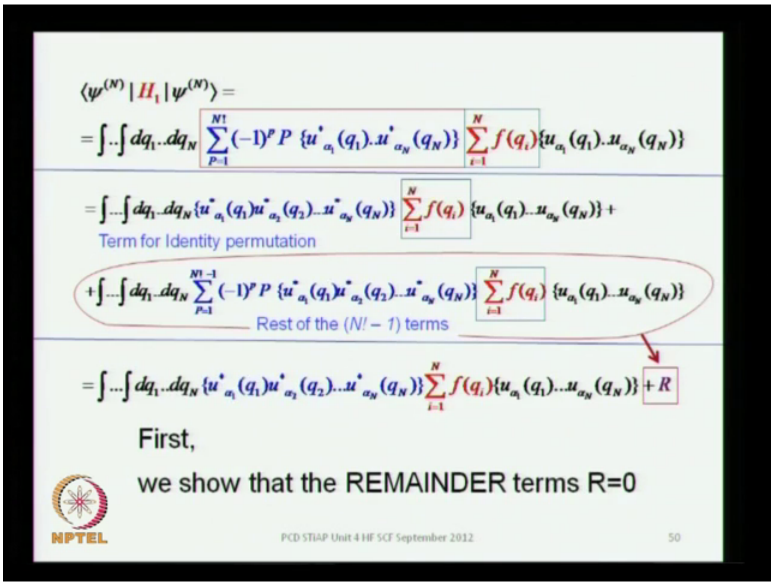

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \int .. \int dq_1 .. dq_N \boxed{\sum_{P=1}^{N!} (-1)^p P \{u^*_{\alpha_1}(q_1) .. u^*_{\alpha_N}(q_N)\}} \boxed{\sum_{i=1}^{N} f(q_i)} \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

$$= \int ... \int dq_1 .. dq_N \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} \boxed{\sum_{i=1}^{N} f(q_i)} \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\} +$$

Term for Identity permutation

$$+ \int ... \int dq_1 .. dq_N \sum_{P=1}^{N!-1} (-1)^p P \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} \boxed{\sum_{i=1}^{N} f(q_i)} \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

Rest of the (N! – 1) terms

$$= \int ... \int dq_1 .. dq_N \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) ... u^*_{\alpha_N}(q_N)\} \sum_{i=1}^{N} f(q_i) \{u_{\alpha_1}(q_1) ... u_{\alpha_N}(q_N)\} \boxed{+R}$$

First,

we show that the REMAINDER terms R=0

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So, let us bring it up to the top of next slide, which is here and you recognize the different places in the integral, this is the psi star, this is the operator omega, which is the h 1 and this is the product of diagonal elements in the slated determinant. So, this is the integration that we have to analyze, now here you have got factorial n permutations. And you know there all are permutation actually form a group, but that is we do not want to have get in into that it will consist of an identity permutation and then rest of that. So, write the terms of corresponding is to the identity first and then the rest.

So, the first corresponds to the identity, so for the identity I will have a u alpha 1 star q 1 u alpha star q 2, u alpha star alpha n q n, this is the just the complex conjugate of what you have on this side. That is one which comes from the identity, and then you have got the remaining permutation, and how are their there are pictorial n minus 1, because the factorial n permutation. It includes the identity that is the one which analyze expression written out, and the remaining terms impact together in the second term.

So, this pack of the residual factorial n minus 1 terms is what I call is the reminder r, so I got a term in the identity permutation plus a reminder, now you recognize what is the remainder is. And then what we are going to do is to discover that the reminder actually goes to 0, that will be, so nice is it not, that what I told you that it is getting better it really does. And it is not at all difficult to see that the reminder varnishes, let us see how, let us ask ourselves what really happens to the reminder there are so many terms factorial n minus 1, it is a huge number.

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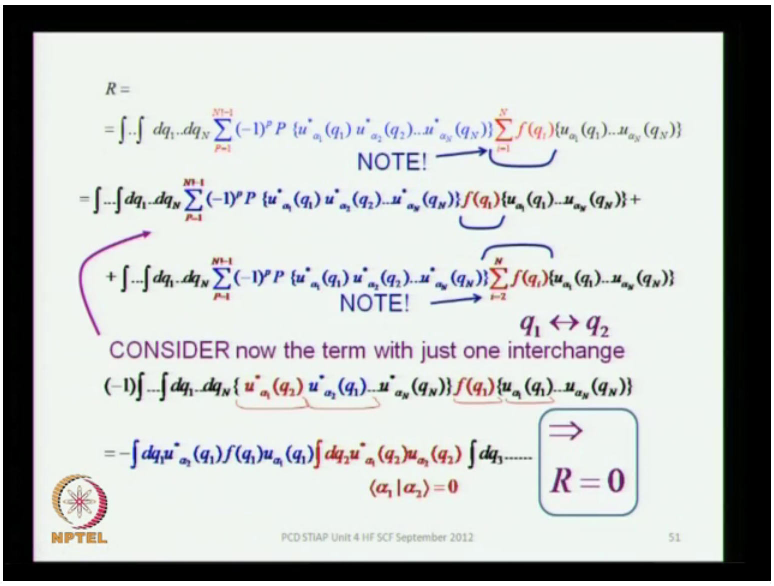

$R =$

$$= \int..\int dq_1..dq_N \sum_{P=1}^{N!-1} (-1)^p P\, \{u^*_{\alpha_1}(q_1)\, u^*_{\alpha_2}(q_2)...u^*_{\alpha_N}(q_N)\} \underbrace{\sum_{i=1}^{N} f(q_i)}_{} \{u_{\alpha_1}(q_1)..u_{\alpha_N}(q_N)\}$$

NOTE!

$$= \int...\int dq_1..dq_N \sum_{P=1}^{N!-1} (-1)^p P\, \{u^*_{\alpha_1}(q_1)\, u^*_{\alpha_2}(q_2)..u^*_{\alpha_N}(q_N)\} \underbrace{f(q_1)}_{} \{u_{\alpha_1}(q_1)..u_{\alpha_N}(q_N)\} +$$

$$+ \int...\int dq_1..dq_N \sum_{P=1}^{N!-1} (-1)^p P\, \{u^*_{\alpha_1}(q_1)\, u^*_{\alpha_2}(q_2)..u^*_{\alpha_N}(q_N)\} \overbrace{\sum_{i=2}^{N} f(q_i)}^{} \{u_{\alpha_1}(q_1)..u_{\alpha_N}(q_N)\}$$

NOTE!

$$q_1 \leftrightarrow q_2$$

CONSIDER now the term with just one interchange

$$(-1)\int...\int dq_1..dq_N \{\underbrace{u^*_{\alpha_1}(q_2)}_{}\, \underbrace{u^*_{\alpha_2}(q_1)..}_{}u^*_{\alpha_N}(q_N)\} \underbrace{f(q_1)}_{} \{\underbrace{u_{\alpha_1}(q_1)}_{}..u_{\alpha_N}(q_N)\}$$

$$= -\int dq_1 u^*_{\alpha_2}(q_1) f(q_1) u_{\alpha_1}(q_1) \int dq_2 u^*_{\alpha_1}(q_2) u_{\alpha_2}(q_2) \int dq_3......$$

$$\langle \alpha_1 | \alpha_2 \rangle = 0$$

$$\boxed{\Rightarrow R = 0}$$

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Now, let us look at this, so these are the remaining terms, so this is the reminder r, which is equal to all of these remaining permutation except identity, and he have got operator h 1, which contains the single particle operators for all the n electrons. And now, what I do is to separate this i equal to one to n again in 2 pieces, one for f of q 1 and the other piece for the remaining electrons, which is i equal to 2 to n. I will just split that summation into 2 parts, one consisting of the operator corresponding to just the electron at q 1, and now look at these terms.

So, let us have look at the first-round, which is this one, which is the upper 1 the remaining corresponds to the other electron in the operator. So, let us look at term the this over here, now this is got all the remaining permutations, everything except for the identity because the identically we have right already separated out. So, we have all the remaining permutation, and the remaining permutation will have at least one interchange, because the identity is only one which does not have and interchange, and we have already separated that term.

So, it will have at least one interchange, so let us consider the term corresponding to just one interchange, and let us do that for the first term, so now one interchange will give you instead of u alpha 1 star q 1, it will give you u alpha 1 star q 2. So, I consider the interchange between q 1 and q 2, so this is the interchange, so I have got u alpha 1 star q 2, I have got u alpha 2 star q 1. What about u alpha 3 star, the argument will be q 3, because there is only one interchange that we are restricting ourselves, u alpha 4 star it will have the argument will be q 4, so may not touching the remaining once only one interchange.

And now, you have this multiple integral, what is the integration over integration is over q 1 q 2 q 3 up to q n, and these are independent degrees of freedom, so you can carry of this integrations separately, so take the integration over q 1. What do you have the integral, you have got over q 1, you have got u alpha 2 star q 1, this is the thing which got argument in q 1, this operator is f of q 1.

And this function u alpha 1 q 1 is here what about the remaining term, integration over q 2 will involve u alpha 1 star q 2, and then you will have u alpha 2 q 2, but then this integration will vanish, because alpha 1 and alpha 2 are orthogonal states. So, it does not matter what is the value of this integral you are going to take some number multiplied by 0, the result is 0 even in a atomic physics, you cannot have.

Now, the same thing is going to happen to the remaining terms, and if you look at the remaining terms the whole reminder varnish, for exactly this reason and the reason is very simple. The whole reminder varnish, because you will have exactly this kind of thing happening from the remaining terms over here, you will be able to factor out one term and then fines it been multiplied by an orthogonal integral, which you know at outside will be 0.

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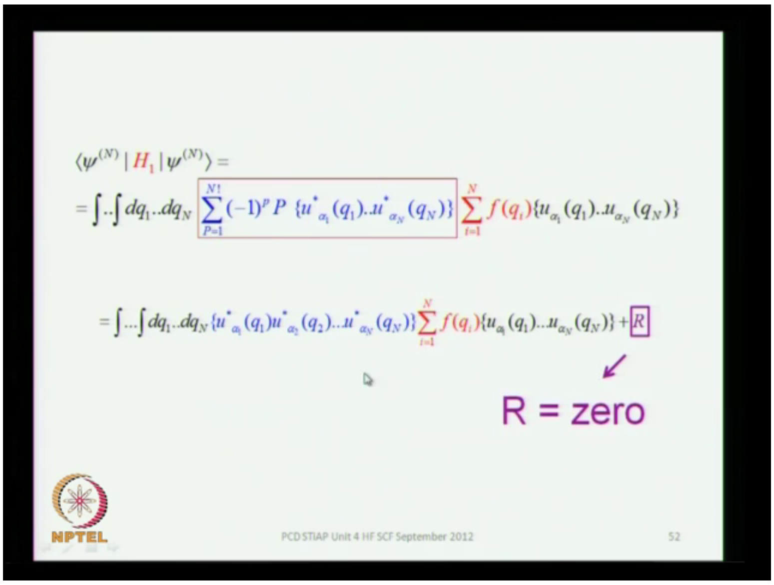

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \int .. \int dq_1 .. dq_N \boxed{\sum_{P=1}^{N!} (-1)^p P \; \{u^*_{\alpha_1}(q_1) .. u^*_{\alpha_N}(q_N)\}} \sum_{i=1}^{N} f(q_i) \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

$$= \int ... \int dq_1 .. dq_N \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) ... u^*_{\alpha_N}(q_N)\} \sum_{i=1}^{N} f(q_i) \{u_{\alpha_1}(q_1) ... u_{\alpha_N}(q_N)\} + \boxed{R}$$

R = zero

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So, the reminder varnishes, what does do to versa, that this whole complex expression that we had, which we factor in to this, and reminder we have the reminder going to 0, and we have only this term to work with it is a lot of simplification now.

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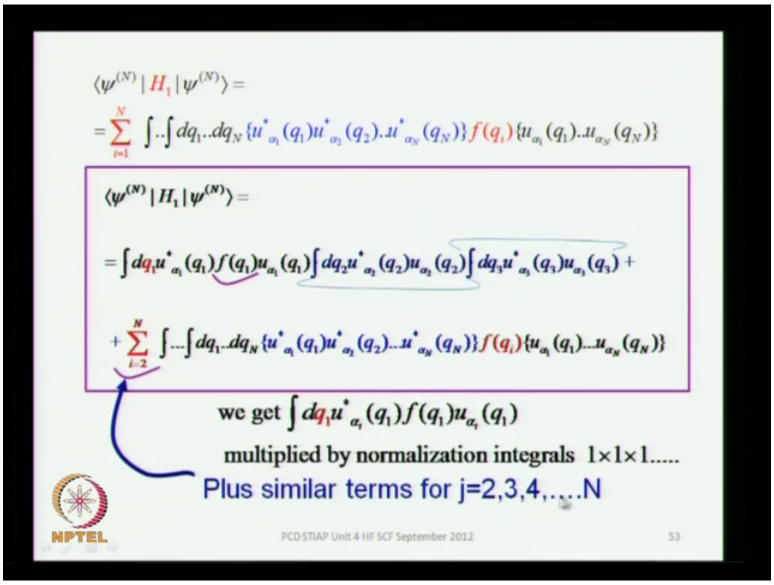

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \sum_{i=1}^{N} \int .. \int dq_1 .. dq_N \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} f(q_i) \{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$

$$= \int dq_1 u^*_{\alpha_1}(q_1) f(q_1) u_{\alpha_1}(q_1) \int dq_2 u^*_{\alpha_2}(q_2) u_{\alpha_2}(q_2) \int dq_3 u^*_{\alpha_3}(q_3) u_{\alpha_3}(q_3) +$$

$$+ \sum_{i=2}^{N} \int ... \int dq_1 .. dq_N \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) ... u^*_{\alpha_N}(q_N)\} f(q_i) \{u_{\alpha_1}(q_1) ... u_{\alpha_N}(q_N)\}$$

we get $\int dq_1 u^*_{\alpha_1}(q_1) f(q_1) u_{\alpha_1}(q_1)$

multiplied by normalization integrals $1 \times 1 \times 1.....$

Plus similar terms for j=2,3,4,….N

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And here you have integration over n variables, each integration, each variable is set of 3 continues space variables, and one discrete spin variable, so now you can write this as you can separate out the integrations over q 1 q 2 and so on. What does the integration over q 2 will give you, d q 2 u alpha star alpha 2 star 1 q 2 u alpha 1 q 2, this is the normalization integral. So, you have this integral multiplied by 1 into 1 into 1 into 1 into 1 into 1 into 1 in all to do that.

So, what does it will give you can just this integral over q 1, and then you will get similar terms from the remaining electrons. So, this is the term coming from electron 1, because that is what we did the separated the term for the electron 1, and then you have the remaining terms. And now, the remaining terms you will have a similar integral, but then what makes even simpler is that over here that integration variable is a dummy variable. So, it really does not matter, they all are the same, so you just have to some over similar terms, and we have got similar terms for the remaining n minus 1 electron j going from j 2 to n.

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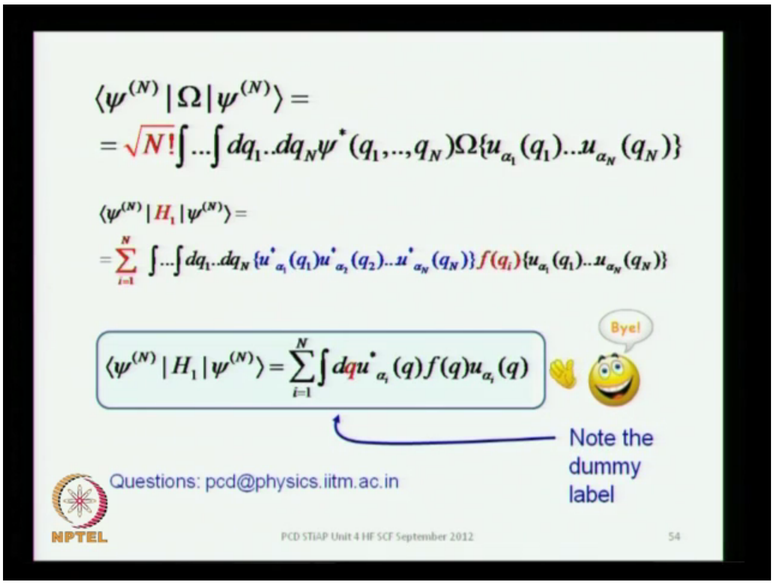

$$\langle\psi^{(N)}|\Omega|\psi^{(N)}\rangle =$$
$$= \sqrt{N!}\int\ldots\int dq_1..dq_N \psi^*(q_1,\ldots,q_N)\Omega\{u_{\alpha_1}(q_1)\ldots u_{\alpha_N}(q_N)\}$$

$$\langle\psi^{(N)}|H_1|\psi^{(N)}\rangle =$$
$$= \sum_{i=1}^{N}\int\ldots\int dq_1..dq_N\{u^*_{\alpha_1}(q_1)u^*_{\alpha_2}(q_2)..u^*_{\alpha_N}(q_N)\}f(q_i)\{u_{\alpha_1}(q_1)..u_{\alpha_N}(q_N)\}$$

$$\boxed{\langle\psi^{(N)}|H_1|\psi^{(N)}\rangle = \sum_{i=1}^{N}\int dq u^*_{\alpha_i}(q)f(q)u_{\alpha_i}(q)}$$

Note the dummy label

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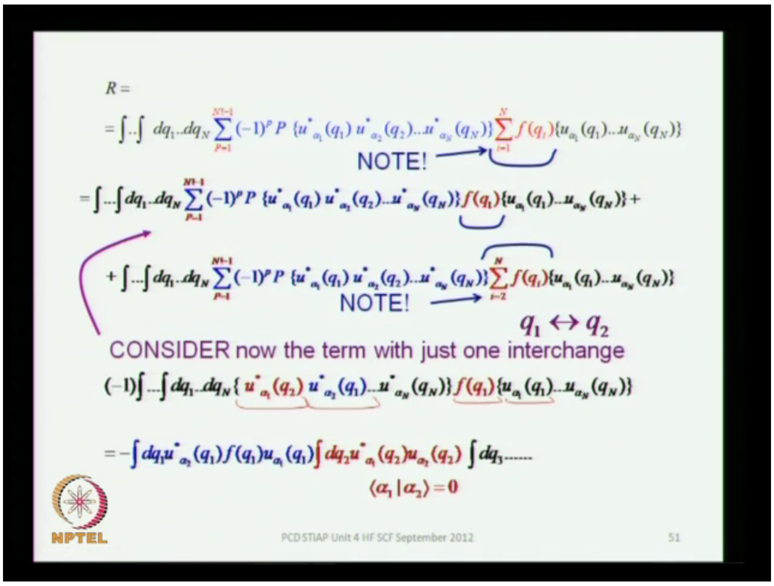
And you can impact all together, but this is your original expression that you began with and for omega equal to h 1, you impact all of these integrations together and you find that it is just a summation over I going from one to n of the single particle integrals. And you do not need to label this as q 1 or q 2 or q 3 and so on, because all of these dummy labels, what you call it rows still no matter what you call. So, the dummy label q replaces this, and we have now arrived at simple expression for the matrix element of one particle operator.

In the next class will deal with two particle operators, then we will do the 2 together, then seek the condition under, which the expectation value of n electron hamiltonian in the n electron slated determinant would varnish. And subject to the constraint that the original single particle spin orbital's remain orthogonal to each other and remain normalized. So, any crush in for today.

Student: last part that reminder going to 0, can you explain that again.

Let us, go back few slides of here, this is the term, so I guess we should be again top of the slide here.

(Refer Slide Time: 48.48)



$R =$

$$= \int .. \int dq_1 .. dq_N \sum_{P=1}^{N!-1} (-1)^p P \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} \underbrace{\sum_{i=1}^{N}}_{} f(q_i)\{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

NOTE! →

$$= \int ... \int dq_1 .. dq_N \sum_{P=1}^{N!-1} (-1)^p P \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} \underbrace{f(q_1)}_{}\{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\} +$$

$$+ \int ... \int dq_1 .. dq_N \sum_{P=1}^{N!-1} (-1)^p P \{u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N)\} \overbrace{\sum_{i=2}^{N} f(q_i)}\{u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N)\}$$

NOTE! →

$q_1 \leftrightarrow q_2$

CONSIDER now the term with just one interchange

$$(-1) \int ... \int dq_1 .. dq_N \{ \underbrace{u^*_{\alpha_1}(q_2)}_{} \underbrace{u^*_{\alpha_2}(q_1)}_{} .. u^*_{\alpha_N}(q_N)\} \underbrace{f(q_1)}_{}\{\underbrace{u_{\alpha_1}(q_1)}_{} .. u_{\alpha_N}(q_N)\}$$

$$= -\int dq_1 u^*_{\alpha_2}(q_1) f(q_1) u_{\alpha_1}(q_1) \int dq_2 u^*_{\alpha_1}(q_2) u_{\alpha_2}(q_2) \int dq_3 ......$$

$$\langle \alpha_1 | \alpha_2 \rangle = 0$$

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And over here what we have done is to separate one of the terms, the f q 1 and the remaining term for I instead of summation going from 1 to n you let it go from 2 to n. And now, you have got factorial n minus 1 terms under this summation, this is a summation of all the permutations, in the original slated determinant, we have got factorial n permutations, but we have the separated identity term. It is only after the suppression of the identity that we had a reminder at all, so whatever you have under the factorial n minus 1 permutations, does not have the identity.

And therefore, it is at least one interchange, if there are more than one interchanges, in fact it becomes easier, because it goes to 0 for more than one region, but even if there is single interchange it goes to 0, that is the main point. Let us consider the term far 1 interchange, and here I have swapped the stage 1 and 2, so here you have got u alpha 1 star q 2 u alpha 2 star q 1. So, that is the interchange that I refer to that there was a one single interchange, all the other 1 electron state are the same.

And now, I separate integration over the different variables, which are q 1 q 2 and q 3, so what is coming under the integration of q 2 is only those functions, whose argument q 2, and the only functions whose argument is q 2 is 1 is over here u alpha 1 star q 2. And then you will have u alpha 1 alpha 2 q 2 coming from here, which is setting in this dots, so there will be u alpha q 2. So, now look at this integral, which is in this red color, this integral is nothing but orthogonality between alpha 1 and alpha 2 that varnishes.

Student: that f of q 1.

F of q 1 will operate only on those functions, whose argument is q 1, f of q 1 you know what precisely what it is it is a kinetic energy operator for electron 1. So, the gradient operator, which is d by d x, it is actually d by d x 1, because it is a coordinate of that particular electron, you are looking at the variation with respect to a particular coordinate.

So, it is not going to operate the gradient operator will do nothing to the other wave functions, so that is the reason this f of q 1 is appears only in this integral and nothing else. And the other integrals involve this there will be an integration over q 3, which will give a unity because that did not involving any interchange, so it will give you the corresponding normalization integral. But, so what means you have got a product number of factors, one of which is 0, and you are happy enough to throw the whole term, without even looking what else there is. So, the moral of the story is that 0, multiplied by anything any number is 0.

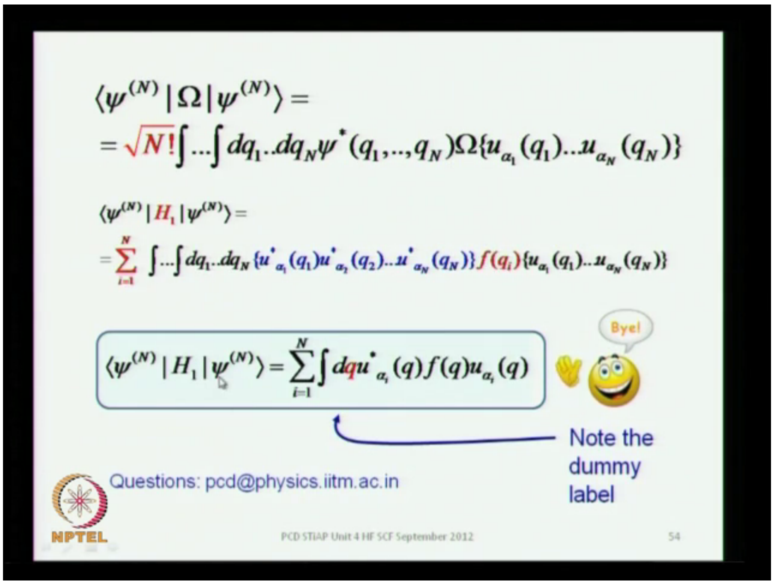
Student: Other integral whether it is goes to perfectly go to infinity.

No, it does all the other integrals will have exactly the same kind of factors, it will have one factor that involving.

Student: We do not anything about it first term, it is integration is.

No, there is no reason for it, to generate a singularity, there is no reason for it to blow up, because these are normalized wave functions or you are all not doing anything crazy to them. See you do a have a point that you might want to worry about you know the rest of integrals of course, unity you know precisely what they are, but this one it really does not matter what it is. So, you get a 0 for the reminder, and that really simplify your expression very much.

(Refer Slide Time: 54.28)



$$\langle \psi^{(N)} | \Omega | \psi^{(N)} \rangle =$$
$$= \sqrt{N!} \int \ldots \int dq_1 .. dq_N \psi^*(q_1, \ldots, q_N) \Omega \{ u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N) \}$$

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle =$$
$$= \sum_{i=1}^{N} \int \ldots \int dq_1 .. dq_N \{ u^*_{\alpha_1}(q_1) u^*_{\alpha_2}(q_2) .. u^*_{\alpha_N}(q_N) \} f(q_i) \{ u_{\alpha_1}(q_1) .. u_{\alpha_N}(q_N) \}$$

$$\boxed{\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle = \sum_{i=1}^{N} \int dq u^*_{\alpha_i}(q) f(q) u_{\alpha_i}(q)}$$

Bye!

Note the dummy label

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So, now, you find that your net result what we have at the end, which is here that the matrix element of the single particle operator is now just the sum of these, over these n, I am going from 1 to n of these single particle integrals. This is all just single particle integral, there is a just one gradient operator here, there is a potential energy term and you integrated over the n 1 electron orbital's.

So, in the next class we will deal with the 2 electron part the h 2, and then we will proceed to the variation calculus, so essentially this is the problem. Now, in variation calculus, and this is now you can stated as variation problems, how to find the extreme of a function subjected certain constraints. So, you will use the method of Lagrangian method a variation multiplies.

Student: ((refer time: 55:32))

Because, what an operator does to operant is that it will operate on everything that is there on the in the operant, if it is within range of operation. And what a permutation operator does is to carry out an interchange either 1 or more of none, if it is an identical permutation, it is the potential to interchange either once or many times. So, when you move the permutation operator from right to left, you have to make sure that whatever it operates on it as the potential to operate on everything is right.

Now, we have we need to do this complication only in the phi star not in this one, that is the reason I put the term in a bracket, because the range of applicability of that operation is to be restricted to that. And when the permutation operator operates on phi star, it will give you minus 1 to the power p time phi star, so that is the extra minus 1 to the power p that we got, but then there was a 1 minus 1 to the power p already. So, together we got minus 1 to the power 2 p, and then we dint want worry about whether it was plus 1 or minus 1, because minus 1 2 p is always plus 1, any other question?

So thank you all very much.