Select/Special Topics in Atomic Physics
Prof. P. C. Deshmukh
Department of Physics
Indian Institute of Technology, Madras

Lecture - 23
Many-Electron Atoms
Hartree-Fock self - Consistent Field Formalism

Greeting, so we have come a long way in our discussion on the Hartree-Fock Self Consistent Field Formalism, and I had mentioned in our previous class that, student in a similar class had done a project on this, this is a report on that. So, this is from IIT, Madras, M.Sc physics report of V. Lakshmi who developed photon code to get the Hartree-Fock self consistent field solutions, and in fact the full report is in this it includes the program that she wrote, some of you would like to try it out, you are welcome to do that. Essentially what we have learnt so far is, that we recognized that the Hartree-Fock equation is in fact, a condition which must be satisfied; it is a necessary and sufficient condition for us to reach our goal.

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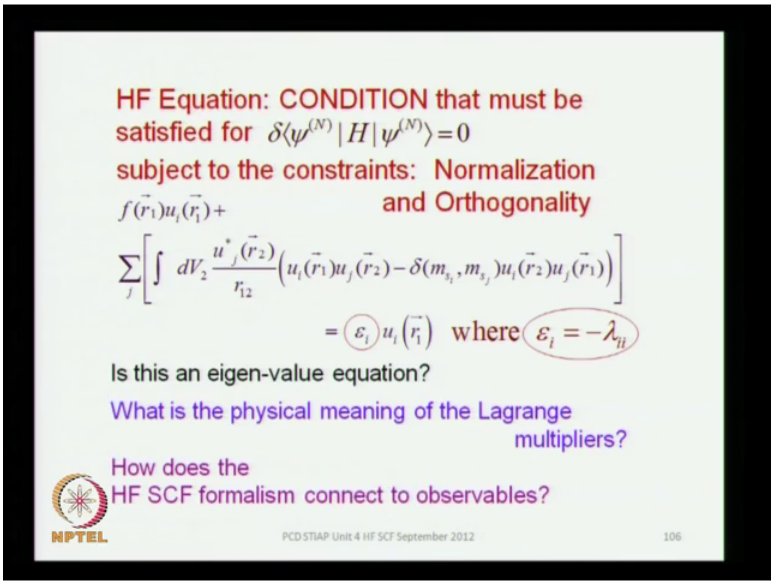

HF Equation: CONDITION that must be satisfied for $\delta\langle\psi^{(N)}|H|\psi^{(N)}\rangle=0$

subject to the constraints: Normalization and Orthogonality

$$f(\vec{r}_1)u_i(\vec{r}_1)+\sum_j\left[\int dV_2\frac{u^*_j(\vec{r}_2)}{r_{12}}\left(u_i(\vec{r}_1)u_j(\vec{r}_2)-\delta(m_{s_i},m_{s_j})u_i(\vec{r}_2)u_j(\vec{r}_1)\right)\right]=\boxed{\varepsilon_i}u_i(\vec{r}_1)\ \text{where}\ \boxed{\varepsilon_i=-\lambda_{ii}}$$

Is this an eigen-value equation?

What is the physical meaning of the Lagrange multipliers?

How does the HF SCF formalism connect to observables?

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And our goal is to get self consistent field solutions to the n electron problem, and we do so by using the variation technique by seeking an extremum of the expectation value of the Hamiltonian, in the antisymmetrize wave function. Subject to the constraints of normalization and orthogonality, and the condition that emerges is what we call is a Hartree-Fock equation, which is a actually a family of n coupled integral differential definitely equations.

And there are couple of questions that we raise towards the end of the previous class, we asked if this is an Eigen value problem, it has some resemblance to an Eigen value problem, so we need to study this on some detail. And then we want to ask how the formalism, how the Hartree-Fock theory connects to experiments, because at some level the main purpose of doing this, is to see how it connects to experimental observations. And there would be some short of physical connection between the theory and the experiment. So, that these questions are the ones that we shall take for our discussion today.

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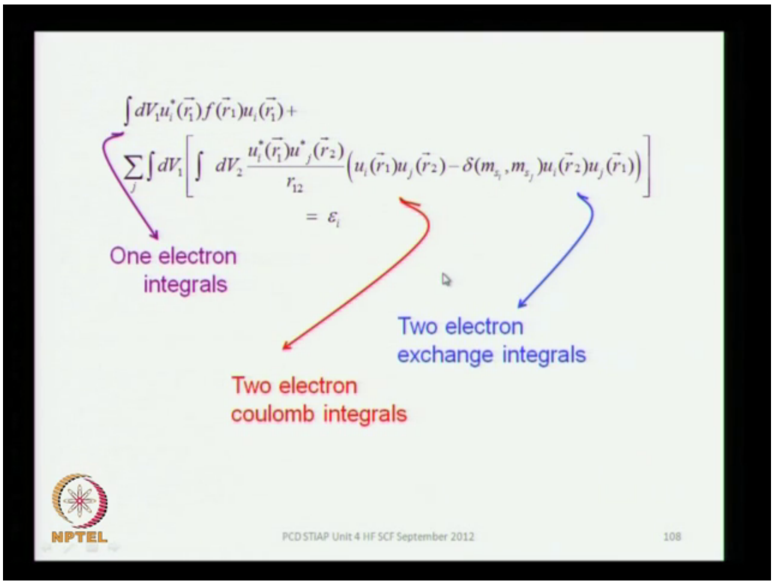

$$\int dV_1 u_i^*(\vec{r}_1) f(\vec{r}_1) u_i(\vec{r}_1) + \sum_j \int dV_1 \left[\int dV_2 \frac{u_i^*(\vec{r}_1) u^*_j(\vec{r}_2)}{r_{12}} \left(u_i(\vec{r}_1) u_j(\vec{r}_2) - \delta(m_{s_i}, m_{s_j}) u_i(\vec{r}_2) u_j(\vec{r}_1) \right) \right] = \varepsilon_i$$

One electron integrals

Two electron exchange integrals

Two electron coulomb integrals

So, to answer these questions, let us begin with look at the Hartree-Fock equation that we got in the previous class, this is the Hartree-Fock equation in the diagonal form, as you will remember. This is in the basis in which the matrix of Lagrange parameters, the variation parameters is diagonal and we will do a little bit of simple rearrangement of terms, to extract some very interesting physics out of it. So, you multiply this by the complex conjugate of u i function, the i th function; and then integrate over r 1, so that is what we have done here.

You multiply this first term by u i star r 1 and then integrate over the volume element for V 1, and you do the same for the remaining terms as well. So, every term is treated by the same prescription and you find that, here you get the normalization integral which is equal to unity, so the right hand side is a very simple one. And the rest of the terms we will handle very carefully, so the first term that you get are the1electron integrals and then you get the2electron integrals, because there is a double integration over V 1 and V 2, V 2 was already there and now we have included an integration over V 1. So, now you have the coulomb and their exchange integrals coming from these double integral integrations, so let us look at this form.

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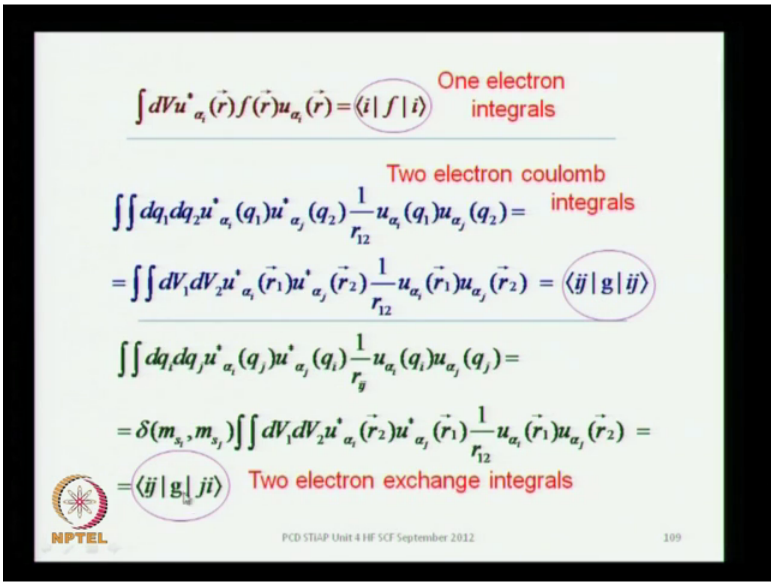

$$\int dV u^*_{\alpha_i}(\vec{r}) f(\vec{r}) u_{\alpha_i}(\vec{r}) = \langle i | f | i \rangle$$

One electron integrals

Two electron coulomb integrals

$$\iint dq_1 dq_2 u^*_{\alpha_i}(q_1) u^*_{\alpha_j}(q_2) \frac{1}{r_{12}} u_{\alpha_i}(q_1) u_{\alpha_j}(q_2) =$$

$$= \iint dV_1 dV_2 u^*_{\alpha_i}(\vec{r}_1) u^*_{\alpha_j}(\vec{r}_2) \frac{1}{r_{12}} u_{\alpha_i}(\vec{r}_1) u_{\alpha_j}(\vec{r}_2) = \langle ij | g | ij \rangle$$

$$\iint dq_i dq_j u^*_{\alpha_i}(q_j) u^*_{\alpha_j}(q_i) \frac{1}{r_{ij}} u_{\alpha_i}(q_i) u_{\alpha_j}(q_j) =$$

$$= \delta(m_{s_i}, m_{s_j}) \iint dV_1 dV_2 u^*_{\alpha_i}(\vec{r}_2) u^*_{\alpha_j}(\vec{r}_1) \frac{1}{r_{12}} u_{\alpha_i}(\vec{r}_1) u_{\alpha_j}(\vec{r}_2) =$$

$$= \langle ij | g | ji \rangle$$

Two electron exchange integrals

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Now, let me remind you that the1electron integrals can be written in a more compact fashion in the Dirac notation, so we will go over to the Dirac notation, because on it is much nicer and easier to write the relations. Likewise the2electron integrals, the first is the coulomb integral which is sometime called as a direct integral, so this is the coulomb integral we have spent considerable time discussing this. So, we have got the coulomb integral which is a i j g i j and then we have the exchange which is the2electron exchange integral, which is i j g j i. So, that is the notation, this will remind us that this is an exchange integral. So, these 3 terms appear in the equation that we got, so this is the Dirac notation, this is the i f i matrix element, this is the i j g i j and this is the i j g j i.

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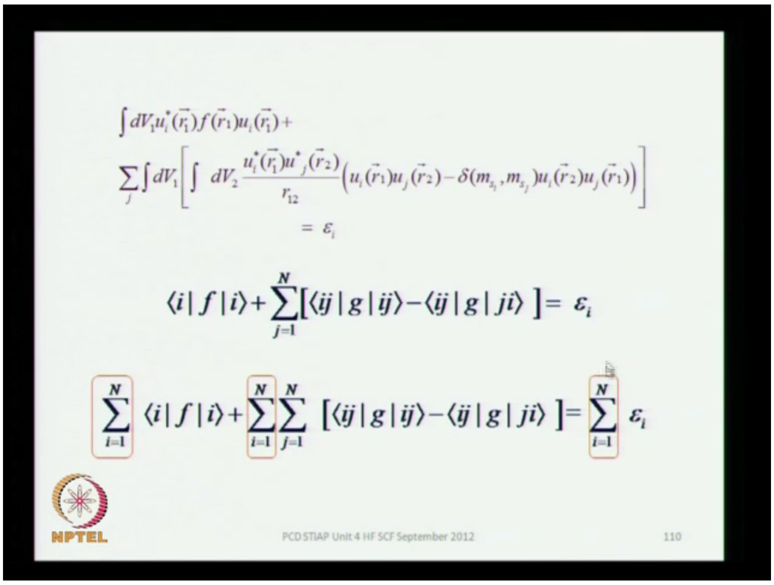

$$\int dV_1 u_i^*(\vec{r}_1) f(\vec{r}_1) u_i(\vec{r}_1) +$$

$$\sum_j \int dV_1 \left[\int dV_2 \frac{u_i^*(\vec{r}_1) u^*{}_j(\vec{r}_2)}{r_{12}} \left(u_i(\vec{r}_1) u_j(\vec{r}_2) - \delta(m_{s_i}, m_{s_j}) u_i(\vec{r}_2) u_j(\vec{r}_1) \right) \right]$$

$$= \varepsilon_i$$

$$\langle i | f | i \rangle + \sum_{j=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle] = \varepsilon_i$$

$$\boxed{\sum_{i=1}^{N}} \langle i | f | i \rangle + \boxed{\sum_{i=1}^{N}} \sum_{j=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle] = \boxed{\sum_{i=1}^{N}} \varepsilon_i$$

And in terms of these the Hartree-Fock equation which we got, can be written in a rather simple compact fashion using the Dirac notation, and now the next thing I am going to do is to sum over the index i. So, this equation there is such an equation which holds for every i, i goes from 1 through n, so i sum over all the terms from 1 through n, so i going from1through n is summed over and the right hand side as well.

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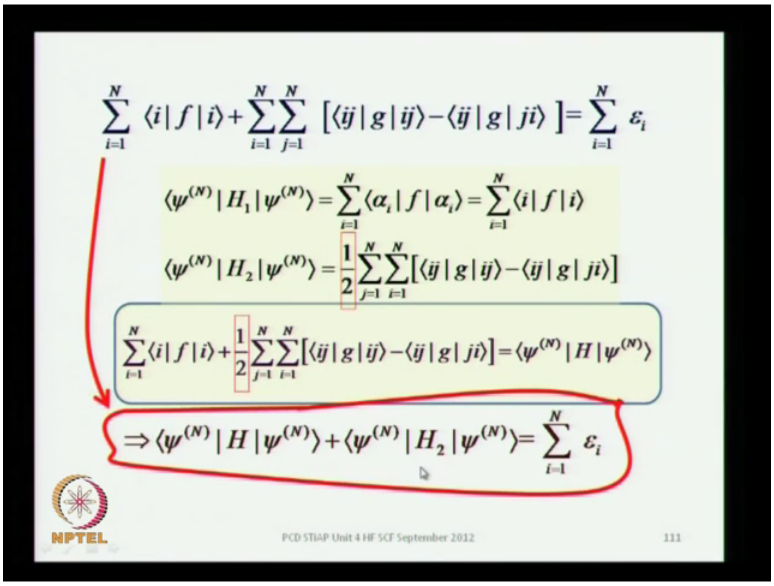

$$\sum_{i=1}^{N} \langle i | f | i \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle] = \sum_{i=1}^{N} \varepsilon_i$$

$$\langle \psi^{(N)} | H_1 | \psi^{(N)} \rangle = \sum_{i=1}^{N} \langle \alpha_i | f | \alpha_i \rangle = \sum_{i=1}^{N} \langle i | f | i \rangle$$

$$\langle \psi^{(N)} | H_2 | \psi^{(N)} \rangle = \boxed{\frac{1}{2}} \sum_{j=1}^{N} \sum_{i=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle]$$

$$\boxed{\sum_{i=1}^{N} \langle i | f | i \rangle + \boxed{\frac{1}{2}} \sum_{j=1}^{N} \sum_{i=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle] = \langle \psi^{(N)} | H | \psi^{(N)} \rangle}$$

$$\boxed{\Rightarrow \langle \psi^{(N)} | H | \psi^{(N)} \rangle + \langle \psi^{(N)} | H_2 | \psi^{(N)} \rangle = \sum_{i=1}^{N} \varepsilon_i}$$

So, here we are, this is the summation of those terms the coulomb in the exchange terms are summed over both i and j, the other terms are summed over only the i index. And this will remind you of the expectation value of the1electron operator in the2electron operator; these expressions we had obtained earlier. And the expectation value of the1electron operator is sum over i going from 1 through n of this matrix element, which is what you find over here. So, this is obviously, the expectation value of the1electron part of the Hamiltonian, this is somewhat similar to this, but not quite.

Because, there is a factor of half here, if you sum these2what would you get, you would get the energy of the system, because you will get the expectation value of the Hamiltonian in the n electron system. So, you would get the energy by adding these2pieces, which is this over here and it is not quite equal to what you get from this equation. So, the sum of i going from 1 through n of these epsilon i, which came as the diagonal element in the matrix of the Lagrange matrix, that if you add up all of those you do not really get the total energy of the n electron system.

What is the difference, you have got a factor of half over here whereas, over here this multiplied as unity, so if you take this expression and add to it another half, then you get the left hand side of this. So, that is what you have, you take the expectation value of the Hamiltonian add to it the expectation value of H 2 and that is what gives you the right hand side, which is the sum of this epsilon i which appear in the Hartree-Fock equation.

Now, we are heading toward extracting the physical meaning of the Lagrange multipliers, is there a Lagrange multiplier in this equation, yes it is the epsilon i, epsilon i is minus lambda i i. So, since we have done the diagonalization, you do not need the row index and the column index it is the same value along the diagonal element. So, there is a single index which is the i th index, and this epsilon i is really coming from the Lagrange multiplier, so this is what you have got.

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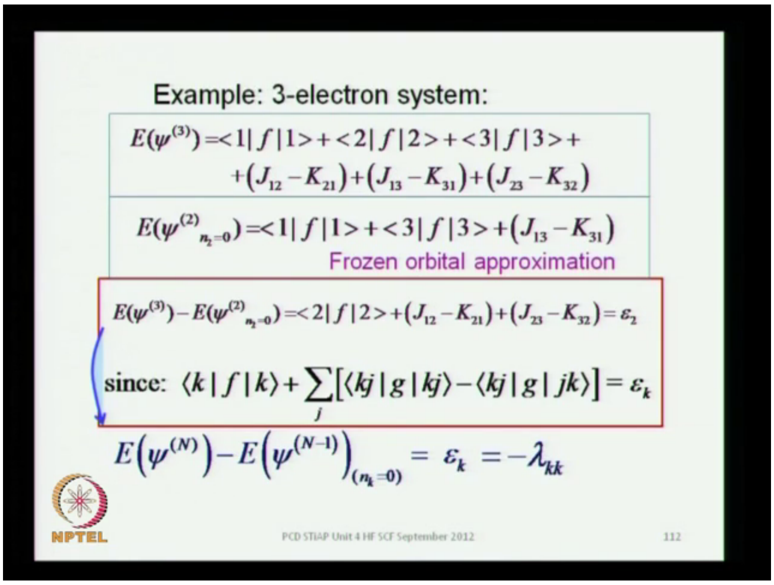

Example: 3-electron system:

$$E(\psi^{(3)}) = <1|f|1> + <2|f|2> + <3|f|3> + \\ + (J_{12} - K_{21}) + (J_{13} - K_{31}) + (J_{23} - K_{32})$$

$$E(\psi^{(2)}{}_{n_2=0}) = <1|f|1> + <3|f|3> + (J_{13} - K_{31})$$

Frozen orbital approximation

$$E(\psi^{(3)}) - E(\psi^{(2)}{}_{n_2=0}) = <2|f|2> + (J_{12} - K_{21}) + (J_{23} - K_{32}) = \varepsilon_2$$

since: $\langle k|f|k\rangle + \sum_j [\langle kj|g|kj\rangle - \langle kj|g|jk\rangle] = \varepsilon_k$

$$E\left(\psi^{(N)}\right) - E\left(\psi^{(N-1)}\right)_{(n_k=0)} = \varepsilon_k = -\lambda_{kk}$$

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Now, let us take an example of a 3 electron system, just to get some feel for these numbers, so for the 3 electron system the energy expression which we wrote on the previous slide. This will add up to these integrals there are these1electron integrals, which is the matrix element of the 1electron operator, in the state 1, 2 and 3. And then there will be pairs of terms the coulomb minus the exchange, which is how they come in pairs, the coulomb minus the exchange between electron1and electron 2, electron 1and electron 3 and electron 2 and electron 3. So, this is the total energy going just by the complete expression that we had for an arbitrary value of n.

So, we will just specialize it for a small system like the n electron system, the specialization we are considering is for the 3 electron system, just to take a very small system, and to see what it does. Now, suppose from these 3 electrons you remove one, so there is an quantum state 1, there is1electron in quantum state 2, and there is an another electron, and in third quantum state there is a third electron, there are 3 electrons. You remove the1in the middle, pluck it out how would you do that, you will have to supply some energy to the system, because it will be bound to the system, so you have to overcome the binding energy.

You can do so by having electromagnetic radiation of appropriate energy shine on it, and once the atom absorbs it, the electron in a particular sub shell can be removed. Like if you have the lithium atom or berilium atom, berilium has got four electrons, and if you give energy as much as the binding energy of the 1 s electron, you will remove the 1 s electron from the berilium. So, you remove the electron in the quantum state that we have labeled as 2, mind you that each quantum label is actually a set of 4 quantum numbers here, whatever they are.

They could be n l m l m s if you like, so there are 4 quantum numbers each quantum number each index over here, whether it is 1 or 2 or 3 is a set of four quantum numbers. And you are creating a vacancy by supplying some external energy to the atom and creating a hole in that state, in the n 2 equal to, so the occupation number of the quantum state 2 will become 0, so n 2 become 0. So, this is a 2 electron system with n 2 equal to 0, but n 1 is equal to 1, n 3 is also equal to 1, so you are not touching those quantum numbers.

What you are assuming is the frozen orbital approximation, when you are creating this cavity,1would expect that the other orbital's flex they would relax, those charge density will also be affected, because removal of an electron is removal of an electron charge. And you have got a certain charge there are 3 electrons in a certain region of space, out of which1electron has been scooped out. And therefore, the remaining2electrons would have their probability amplitudes functions, and the probability densities they will need to flex and readjust, because of the removal of1charge.

And the frozen orbital approximation tells us that, we are going to pretend in this approximation that these other orbital's do not flex, they will remain as they were when you consider the 3 electron system, that is the essence of the frozen orbital approximation. So, then the same integrals 1 f 1, 2 f 2 this wave function for the state 2 is not going to change, and then you are left with these 3 terms, because n 2 is equal to 0. So, there are no pair interactions between electron1and 2 or between 2 and 3, because electron 2 is the1which has been removed.

And you are left with only the pair electron terms between 1 and 3, and then the1electron integrals for the 1 and the state 3, so this is what you get for the2electron system. Now, if you take the difference just subtract this from what is that the term, so e psi 3 minus e psi 2 what you get, you take the difference cancel the common terms and the reason you are able to cancel them is because of the frozen orbital approximation. If the orbital's were not frozen you could not cancel those terms, now under the frozen orbital approximation you cancel those terms.

And you find that on the right hand side this these 3 terms are nothing but what epsilon k represents in the Hartree-Fock equation. Now, epsilon k had entered our analysis why are the Lagrange multiplier, it is just a name epsilon k is minus lambda k k, and because you do not need2indices, it is lambda in the diagonal form there is a single index k. So, epsilon k is the Lagrange multiplier, this is the variation parameter and this gives you on the right hand side it is epsilon 2, which is the Lagrange multiplier on the left hand side you have got the energy difference.

This is the energy difference between the 3 electron system and the2electron, and it is exactly equal to the energy that you have to give, to pull out the electron from the state 2. In common terms it is ionization potential for the state 2, it is the binding energy of the state 2, it is something that you can measure and this is related to the Lagrange multiplier epsilon k within the applicability of the frozen orbital approximation. So, this is the key result that, if you generalize it not just for 3 electron system, but for an n electron system, you remove 1 electron from the k th state.

So, n k equal to 0, all the other occupation number remain the same, the energy difference between these2which is actually the ionization potential of the k th state. The binding energy of the k th electron, this is exactly equal to epsilon k, which is the k th Lagrange multiplier or minus of that, epsilon k is minus lambda k k. Now, you can develop this general image, I illustrated it for the 3 electron system.

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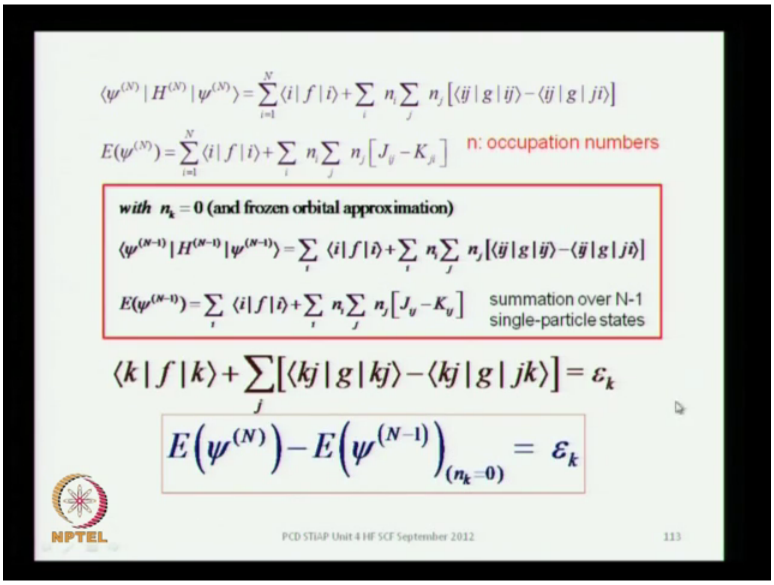

$$\langle\psi^{(N)}|H^{(N)}|\psi^{(N)}\rangle=\sum_{i=1}^{N}\langle i|f|i\rangle+\sum_i n_i\sum_j n_j\left[\langle ij|g|ij\rangle-\langle ij|g|ji\rangle\right]$$

$$E(\psi^{(N)})=\sum_{i=1}^{N}\langle i|f|i\rangle+\sum_i n_i\sum_j n_j\left[J_{ij}-K_{ji}\right]$$

n: occupation numbers

with $n_k=0$ (and frozen orbital approximation)

$$\langle\psi^{(N-1)}|H^{(N-1)}|\psi^{(N-1)}\rangle=\sum_i\langle i|f|i\rangle+\sum_i n_i\sum_j n_j\left[\langle ij|g|ij\rangle-\langle ij|g|ji\rangle\right]$$

$$E(\psi^{(N-1)})=\sum_i\langle i|f|i\rangle+\sum_i n_i\sum_j n_j\left[J_{ij}-K_{ij}\right]$$

summation over N-1 single-particle states

$$\langle k|f|k\rangle+\sum_j\left[\langle kj|g|kj\rangle-\langle kj|g|jk\rangle\right]=\varepsilon_k$$

$$\boxed{E\left(\psi^{(N)}\right)-E\left(\psi^{(N-1)}\right)_{(n_k=0)}=\varepsilon_k}$$

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And it is easy to write it for an n electron system, and the way to do it is to multiply these terms by the occupation numbers n i n n j, n i is the occupation number of the i th state n j is the occupation number of the j th state. And these occupation numbers, because these are fermion particles, these occupation numbers will be either 0 or 1, they can be only either 0 or 1. So, you have the energy of the n electron system, you can write the corresponding expression for the n minus 1 system, which is a completely identical expression.

Except for the fact that all terms for which n i is equal to n k for, which i is equal to k that n k would be 0 and those are the terms which will be removed, and you are summing over all the other indices, all the other states only the1for i equal to k is 0. And if you then take the difference, you find that it will give you the k th Lagrange multiplier, what I illustrated for the 3 electron case, is generalized here for the n electron case. And the difference between the n electron system and the n minus 1 electron system, which is got the hole in the k th state which is ionization potential of the k th state is then equal to the k th Lagrange multiplier in the diagonal representation.

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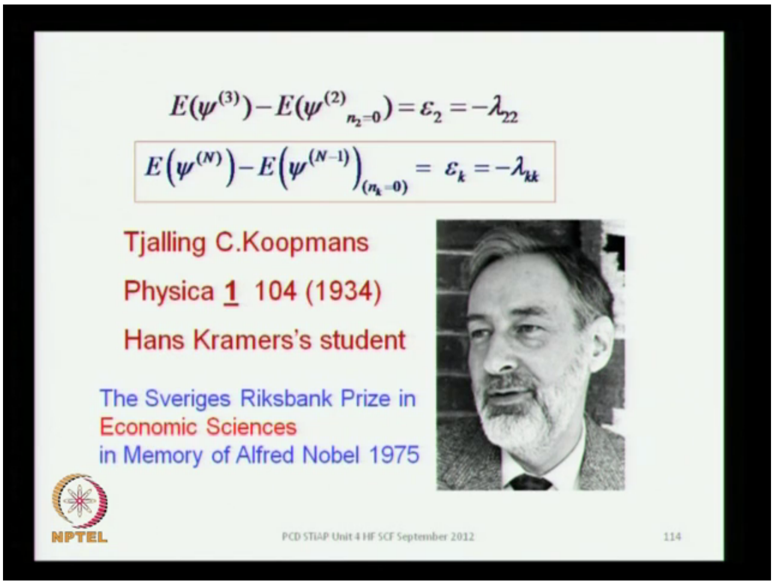

$$E(\psi^{(3)})-E(\psi^{(2)}{}_{n_2=0})=\varepsilon_2=-\lambda_{22}$$

$$\boxed{E\left(\psi^{(N)}\right)-E\left(\psi^{(N-1)}\right)_{(n_k=0)}=\varepsilon_k=-\lambda_{kk}}$$

Tjalling C.Koopmans

Physica <u>1</u> 104 (1934)

Hans Kramers's student

The Sveriges Riksbank Prize in
Economic Sciences
in Memory of Alfred Nobel 1975

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This theorem is known as a Koopmans theorem, Koopmans has been written correctly, there is no apostrophe s, that s is a part of his name. So, if you want to put an apostrophe, it will have to be after this s not before, so this is called as a Koopmans theorem. A very interesting person Koopmans, student of Kramers, and Kramers suggested this problem to him which he solved and he wrote a paper in physical. And this is presumably the only paper he wrote in physics and then he nevertheless was a very smart fellow, and he went on to get what is equivalent of the Nobel prize in economics.

So, he got this is not called as a Nobel prize, but it is called as a Sveriges Riksbank prize in memory of Alfred Nobel. So, it was not instituted by Nobel, but instituted in his memory and it is considered to be equivalent to a Nobel prize, so Koopmans got this prize, but not for this theorem.

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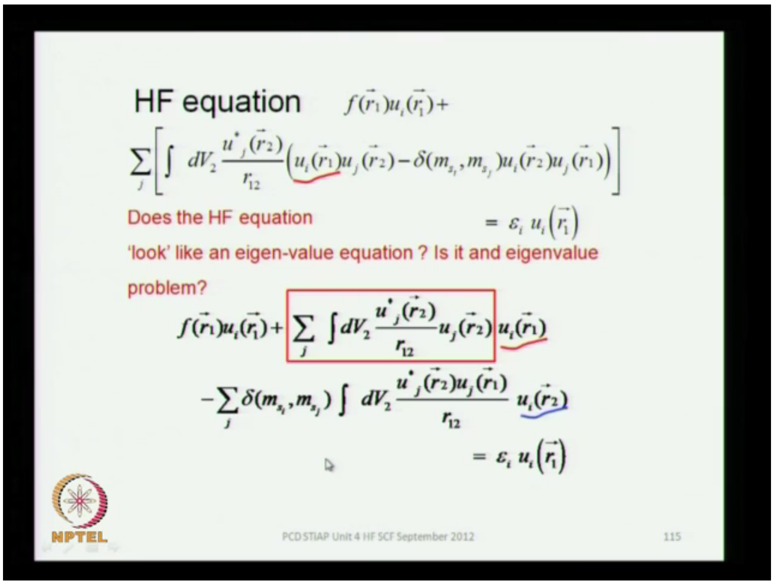

HF equation $f(\vec{r}_1)u_i(\vec{r}_1)+$

$$\sum_j \left[\int dV_2 \frac{u^*_j(\vec{r}_2)}{r_{12}} \left(\underline{u_i(\vec{r}_1)} u_j(\vec{r}_2) - \delta(m_{s_i}, m_{s_j}) u_i(\vec{r}_2) u_j(\vec{r}_1) \right) \right]$$

Does the HF equation $= \varepsilon_i \, u_i(\vec{r}_1)$

'look' like an eigen-value equation ? Is it and eigenvalue problem?

$$f(\vec{r}_1)u_i(\vec{r}_1) + \boxed{\sum_j \int dV_2 \frac{u^*_j(\vec{r}_2)}{r_{12}} u_j(\vec{r}_2)} \underline{u_i(\vec{r}_1)}$$

$$- \sum_j \delta(m_{s_i}, m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2) u_j(\vec{r}_1)}{r_{12}} \underline{u_i(\vec{r}_2)}$$

$$= \varepsilon_i \, u_i(\vec{r}_1)$$

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But, this theorem is a very powerful theorem, and we will address some other questions connected with a Hartree-Fock equation, we also asked if this is an Eigen value problem, it does have some similarity with an Eigen value problem. Because, on the right hand side you have got an energy kind of term, we already know that this is energy, it came as the difference of e n minus e n minus 1, so it is an energy term. So, the right hand side looks like, the right hand side of a typical shorting equation x psi equal to e psi, the left hand side is an operated, the1electron operator operating of the same function. So, it really it looks like an Eigen value equation.

The coulomb term also has similar structure, you can see that, if you just look at this box everything whose argument is to r 2 is integrated out. So, you are going to have an operator which is just a function of 1, 2 is a dummy index which gets integrated out and then you some over r j. And then the coulomb term also suggest that you can put it in form, so that an Eigen value equation would possibly develop, but then if you look at the exchange term there are other issues Because, what you have over here is u i which this is for the same quantum state i which is on the right hand side. But, the argument for the i th quantum state is r 2 a not r 1, so we have to be careful in handling this term.

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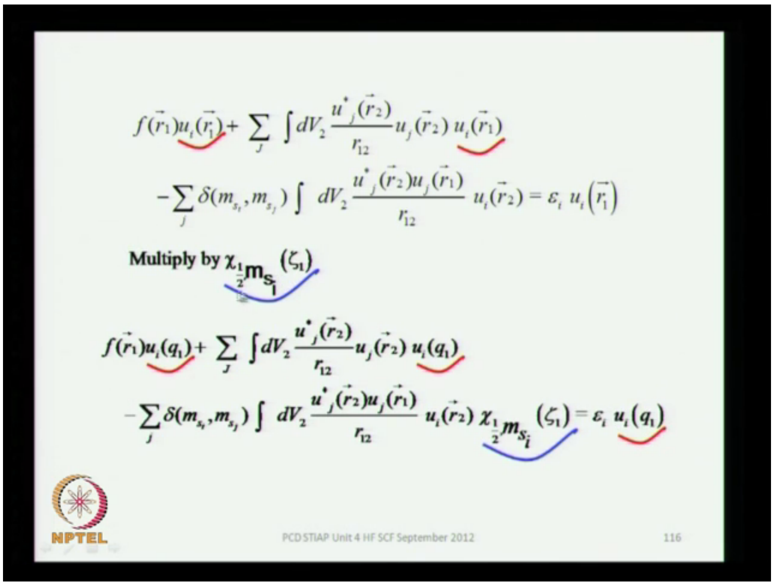

$$f(\vec{r}_1)\underline{u_i(\vec{r}_1)} + \sum_j \int dV_2 \frac{u^*_j(\vec{r}_2)}{r_{12}} u_j(\vec{r}_2)\, \underline{u_i(\vec{r}_1)}$$

$$-\sum_j \delta(m_{s_i}, m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2) u_j(\vec{r}_1)}{r_{12}} u_i(\vec{r}_2) = \varepsilon_i\, u_i(\vec{r}_1)$$

Multiply by $\underline{\chi_{\frac{1}{2} m_{s_i}}(\zeta_1)}$

$$f(\vec{r}_1)\underline{u_i(q_1)} + \sum_j \int dV_2 \frac{u^*_j(\vec{r}_2)}{r_{12}} u_j(\vec{r}_2)\, \underline{u_i(q_1)}$$

$$-\sum_j \delta(m_{s_i}, m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2) u_j(\vec{r}_1)}{r_{12}} u_i(\vec{r}_2)\, \underline{\chi_{\frac{1}{2} m_{s_i}}(\zeta_1)} = \varepsilon_i\, \underline{u_i(q_1)}$$

So, what we will do is first multiply by this spin function, this hole equation we will multiplied by this, so when you multiply this term by the spin function what you get. You get the complete spin orbital, this is the orbital part, you are multiplied it by the spin part you get the orbital the complete spin orbital. And therefore, the argument is written as q 1 instead of r 1, r 1 is just a set of 3 space coordinates, q 1 is a set of 4 coordinates, corresponding to the 3 space coordinates, and 1 spin coordinate. So, by multiplying this by the spin function, you get u i q 1 here, likewise from this u i r 1, you get u i q 1 here, and the right hand side from this u i r 1 you get the u i q 1 here, and here you multiplied it by this spin function which I have written as it is.

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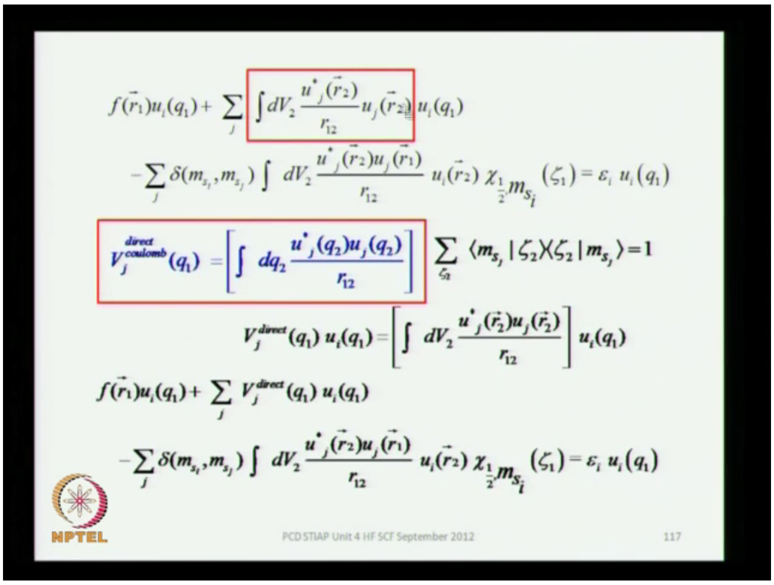

$$f(\vec{r}_1)u_i(q_1)+\sum_j \boxed{\int dV_2 \frac{u^*_j(\vec{r}_2)}{r_{12}} u_j(\vec{r}_2)} u_i(q_1)$$

$$-\sum_j \delta(m_{s_i},m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2)u_j(\vec{r}_1)}{r_{12}} u_i(\vec{r}_2)\, \chi_{\frac{1}{2}m_{s_i}}(\zeta_1)=\varepsilon_i\, u_i(q_1)$$

$$\boxed{V_j^{\substack{direct\\coulomb}}(q_1)=\left[\int dq_2 \frac{u^*_j(q_2)u_j(q_2)}{r_{12}}\right]} \quad \sum_{\zeta_2} \langle m_{s_j}|\zeta_2\rangle\langle\zeta_2|m_{s_j}\rangle=1$$

$$V_j^{direct}(q_1)\, u_i(q_1)=\left[\int dV_2 \frac{u^*_j(\vec{r}_2)u_j(\vec{r}_2)}{r_{12}}\right] u_i(q_1)$$

$$f(\vec{r}_1)u_i(q_1)+\sum_j V_j^{direct}(q_1)\, u_i(q_1)$$

$$-\sum_j \delta(m_{s_i},m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2)u_j(\vec{r}_1)}{r_{12}} u_i(\vec{r}_2)\, \chi_{\frac{1}{2}m_{s_i}}(\zeta_1)=\varepsilon_i\, u_i(q_1)$$

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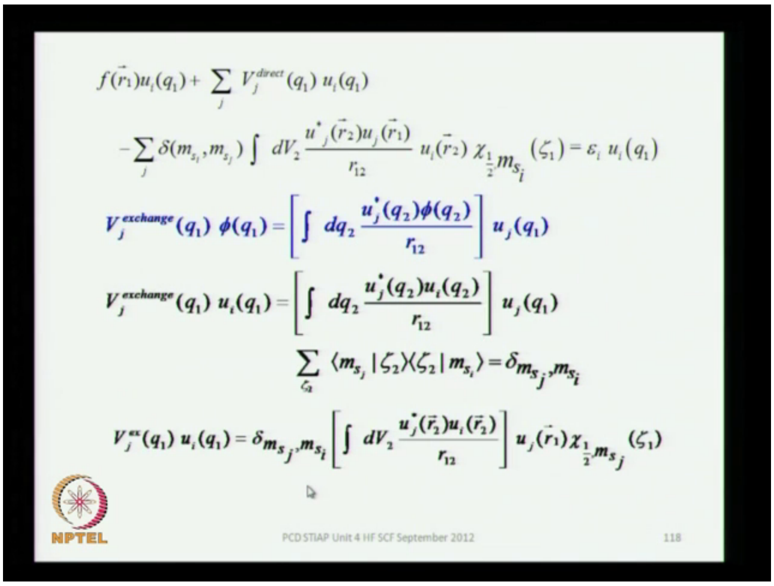
So, this is what I have written as it is, all the other terms wherever I could write this spin orbital as a product of the orbital part, as well as the spin part has been written already. So, let us look at this operator in the box, and this operator is sometimes referred to as the direct coulomb operator, this is got the index j it is specific to j, what is inside in this box is specific to j and then you can sum over this j and get1which is summed over hole the particles. So, this is the V j operator, this is the coulomb operator, using this you can write this equation in a slightly compact fashion.

Because, this involves integration over the space variables and summation over the spin, now what is the summation over the spin part 1 over r 1 2 is nothing do a spin. So, you carry of the spin over the spin coordinate 2, both of these are states j, so this is the spin state m s j zeta 2 and this is the complex conjugate of that and you find that this is equal to 1 right; you got the unit operator sandwiched between these2states, which is normalized. So, this integral reduces very easily to just the space integral, because the spin part gives you a fact of unity.

So, the spin part gives you a fact of unity and the direct coulomb operator can also be written in terms of this integration over the space part alone, so this is just a triple integral; whereas, over here it is the triple integral and also a summation over the spin. So, this is the direct part and using this direct part this term can now be written in terms of this coulomb operator, which is the v j direct all the other terms have been written just as they were. The only difference i have made over here is to this term, which has now been written in terms of this v j and then there is a summation over j, that we will maintain.

(Refer Slide Time: 26:28)



$$f(\vec{r}_1)u_i(q_1) + \sum_j V_j^{direct}(q_1)\, u_i(q_1)$$

$$-\sum_j \delta(m_{s_i}, m_{s_j}) \int dV_2 \frac{u^*_j(\vec{r}_2)u_j(\vec{r}_1)}{r_{12}}\, u_i(\vec{r}_2)\, \chi_{\frac{1}{2} m_{s_i}}(\zeta_1) = \varepsilon_i\, u_i(q_1)$$

$$V_j^{exchange}(q_1)\, \phi(q_1) = \left[\int dq_2 \frac{u_j^*(q_2)\phi(q_2)}{r_{12}}\right] u_j(q_1)$$

$$V_j^{exchange}(q_1)\, u_i(q_1) = \left[\int dq_2 \frac{u_j^*(q_2)u_i(q_2)}{r_{12}}\right] u_j(q_1)$$

$$\sum_{\zeta_2} \langle m_{s_j} | \zeta_2 \rangle\langle \zeta_2 | m_{s_i} \rangle = \delta_{m_{s_j}, m_{s_i}}$$

$$V_j^{ex}(q_1)\, u_i(q_1) = \delta_{m_{s_j}, m_{s_i}} \left[\int dV_2 \frac{u_j^*(\vec{r}_2)u_i(\vec{r}_2)}{r_{12}}\right] u_j(\vec{r}_1)\chi_{\frac{1}{2} m_{s_j}}(\zeta_1)$$

NPTEL

Let us being into the top the next slide and now let us define an operator, which is called as the exchange operator and it is defined by the reservation here. It is defined in a such a way, that whenever it operates an arbitrary function of q 1 it will generate this quantity on the right-hand side that is the definition of the exchange operator. There is a certain exchange which is involved, that what it, what appears in the integral is phi q 2 and then what gets multiplied or what gets operated upon is u j of q 1. So, the j index is the same everywhere, wherever you have the 1 electron spin orbital the j index is always the same.

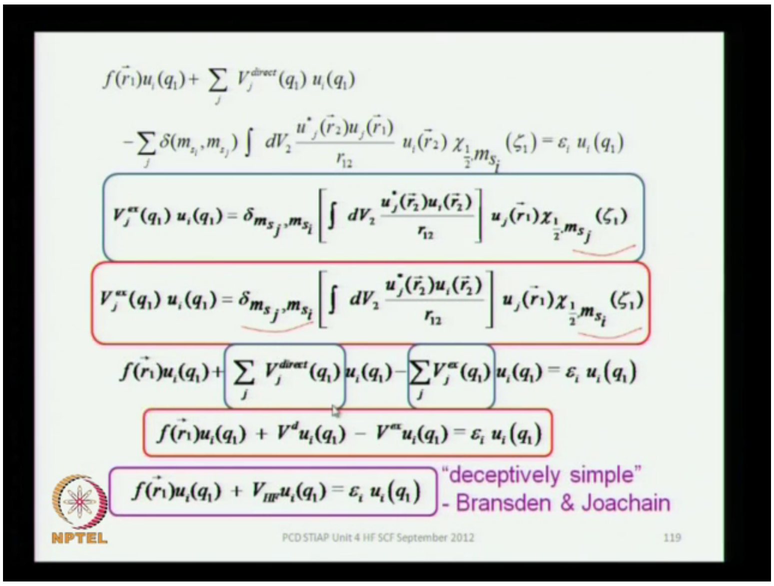
So, this is j, this is j, and this is j ((Refer Time:27:30)) this is on arbitrary function of q 2 this is the definition of the exchange operator and since this holds for any phi it will also hold for u j of q 1. So, we will operate by the exchange operator on the i th spin orbital this is the spin orbital. So, when you operate on the i th spin orbital in place of this phi q 2 you will have u j q 2 and this u j q 1 will come here as an operant as before, this is your definition of the exchange operator.

And using this you can see that here again you have an integration over q 2, which is a triple integral over the space variables and the summation over the spin, which can be done separately because 1 over r 1 2 does not touch the spin part. So, the summation over the spin part is given by over here and what is this, here the index is j and here the index is i. So, you will get a delta m s j m s i out of this.

So, in the when we dealt with similar expression for the coulomb or the direct term, we got unity. In this case we get a chronicle delta which will be equal to 1 in the case of parallel spins, otherwise it will be 0 right. So, we can carry out the summation over the spin part separately and write this chronicle delta which is written over here then you have only the space integration left, because the summation over the spin part has been carried out that is1which gave us this chronicle delta. The integration over the space part is just this integral with q 2 is replaced by r 2 and the volume element d q 2 replaced by the 3 dimensional space volume element d v 2.

So, this is your expression, which you can now put over here, but then there is1worry because here you had m s i, but here you have m s j, but that is not worry because this term is going to be non zero only when m s i is going to be m s j right. So, that would not create any as off.

(Refer Slide Time: 30:10)



$$f(\vec{r}_1)u_i(q_1)+\sum_j V_j^{direct}(q_1)\,u_i(q_1)$$

$$-\sum_j \delta(m_{s_i},m_{s_j})\int dV_2\frac{u^*_j(\vec{r}_2)u_j(\vec{r}_1)}{r_{12}}\,u_i(\vec{r}_2)\,\chi_{\frac{1}{2},m_{s_i}}(\zeta_1)=\varepsilon_i\,u_i(q_1)$$

$$\boxed{V_j^{ex}(q_1)\,u_i(q_1)=\delta_{m_{s_j},m_{s_i}}\left[\int dV_2\frac{u_j^*(\vec{r}_2)u_i(\vec{r}_2)}{r_{12}}\right]u_j(\vec{r}_1)\chi_{\frac{1}{2},m_{s_j}}(\zeta_1)}$$

$$\boxed{V_j^{ex}(q_1)\,u_i(q_1)=\delta_{m_{s_j},m_{s_i}}\left[\int dV_2\frac{u_j^*(\vec{r}_2)u_i(\vec{r}_2)}{r_{12}}\right]u_j(\vec{r}_1)\chi_{\frac{1}{2},m_{s_i}}(\zeta_1)}$$

$$f(\vec{r}_1)u_i(q_1)+\boxed{\sum_j V_j^{direct}(q_1)}u_i(q_1)-\boxed{\sum_j V_j^{ex}(q_1)}u_i(q_1)=\varepsilon_i\,u_i(q_1)$$

$$\boxed{f(\vec{r}_1)u_i(q_1)+V^d u_i(q_1)-V^{ex}u_i(q_1)=\varepsilon_i\,u_i(q_1)}$$

$$\boxed{f(\vec{r}_1)u_i(q_1)+V_{HF}u_i(q_1)=\varepsilon_i\,u_i(q_1)}$$

"deceptively simple"
- Bransden & Joachain

So, let us do that, so this is what we got from the exchange term and then we can replace this term this spin function for m s j by the 1 for m s i because it is nonzero only for parallel spins. And now we have exactly the term which appeared in the second term what is it give us, you get the direct operator operating on u i q 1 minus this is the minus sign, the rest of it is nothing but the exchange operator operating on u i q 1. And now you can combine these terms, because you can both all operating on u i q 1 you can sum over j to give you this operator v with the superscript d for direct and this operator v with the super script x for exchange.

And you have got this coulomb minus the exchange operator and you find that this is written in a form which looks like an Eigen value equation and in this form Bransden and Joachain the book they write very nicely that it is deceptively simple form it is looks like an Eigen value equation. If you look that this equation you would not doubt that it is an Eigen value equation, you got an operator operating on a function giving you a scale or time ascends function, but it is not an Eigen value function we know it from the very big right. The reason it is not an Eigen value equation is because of the exchange term which is a global term.

So, let us discuss this connection with the experiment further, because within the frozen orbital approximation we found that this difference in the energy, if you produce of whole in the K th state, which is ionization potential for the k th state, here is you the Lagrange multiplier. And you can therefore, actually measure it and I presume that some of you are doing some projects in material science or conducts meta physics molecular physics or some other branch of solicit physics and maybe you produce some new materials you want to characterize it.

And1of the very powerful tools for material characterization is photoelectron spectroscopy, which is also called as ESCA the Electron Spectroscopy for Chemical Analysis, is an anybody over here who are used it not yet, but some of you perhaps soon well. So, the electron spectroscopy for chemical analysis is a very powerful technique.

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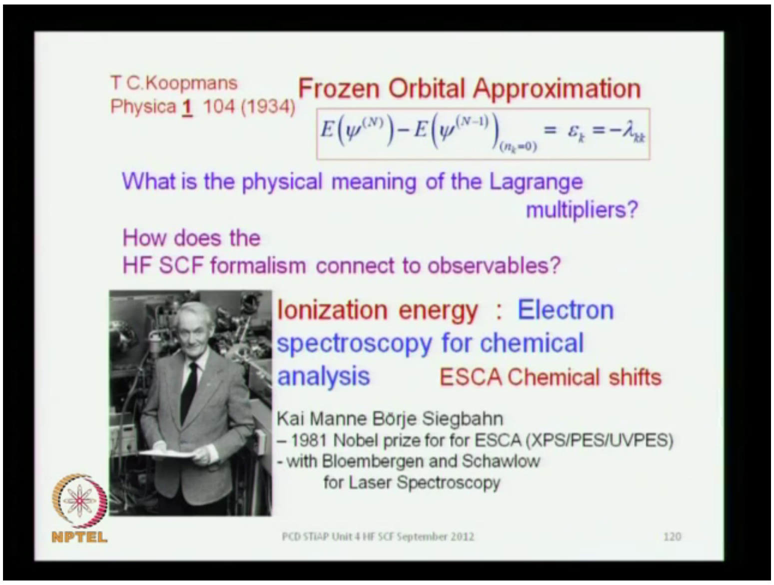

T C.Koopmans
Physica **1** 104 (1934)

Frozen Orbital Approximation

$$E\left(\psi^{(N)}\right) - E\left(\psi^{(N-1)}\right)_{(n_k=0)} = \varepsilon_k = -\lambda_{kk}$$

What is the physical meaning of the Lagrange multipliers?

How does the HF SCF formalism connect to observables?

Ionization energy : Electron spectroscopy for chemical analysis ESCA Chemical shifts

Kai Manne Börje Siegbahn
– 1981 Nobel prize for for ESCA (XPS/PES/UVPES)
- with Bloembergen and Schawlow
for Laser Spectroscopy

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And this was developed by Kai Siegbahn who got the Nobel prize for it an 1981 is dad got a Nobel prize I forget the year, but that was for x-ray spectroscopy and Kai Siegbahn also, got a Nobel prize because he developed this technique. And what you do in this technique is if you want to know like compare any2materials you have some something like ((Refer Time: 33:46)); and you look at the energy of the1s electron in gallium.

Now is the energy of the1s electron in gallium the same as what it is in gallium arsenide, it folly would be different how would you know that, how would you find out what the differences. The way to do it is to expose the sample of gallium arsenide to electro medic radiation and find out the binding energy by checking the ionization potential you do spectroscopy.

You do spectroscopy do it over a range of electromagnetic frequencies or wave lines right usually these experiments are done using powerful light sources like synchrotron. And using synchrotron radiation or you can also use lasers or some other conventional laboratory light sources well, you can do spectroscopy and find out what is the energy of the 1 s electron in gallium is it the same as it is gallium arsenide. And if you do not know the compensation of a compound, but you know that there is a certain atom which is present there. Suppose you know that oxygen is presented in a certain compound and you want to find out what is it is environment.

And by environment I mean the physicochemical environment what are the other does it as a participated in some chemical bonds, what is the physical structure this is the crystallographic structure. What kind of symmetry is it in, is it in octahedral symmetry, is it in tetrahedral symmetry, what is the symmetry, that is the physical environment; and the chemical environment is what are the other items to which it is bundle.

So, the physicochemical environment will be responsible to shift the energy state of a particular electron the 1 s electron of oxygen will have different energies in different compounds in sulphur dioxide it might could be something else and carbon dioxide it will be something else because the environment is different. And by measuring this difference you would know what you are looking at.

So, when you are looking at an unknown compound, when you produce new materials for technology you want to know what is the composition, a powerful tool for material characterization is Photoelectron Spectroscopy, it is P E S sometimes it is done using x-ray then it is called as x-ray photoelectron spectroscopy or with ultraviolet radiation then it is called as ultraviolet photoelectron spectroscopy. Sometimes it is called as ARPES which is Angle Resolved Photoelectron Spectroscopy, because then you find an what angle as the electron come out.

So, there are very many sophisticated off shores of this technique, which is wide such a powerful technique and Koopmans theorem connected, so nicely to the self consistent field theory, within the demine of the frozen orbital approximation. But, then of course, there are techniques to improve upon the frozen orbital approximation, I will mention some of it. So, now that this is something which relates in majorly to experimental observations, and to very important and very useful techniques, mind you this is not of important just on atomic physics.

But, in all branches of contents meta physics, which you take a small piece of cooper if you like, a small piece of gallium arsenide or small piece of semi-conductor, you want to know it is man structure. How are you going to do that, how many electrons do you have in a small unit volume, you got like Avogadro number huge number, and they are all interacting with each other.

And if you want to think of something like the chronic piney model, I assume on that you are familiar with that are you, that the chronic piney model is a single electron equation, which is so much removed from the physical reality of any many electron system. The solid that you are talking about, you want to get the man structure of something like gallium arsenide or some silicon or some semi-conductor are some dielectric or whatever it is; it could be a medal, it could be a semi medal.

Now, you have a huge number of electrons and there is no way you can separate the dynamics of1electron from that of the other, because each electron interact with other electron through the 1 over r 1 2 term, that is what we plugged in the Hartree-Fock theory. We had the 1 over r 1 2, we had the anti-symmetric wave function, so the starting point for band structure calculations of solids or molecular orbital calculations in quantum chemistry. For everything the starting point for getting the electron structure is the Hartree-Fock formalism which is why it is, so important, and the Koopmans theorem is very important. But, then when I has to go beyond the Hartree-Fock and there are many directions for that.

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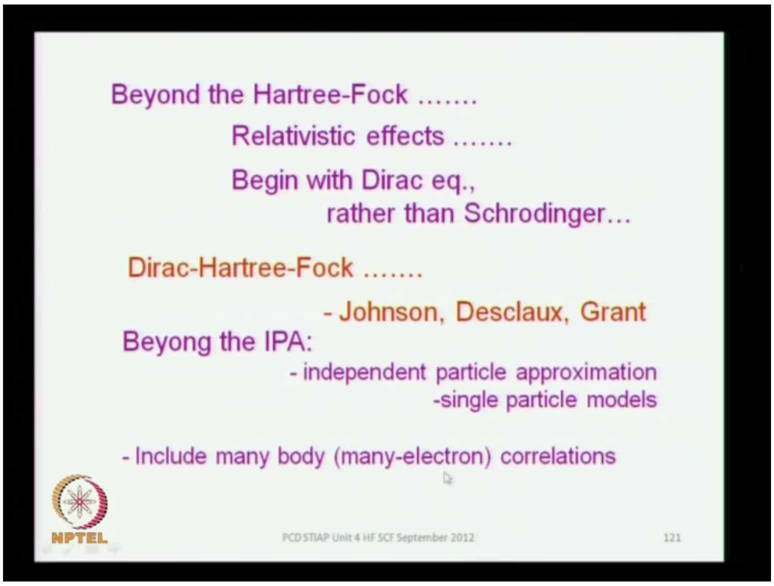

Beyond the Hartree-Fock ....

Relativistic effects ....

Begin with Dirac eq.,
rather than Schrodinger…

Dirac-Hartree-Fock ....

- Johnson, Desclaux, Grant

Beyong the IPA:

- independent particle approximation
-single particle models

- Include many body (many-electron) correlations

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Now, first thing is1should be given with Dirac equation, rather than the Schrodinger, what we did in the Hartree-Fock is to begin with the Schrodinger equation. So, when you do that you get what is called is the Dirac Hartree-Fock, and Hartree-Fock formalism was developed in around 1928, 29, 1930 around the time. The relativistic self consistent fields, some other earliest work I believe the first paper was by Voltaire Johnson in 1960 and then Dechko and

Grant, they also developed the relativistic self consistent field formalism around the same time.

But, then what is Johnson went on to do, so many other things Grant focused on the many electron relativistic solutions, and right from 1960, until now, for 50 years he is working on the n electron problem, atomic and molecular problem, getting relativistic self consistent fields. And huge technology and I was mentioning yet to someone over here, that over these 50 years he want worked with 50 young people, intelligent minds like you, who have all contributed to the technology.

And the number of PIG students and number of course dogs, so in 50 years a whole missionary has been developed by Grant and his collaborators. Then you need to include the many electron correlations and this I mentioned that the very outside, that in the Hartree-Fock theory certain correlations are included, and some correlations are not included. If you remember, I had mentioned that the exchange correlations are included, and because of the frozen orbital approximation, you have pretended the other electrons will not respond to any changes in the occupation of1electron orbital.

So, you need to go beyond the Hartree-Fock, because this is obviously, on approximation and the correlation energy is what you miss out when you do the Hartree-Fock, because in the Hartree-Fock, because of the frozen orbital approximation, you have left out the electron correlations the coulomb correlations. And these are left out in the self consistent field from nevertheless you are able to write your wave function, as a product of single particle wave functions that is exactly what you have done, we have worked with an n electron wave function, which is the product of1electron wave functions.

What I have added to that antisymmetric, our n electron wave function was made up of a product of1electron wave functions the only thing we added to that was the anti-symmetry. So, we did include the exchange correlations, but we did not include the coulomb correlations, and therefore one has to go beyond the independent particle approximations. The single particle model it works beautifully, it does give excellent results, but then it has certain limitations and1has to go really beyond it. So, you need to include many body correlations.

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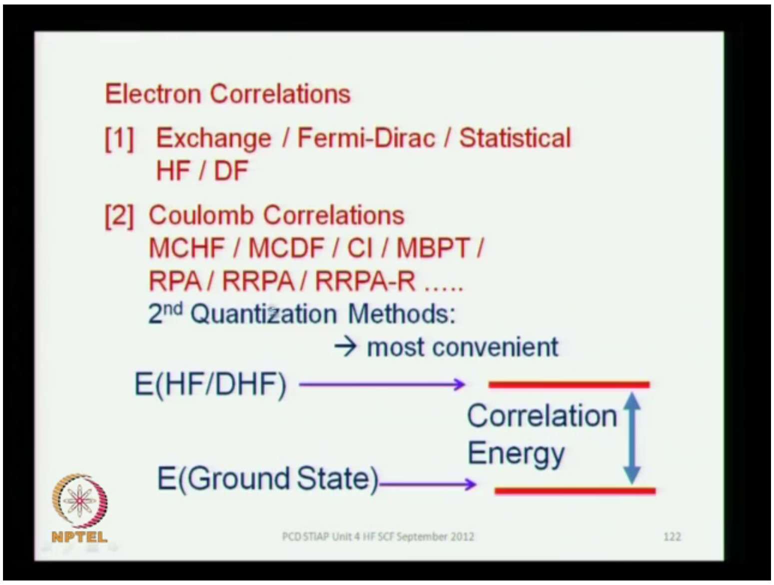

Electron Correlations

[1] Exchange / Fermi-Dirac / Statistical
HF / DF

[2] Coulomb Correlations
MCHF / MCDF / CI / MBPT /
RPA / RRPA / RRPA-R .....
2nd Quantization Methods:
→ most convenient

And1does it by different mechanisms, the exchange correlations are also called as Fermi Dirac correlations or statistical correlations, and the terminology is obvious. To include the coulomb correlations you can do what is called as MCHF, which stands for Multi-Configurational Hartree-Fock or MCDF, which stands for Multi-Configurational Dirac form, Dirac Hartree-Fock is the relativistic version of the Schrodinger self consistent field Hartree-Fock.

Then there are other techniques, which comes from anybody perturbation theory MBPT, you can use methods of second quantization, quantum field theory and this is a fairly large subject by itself. And this goes beyond this course, I am planning to expect address some of these techniques in another course, which I will be given in the next semester, in which I will discuss some of these techniques, the many body techniques. But, at this point I would like to mentioned that you need more powerful techniques like second quantization, fields theoretical methods to addressed those issues, which go beyond the Hartree-Fock which go beyond the frozen orbital approximations.

So, that you can include the coulomb correlations, they are the ones we should a responsible further fact, that the actual ground state is not the same as the Hartree-Fock or the Dirac Hartree-Fock ground state. You miss out on something, and what you miss out is typically called as the correlation energy. So, the subject is very worst subject and I will like to draw your attention to2excellent books1by Walter Johnson and the other by A.M. Grant. And these books I am got good summary of relativistic many body methods, which are used and atomic and molecular physics. And Grant as I mentioned he has developed the huge technology over the last 50 years, and now there is a package which is what people use at the front end of atomic physics, which is commonly called as grist which is general-purpose relativistic atomic structure program.

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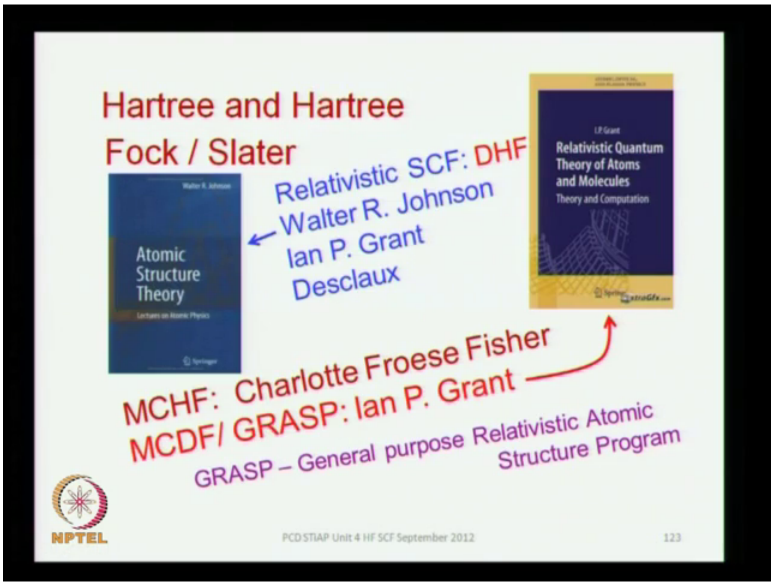

Hartree and Hartree Fock / Slater

Relativistic SCF: DHF
Walter R. Johnson
Ian P. Grant
Desclaux

MCHF: Charlotte Froese Fisher
MCDF/ GRASP: Ian P. Grant

GRASP – General purpose Relativistic Atomic Structure Program

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The various versions of grist this is the matter of detail, for those of you want to get into computational atomic physics. So, you will be using some of these tools, there is a among another techniques, I mentioned there is this the many body perturbation theory methods, which were developed by U. Kelly and there are so many others contributors. So, that there is a random phase approximation and it is relativistic version, the relativistic random phase approximation and many many developments, which go beyond the Hartree-Fock and also beyond the Dirac Hartree-Fock.

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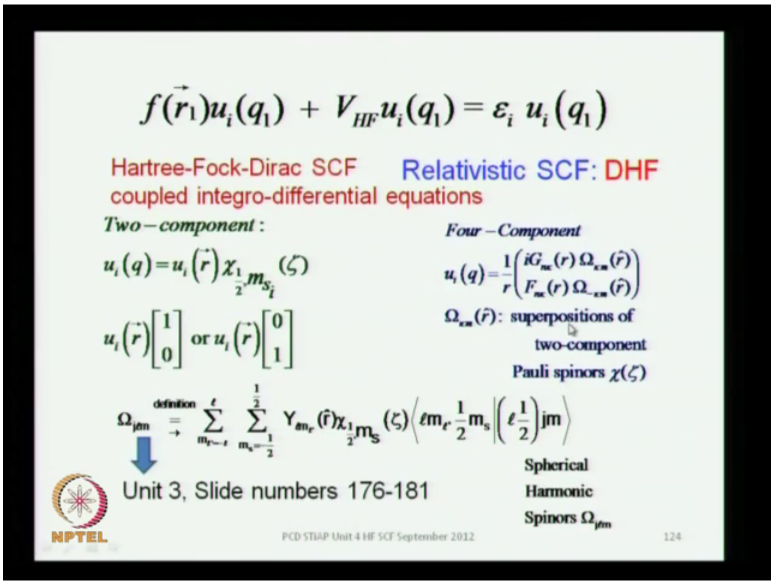

$$f(\vec{r}_1)u_i(q_1) + V_{HF}u_i(q_1) = \varepsilon_i\, u_i(q_1)$$

Hartree-Fock-Dirac SCF
coupled integro-differential equations

Relativistic SCF: DHF

Two – component:

$$u_i(q) = u_i(\vec{r})\,\chi_{\frac{1}{2},m_{s_i}}(\zeta)$$

$$u_i(\vec{r})\begin{bmatrix}1\\0\end{bmatrix} \text{ or } u_i(\vec{r})\begin{bmatrix}0\\1\end{bmatrix}$$

Four – Component

$$u_i(q) = \frac{1}{r}\begin{pmatrix} iG_{n\kappa}(r)\,\Omega_{\kappa m}(\hat{r}) \\ F_{n\kappa}(r)\,\Omega_{-\kappa m}(\hat{r})\end{pmatrix}$$

$\Omega_{\kappa m}(\hat{r})$: superpositions of
two-component
Pauli spinors $\chi(\zeta)$

$$\Omega_{j\ell m} \overset{\text{definition}}{\underset{\rightarrow}{=}} \sum_{m_\ell=-\ell}^{\ell} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} Y_{\ell m_\ell}(\hat{r})\,\chi_{\frac{1}{2}m_s}(\zeta)\left\langle \ell m_\ell \tfrac{1}{2} m_s \middle| \left(\ell \tfrac{1}{2}\right) jm \right\rangle$$

Unit 3, Slide numbers 176-181

Spherical
Harmonic
Spinors $\Omega_{j\ell m}$

Essentially what we have is the relativistic version, which is the Dirac Hartree-Fock, very often people call it as Dirac Fock, and I must apologize that I also may have use that term Dirac Fock. Sometimes, but as my friend and colleague and collaborator other, which always reminds me, that it is injustice to Hartree not to mention his name. So, it should be called as Dirac Hartree-Fock and not just as Dirac Fock. So, here the spin orbital that we used in our analysis are the2component functions, now your expression relativistic quantum mechanics, which we did in unit 3.

So, instead of the2component formalism, you can use the four component wave functions and you have got the radial part the G and F function you remember them. We had them from the solutions of the Dirac equation and then you had these spherical harmonic spinors. So, using these you can go through the exactly the same procedure, the same logic and you would have effectively learn the relativistic Hartree-Fock as well, everything is exactly the same. The hole approach to the relativistic problem is essentially the same.

So, in1go we have essentially developed some familiarity with both the non relativistic, as well as the relativistic models, the only thing is that you have to make use of these four components functions, you will remember that we use these spherical harmonic spinners. And these are the ones which will go into the four component functions, so using these you can develop the relativistic forms. Now, here you remember that it was this exchange term, which prevented as from identifying this as an Eigen value equation.

Because, here the argument of the i th orbital is 1, here the argument of i th orbital is 2, where is the argument1it is over here, and it is coming with the index j and then the j index also has this r 2 which is integrated over the whole space. So, it is a global term and it means although other solutions, so this exchange term makes an impossible to write this operator as a function of just1coordinate.

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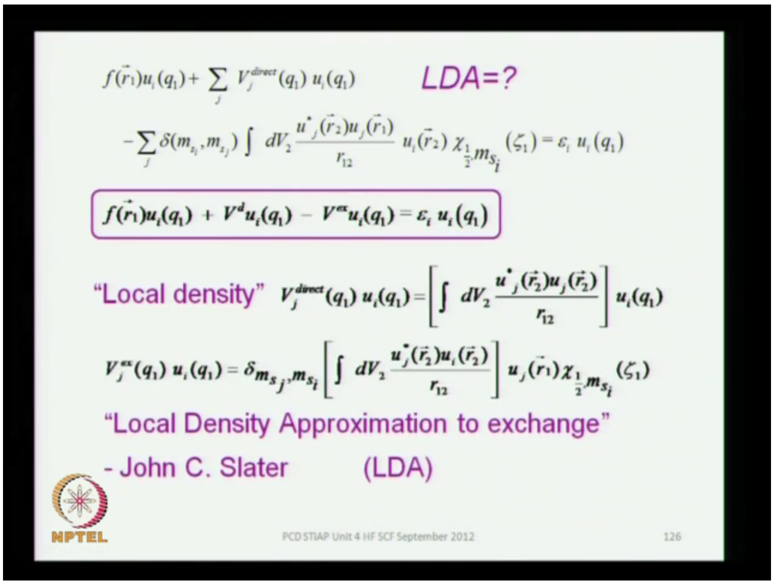

$$f(\vec{r}_1)u_i(q_1)+\sum_j V_j^{direct}(q_1)\,u_i(q_1)$$

LDA=?

$$-\sum_j \delta(m_{s_i},m_{s_j})\int dV_2\frac{u^*_j(\vec{r}_2)u_j(\vec{r}_1)}{r_{12}}u_i(\vec{r}_2)\,\chi_{\frac{1}{2},m_{s_i}}(\zeta_1)=\varepsilon_i\,u_i(q_1)$$

$$\boxed{f(\vec{r}_1)u_i(q_1)+V^d u_i(q_1)-V^{ex}u_i(q_1)=\varepsilon_i\,u_i(q_1)}$$

"Local density" $V_j^{direct}(q_1)\,u_i(q_1)=\left[\int dV_2\frac{u^*_j(\vec{r}_2)u_j(\vec{r}_2)}{r_{12}}\right]u_i(q_1)$

$$V_j^{ex}(q_1)\,u_i(q_1)=\delta_{m_{s_j},m_{s_i}}\left[\int dV_2\frac{u^*_j(\vec{r}_2)u_i(\vec{r}_2)}{r_{12}}\right]u_j(\vec{r}_1)\chi_{\frac{1}{2},m_{s_i}}(\zeta_1)$$

"Local Density Approximation to exchange"

- John C. Slater (LDA)

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The coulomb term the direct term could be written as a function of just1coordinate which is q 1, would you cannot do it over here. We wrote it in a form Bransden and Joachain called as a deceptively simple form, and the reason it is deceptive, is because here you have got a global integration, which involves the other solutions u j. So, this is the term which really makes it extremely difficult to solve the Hartree-Fock problem numerical.

What you can possibly do is to develop a local density approximation, that is LDA that the exchange term in fact, it is global term as you can see, because this is integration over the hole space. And you can develop some approximation to this exchange term and these approximations are called as local density approximations. And using this you can develop approximate Hartree-Fock formalism which also gives really good results, which is very useful in atomic physics and molecular physics and solicit physics.

So, this is the local density approximation in which you make on approximation to this operator to the exchange term, and this was introduced by John Slater, the first form was introduced by John Slater. But, later on there are many developments following this, so slater approximation is called as a free electronic approximation, but that is a matter of detail, there are other variations like the x alpha method and so on. So, these are some terms which I am passing over here, for those of you would read beyond the Hartree-Fock and beyond the Dirac Hartree-Fock.

And the local density approximations are then the starting point for many more powerful, but approximate techniques like the density functional theory is and so on, in many body problem. So, we are need to conclude this unit 4 at this point, and I thought that I will mention some of this signs for you to go beyond, there are large number of contributors.

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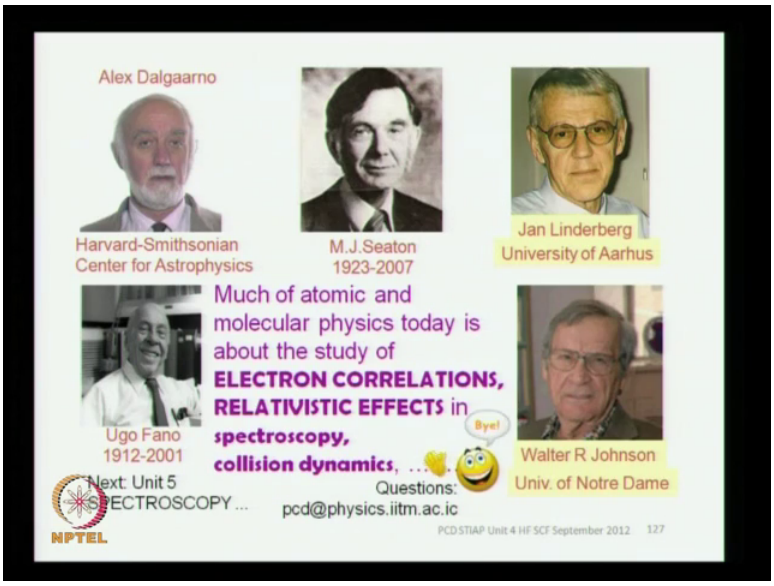

Alex Dalgaarno

Harvard-Smithsonian
Center for Astrophysics

M.J.Seaton
1923-2007

Jan Linderberg
University of Aarhus

Ugo Fano
1912-2001

Much of atomic and molecular physics today is about the study of **ELECTRON CORRELATIONS, RELATIVISTIC EFFECTS** in **spectroscopy, collision dynamics**, ….

Walter R Johnson
Univ. of Notre Dame

Next: Unit 5
SPECTROSCOPY ...

Questions:
pcd@physics.iitm.ac.ic

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And the most exciting problems an atomic and molecular physics are those which involve relativistic effects, electron correlation effect, and now you have some idea about what electron correlation effects are. Lot of work has been done by Alex Delgaarno, Ugo Fano, Mike Seaton and in quantum chemistry, people like Jan Linderberg have contributed a lot, Walter Johnson to atomic physics. So, huge amount of development which goes beyond the Hartree-Fock, and beyond the relativistic Dirac Fock has taken place. And then the exciting problems are in atomic spectroscopy and collision phenomena, because what you have done here is to get the electron structure.

So, this is what is called as the structure studies, now these described electron wave functions for the atomic system, or the molecular system or the solicit system. Now, you have got this system how this system is going to react to electrometric radiation, or how is it going to react if you bombard it by neutrons, how is it going to react if you fire some other projectiles. Because, by carrying out these experiments you get a lot of information about the target, and that is for physics is about that you got a certain system, that is your target how do you investigate it.

So, you need to either shined light with it, or bombard particles it and other than light and particles, what else do you have nothing, so you do either spectroscopy or collisions, and at some level light and particles are also inter-convertible, but that is a matter of detail. But, either you need to do spectroscopy or you need to do collisions that is the only way you can really prove targets. So, these are very powerful techniques the Hartree-Fock and the Dirac Hartree-Fock tell you, how to describe the electronic structure of the quantum system, of a microscopy quantum system; let it be an atom, a molecular, a solid whatever. And then I will conclude this unit over here, the next unit will be on spectroscopy and we will begin to acquaint ourselves with spectroscopy tools, questions.

Student: Why we cannot call that particular equation as an Eigen value equation.

Because, you really cannot solve it as an Eigen value problem, and Eigen value equation is not just how many equation looks, but also in how that mathematical equation is dealt with, it cannot be dealt with as an Eigen value problem. That is specialized the reason Bransden and Joachain call it as a deceptively simple form it looks like, but it is not; that is the disruption. You can make it look like an Eigen value problem, but the operator that you really have, an Eigen value equation is an operator operating on an operant giving you the same operant scaled by some complex number, by scale up.

This operator requires solutions to all the other n minus one problems, and unless you solve them, you cannot set up this Eigen value equation, you cannot solve it as an Eigen value equation. So, it can be solved only self consistently together with all the remaining n minus 1 problems, it is n coupled integral differential equations. And if you make on approximation to the exchange, you can solve it as an Eigen value problem, but then you do not get the exact solutions, you do get useful solutions.

So, slater approximation which is sometimes called as a Hartree-Fock slater method, or H f s, and this 3 names associated with it,1tends to think that this is something better than the Hartree-Fock which it is not. It is slaters approximation to the Hartree-Fock, so there are various ways of the local density methods are quite useful and what typically happens is that, the larger the quantum system is you need to have more approximations. The smaller a quantum system is you can try to go for more exact solutions, so it is not very easy to do relativistic self consistent field for energy bands in solids, but yes you can do it, and people do it.

So, do not get me wrong, you do relativistic self consistent field band structure calculations, you also do the relativist self consistent field molecular orbital calculations. But, it is locked more comment to see non-relativistic approximation or local density approximations in molecular physics or condensed meta physics. Because, the more there is the order it gets, any other question, yes.

Student: ((Refer Time: 58:18))

You can get improvements using various alterations, there are so many different approximation that can be made, but remember what I mentioned at the very beginning of the discussion on the n electron problem. That 3 body problem in classical mechanics as no exact analytical solution, when you put in relativity, you put in quantum mechanics, quantum fields, even vacuum fluctuations you do not have exact analytical solutions, you have to make a approximation.

Vacuum fluctuations lamb shift for example, if you start to calculating the lamb shift and then you make corrections like for the hydrogen atom, we talked about the spin orbital correction, then the kinetic energy correction that the Darwin correction. You start making corrections to the vacuum fluctuations, you make correction 1, correction 2, correction 3, correction 4 people are made something like 12, 13 correction I think. And they still do not have an exact solution, and what is very nicely stated by brown who I quoted earlier, that if you are looking at exact solutions having nobody at all is already to many, even for vacuum you cannot do it.

So, there are large number of many body methods, which are developed and that is way the challenges, the challenge for a many body theories is not to get the exact solution that is beyond his scope. Because, there are existence theorem which tell you, then the solution does not exist what are you going to do, so your challenge is to find the best approximation that you can. And there is a lot of competition in different approximation techniques, but then they also have the limited scope and range of applicability.

So, I do not think anybody is ever going to climb that this approximation is going to give better results in general, I do not believe any many body theorist will make that climb. Because, you could get better results in some domains, but not in every domain, if you did you would have something like a very general solution that is it work, is not that easy I do not think we are any right to close to at least on atomic physics. And therefore, further half in molecular in condensed meta physics.

Student: ((Refer Time: 01:01:02))

LDA is an approximation mind you whatever it is, it is an approximation, it is pretending that the exchange interaction need not be treated exactly, but that the exchange interaction is there. The exchange interaction cannot be wished away, it is coming from the simple fact that electrons, your many body systems consist of electrons, which are fermion. And under an interchange of any two, the wave function must change it sign, you cannot wish it away, and if this interaction which is the exchange interaction is treated only approximately, it means that you are treating the statistics approximately. So, making a certain compromise and by making compromise you are sometimes able to move ahead which is useful, but not strictly correct, but it can be very useful. So, nothing wrong in using local density approximations any other question.

So thank you for now, and then in the next class we will begin that unit 51 spectroscopy.