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

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Lecture 13
Many Body Theory, Electron Correlations

Greetings, we will begin unit 2 today and this will be on many body theory our focus will be on the study of electron correlations and techniques which make use of diagrammatic perturbation theory, the Feynman Goldstone diagrams and so on. So, we will develop these techniques which are of importance in studying atomic collisions and spectroscopy.
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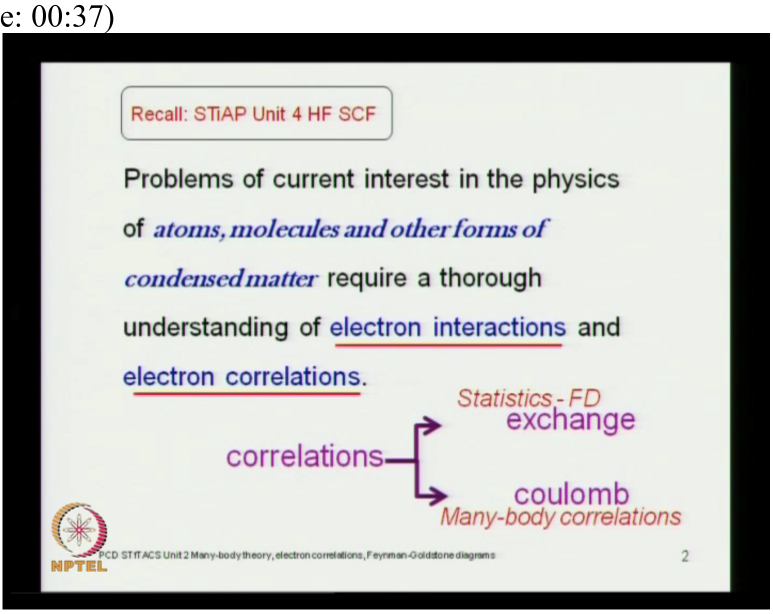

Recall: STiAP Unit 4 HF SCF

Problems of current interest in the physics of *atoms, molecules and other forms of condensed matter* require a thorough understanding of electron interactions and electron correlations.

correlations → Statistics - FD exchange
correlations → coulomb Many-body correlations

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And I will spend a few minutes at the start of this unit recapitulating a few points that we did earlier in the previous course on the special topics and atomic physics in particular I will invoke the discussion on the Hartree Fock formalism which is also a many body theory in a certain sense. It is a many electron theory but then we are going to go well beyond the Hartree Fock in the discussion in unit 2.

So, let me recapitulate a few points from unit 4 of the previous course on atomic physics. And our interest in studying atoms, molecules, condensed matter of any kind is in studying electron interactions and electron correlations and of course how the many body system responds to various probes like electromagnetic radiation or other particles like projectiles electrons, positrons, composite particles and so on.

So, I have underlined the words electron interactions and electron correlations to draw attention to the fact that these two terms will have different connotations in our context okay. And in particular when I refer to correlations I will be referring to two kinds of correlations one are the exchange correlations and the other are Coulomb correlation. So, obviously Coulomb correlations and Coulomb interactions are two different things okay.

Coulomb interaction is the usual one over r12, Coulomb correlations is what many-body theory is about, so that is the focus of unit 2. Now the exchange correlations come from statistics. Exchange correlations they are because of the fact that electrons are Fermi particles Fermi Dirac particles and the statistics they must observe is the Fermi Dirac statistics and that requires that a many electron wave function must be anti symmetric.

So, there is a certain correlation coming in from statistics. In addition to that there is a correlation which is the Coulomb correlation which is not included in the Hartree Fock formalism and that is the one that we are going to talk about. That is a result of what we will refer to as many body correlations or many electron correlations.

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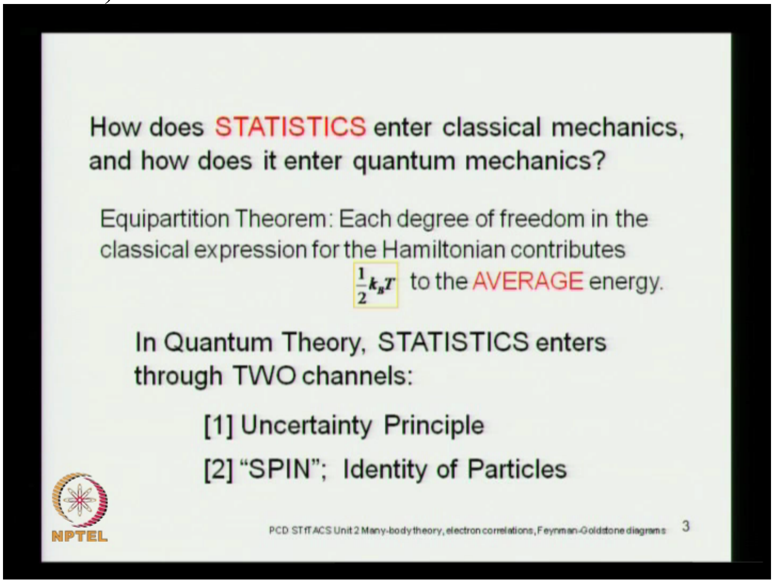

How does STATISTICS enter classical mechanics, and how does it enter quantum mechanics?

Equipartition Theorem: Each degree of freedom in the classical expression for the Hamiltonian contributes $\boxed{\frac{1}{2}k_BT}$ to the AVERAGE energy.

In Quantum Theory, STATISTICS enters through TWO channels:

[1] Uncertainty Principle

[2] "SPIN"; Identity of Particles

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And let me quickly remind you that statistics enters classical mechanics and quantum mechanics in different ways okay. In classical mechanics it enters just because you are dealing with a large number of particles and there is too much of information not all of it all the details are interesting. So, you do some averaging like in principle in classical mechanics since every single particle is distinguishable.

And it obeys dynamical laws in which you can predict the motion using the equation of motion. In principle you can follow the trajectory of every particle. But all this is not interesting what is interesting is what the average kinetic energy is and what it generates is a thermodynamic parameter like the temperature. So, these are average properties and this is how statistics enters classical mechanics.

In quantum mechanics statistics enters because of the uncertainty principle. So, laws of nature are intrinsically statistical there is a probabilistic interpretation that quantum mechanics demands even when you are dealing with a single particle or even when you are dealing with vacuum. So, it is nothing to do with the number of particles, number of particles only makes it more complicated.

But having fewer particles having a single particle does not eliminate statistics. And then you have the spin which is an intrinsic angular momentum for elementary particles and this also leads you to statistical considerations. Because there are two kinds of particles in nature fermions and bosons and they observe different statistics they have different spins.

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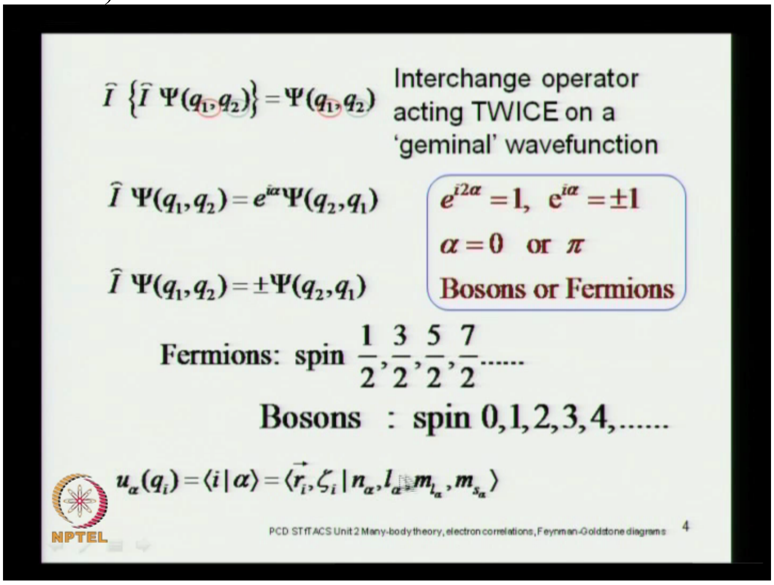

$\hat{I}\,\{\hat{I}\,\Psi(q_1,q_2)\} = \Psi(q_1,q_2)$ Interchange operator acting TWICE on a 'geminal' wavefunction

$\hat{I}\,\Psi(q_1,q_2) = e^{i\alpha}\Psi(q_2,q_1)$

$\hat{I}\,\Psi(q_1,q_2) = \pm\Psi(q_2,q_1)$

$e^{i2\alpha} = 1,\ e^{i\alpha} = \pm 1$

$\alpha = 0$ or π

Bosons or Fermions

Fermions: spin $\frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2}$......

Bosons : spin 0,1,2,3,4,......

$u_\alpha(q_i) = \langle i|\alpha\rangle = \langle \vec{r}_i,\zeta_i \,|\, n_\alpha, l_\alpha, m_{l_\alpha}, m_{s_\alpha}\rangle$

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So, if you have two identical particles and the signature of quantum mechanics so far as many body formalisms are concerned is the fact that these particles are indistinguishable okay. So, if you have two identical particles one at coordinate q1 and the other at coordinate q2. If you interchange these two particles and I is the interchange operator. And on the result you carry out the interchange yet again. So, you are carrying out an interchange twice.

You naturally expect that you will recover the original state. Now this is a geminal wave function which is a wave function for the twin particles. They are completely identical in all respects and you will recover the same function which means that if you interchange only once you can at the most change the phase of this wave function by e to the i alpha right. And e to the 2i alpha must be unity which is what you will get over here.

Which means that alpha is either 0 or pi and depending on it is 0 or pi you have either Bose particles or Fermi particles. Now all particles which have half integer spin are Fermi particles or Fermi Dirac particles. And all particles with integer spins are Bose particles or Bose

Einstein particles. And typically the wave function would be written in terms of the spin quantum number as well.

And then you will have a one electron state written as n, l, ml, ms for a particular state which is alpha. So, you have got a set of commuting operators, so this gives you a complete description, a complete set of commuting operators or a complete set of compatible observables as Dirac calls it CSCO right. And these give you the complete description and this complete description must include the spin.

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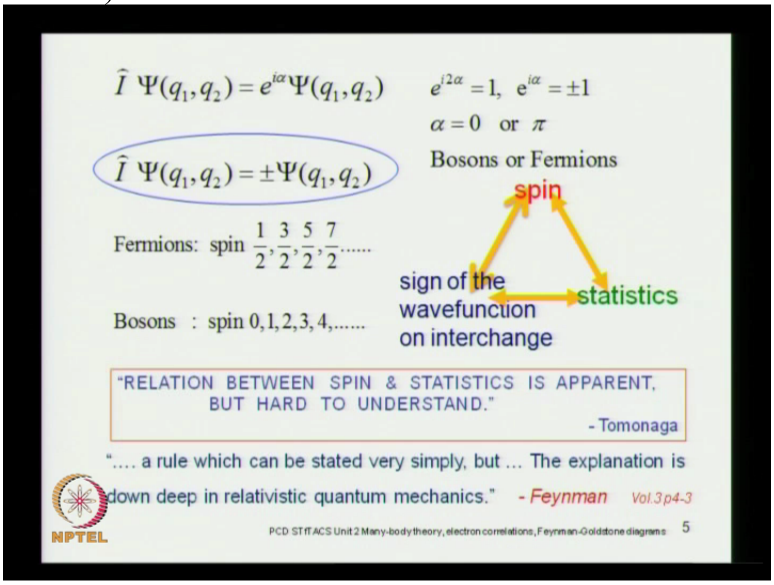

$$\hat{I}\ \Psi(q_1,q_2)=e^{i\alpha}\Psi(q_1,q_2)$$

$e^{i2\alpha}=1,\ e^{i\alpha}=\pm 1$

$\alpha=0$ or π

Bosons or Fermions

$$\boxed{\hat{I}\ \Psi(q_1,q_2)=\pm\Psi(q_1,q_2)}$$

Fermions: spin $\frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2},\ldots\ldots$

Bosons : spin $0,1,2,3,4,\ldots\ldots$

spin

sign of the wavefunction on interchange

statistics

"RELATION BETWEEN SPIN & STATISTICS IS APPARENT, BUT HARD TO UNDERSTAND."

- Tomonaga

".... a rule which can be stated very simply, but ... The explanation is down deep in relativistic quantum mechanics." - Feynman Vol.3p4-3

NPTEL

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Now it is very interesting that you have this connection between statistics, the spin of the particles and the sign of the wave function on interchange. Because on interchange of Bose particles the wave function remains invariant. Whereas on interchange of Fermi particles the wave functions of the geminal changes sign right. So, this connection is rather interesting and it is nevertheless not so very easy to understand as Tomonaga tells us in the statement.

That the relation between spin and statistics is apparent but hard to understand and I would like to quote Feynman one more time over here that you have a rule which can be stated very simply. But the explanation is complicated it lies deep down in relativistic quantum mechanics okay. So, I will not go into those details because our focus in unit 2 is the discussion on how many body correlations are to be treated and what they are in the first place.

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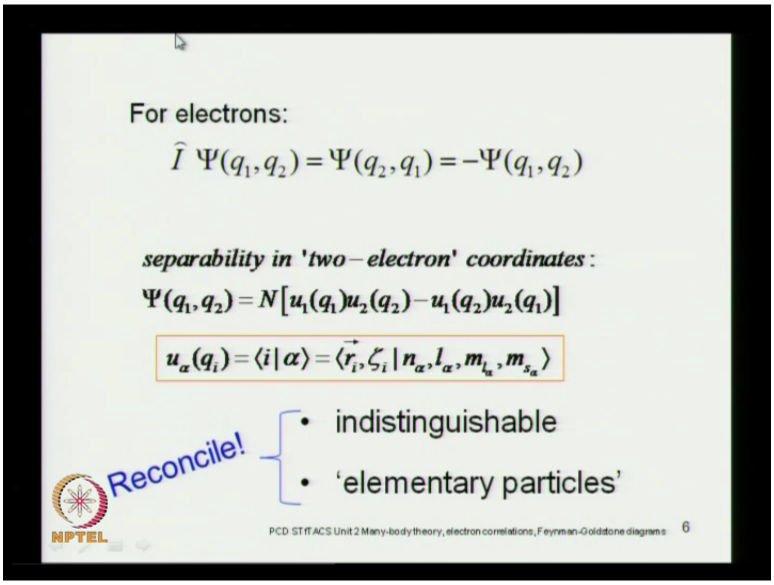

For electrons:

$$\hat{I}\ \Psi(q_1,q_2)=\Psi(q_2,q_1)=-\Psi(q_1,q_2)$$

separability in 'two – electron' coordinates:

$$\Psi(q_1,q_2)=N\left[u_1(q_1)u_2(q_2)-u_1(q_2)u_2(q_1)\right]$$

$$\boxed{u_\alpha(q_i)=\langle i|\alpha\rangle=\langle\vec{r}_i,\zeta_i|n_\alpha,l_\alpha,m_{l_\alpha},m_{s_\alpha}\rangle}$$

Reconcile!

- indistinguishable
- ‘elementary particles’

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So, let us deal with electrons on interchange the electron germinal, the two electron wave function changes at sign and you consider the wave function or which is a function of two electrons q1 and q2 one at q1 the other at q2 to be separable in one particle coordinates okay. So, the two electron wave function is written as a product of 2,1 electron functions but the product must be an anti symmetric product.

As we have discussed in details in our previous course in atomic physics on the discussion on the Hartree Fock. So, you have to reconcile two properties two attributes which can appear to be contradictory the particles are indistinguishable in the sense that you really cannot separate one from the other yet you talk of them as individual elementary particles in which each has an identity of its own as an elementary particle okay.

The elementary particle of nature is the electron not the twin it is not the pair of electrons. So, the elementary particle is still the electron but the two electrons are indistinguishable and this is indicated over here that the two electron wave function is written as a product of one electron functions which respects the elementary nature of the two electrons. But then it is a superposition of these two states electron at q1 in the quantum state 1.

And electron at q2 in the quantum state 2 and the other possibility that the electron at q1 is in the quantum state 2 and the electron at q2 is in quantum state 1. So, these two situations are not distinguishable, so indistinguishability demands that you construct a linear superposition of this and this superposition must be an anti symmetric superposition.

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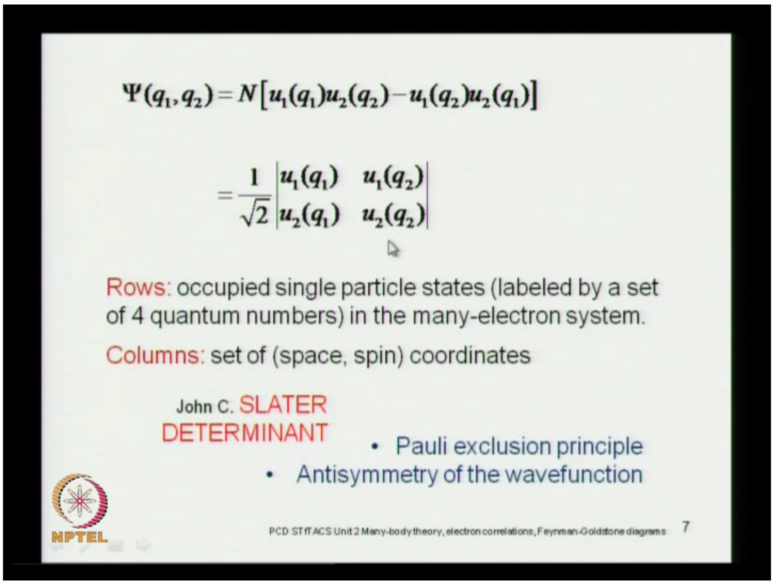

$$\Psi(q_1,q_2)=N\left[u_1(q_1)u_2(q_2)-u_1(q_2)u_2(q_1)\right]$$

$$=\frac{1}{\sqrt{2}}\begin{vmatrix} u_1(q_1) & u_1(q_2)\\ u_2(q_1) & u_2(q_2)\end{vmatrix}$$

Rows: occupied single particle states (labeled by a set of 4 quantum numbers) in the many-electron system.

Columns: set of (space, spin) coordinates

John C. SLATER DETERMINANT

- Pauli exclusion principle
- Antisymmetry of the wavefunction

So, you can see that you can write this as a determinant this is just an equivalent form. And this is the 2 by 2 determinant for the two electron system is called as the Slater determinant you can automatically see that the Pauli exclusion principle and the anti symmetry of the wave function is automatically built into it.

Because if you interchange q1 and q2 the determinant would change its sign and if you have two rows to be the same, the determinant will vanish okay that is the Pauli Exclusion Principle.

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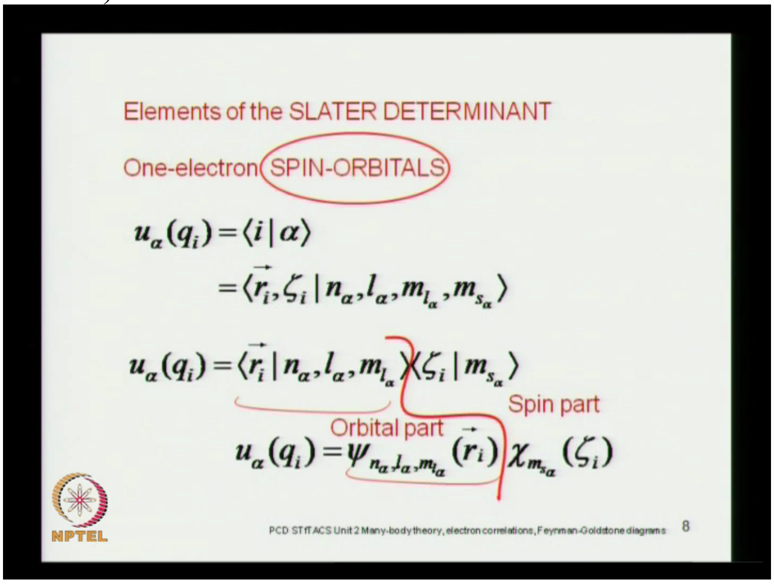

Elements of the SLATER DETERMINANT

One-electron SPIN-ORBITALS

$$u_\alpha(q_i)=\langle i|\alpha\rangle$$

$$=\langle \vec{r}_i,\zeta_i|n_\alpha,l_\alpha,m_{l_\alpha},m_{s_\alpha}\rangle$$

$$u_\alpha(q_i)=\underbrace{\langle \vec{r}_i|n_\alpha,l_\alpha,m_{l_\alpha}\rangle}_{\text{Orbital part}}\langle\zeta_i|m_{s_\alpha}\rangle$$

Spin part

$$u_\alpha(q_i)=\underbrace{\psi_{n_\alpha,l_\alpha,m_{l_\alpha}}(\vec{r}_i)}\chi_{m_{s_\alpha}}(\zeta_i)$$

Now basically the single electron wave functions which are called as spin orbital. These are made up of a spin part and the orbital part okay so there is a separation between spin and orbit part over here. But the spin orbit coupling of course will give you a quantum number which is different.

Because l and s will combine to give you a j right and then j, mj will be good quantum numbers and not ml, ms so, basically you deal with these spin orbitals in the Slater determinant.

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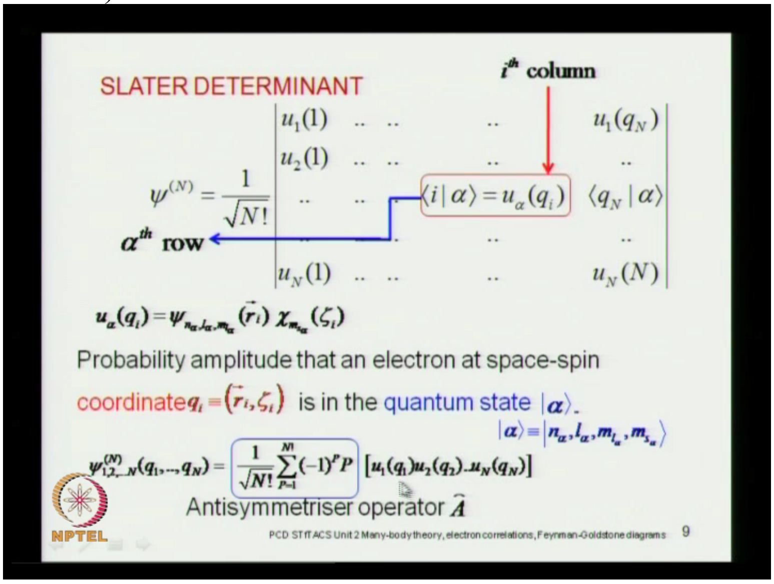

SLATER DETERMINANT

i^{th} column

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & .. & .. & .. & u_1(q_N) \\ u_2(1) & .. & .. & .. & .. \\ .. & .. & .. & \boxed{\langle i|\alpha\rangle = u_\alpha(q_i)} & \langle q_N|\alpha\rangle \\ .. & .. & .. & .. & .. \\ u_N(1) & .. & .. & .. & u_N(N) \end{vmatrix}$$

α^{th} row

$$u_\alpha(q_i) = \psi_{n_\alpha, l_\alpha, m_{l_\alpha}}(\vec{r}_i)\, \chi_{m_{s_\alpha}}(\zeta_i)$$

Probability amplitude that an electron at space-spin coordinate $q_i = (\vec{r}_i, \zeta_i)$ is in the quantum state $|\alpha\rangle$.

$$|\alpha\rangle \equiv |n_\alpha, l_\alpha, m_{l_\alpha}, m_{s_\alpha}\rangle$$

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

Antisymmetriser operator $\hat{A}$

For an N electron system now we go quickly from the two electron system to an N electron system where N is any number it could be 2 or 3 or 4 or whatever. And you have an N by n Slater determinant in which the columns are labelled by the q's which are the coordinates. And the rows are labeled by the quantum numbers these are the complete set of commuting operators and their Eigen values okay.

So, the quantum number is obtained from the Eigen value of the observable which is measurable. And once you have a complete set of commuting observations you get a set and this set is what I call as alpha. So, alpha is not just one quantum number in our case it is 4 quantum numbers right and together this gives us one set.

So, each row in this Slater determinant corresponds to to a particular set of alpha where alpha contains all the 4 quantum numbers, so, these are the 4 quantum numbers in alpha n, l, ml and ms and you can write this determinant also as you can take all the diagonal elements construct a product of this and then carry out the permutations of these. This is how the determinant.

Yes you have a question (Question Time: 13:52) that here subscript corresponding to u means that this subscript combination is different combination from n, l exactly right. So, either one or more quantum numbers will be different when you go from one row to the other. No 2 rows will have the same set of quantum numbers that will violate the Pauli Exclusion Principle and the determinant will vanish.

But if even one of them is different then you are okay right (Question time: 14:24) So that difference is manifested inside the q position I mean each row, each or the; q's go from one column to the next so the first column is q1 the second is q2 and the last column is qn. (Question time: 14:43 not audible) So, in a particular row, for the q upto qn, what are the quantum numbers, are same positions.

Yes basically what you are doing is interchanging the position that is where the indistinguishability of the particles comes in. So, typically this is a measure of the probability amplitude that an electron at coordinate qi is in the quantum state alpha. But in the next row belonging to the same column you will have the probability amplitude that an electron at coordinate qi will be in the quantum state alpha + 1, the next one right.

And that cannot be ruled out because these particles are completely indistinguishable. So, you must construct a superposition of these and this must be an anti symmetric superposition. So that is what this Slater determinant guarantees. So, you can write this; basically you are carrying out these permutations between these coordinates and then you must have the parity of the permutation.

You will have factorial n permutations possible and then 1 over root factorial n is the normalization as you can get if these individual spin orbitals which are elements of the determinant are individually normalized. So, these things we discussed at some length in our previous course on atomic physics.

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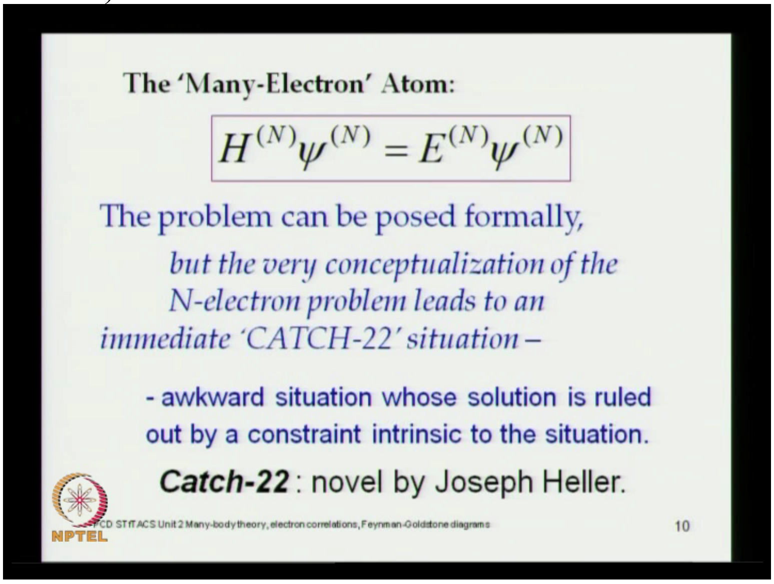

The 'Many-Electron' Atom:

$$\boxed{H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}}$$

The problem can be posed formally,

but the very conceptualization of the N-electron problem leads to an immediate 'CATCH-22' situation –

- awkward situation whose solution is ruled out by a constraint intrinsic to the situation.

Catch-22: novel by Joseph Heller.

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And you may want to refer back to some of those details and I just wanted a very quick recapitulation of that. And the many electron Schrodinger equation is H Psi = E Psi for the N number of particles and this is what we called as the Catch-22 situation, the reason is it is Catch-22 a phrase which is, which comes from the novel by Joseph Heller.

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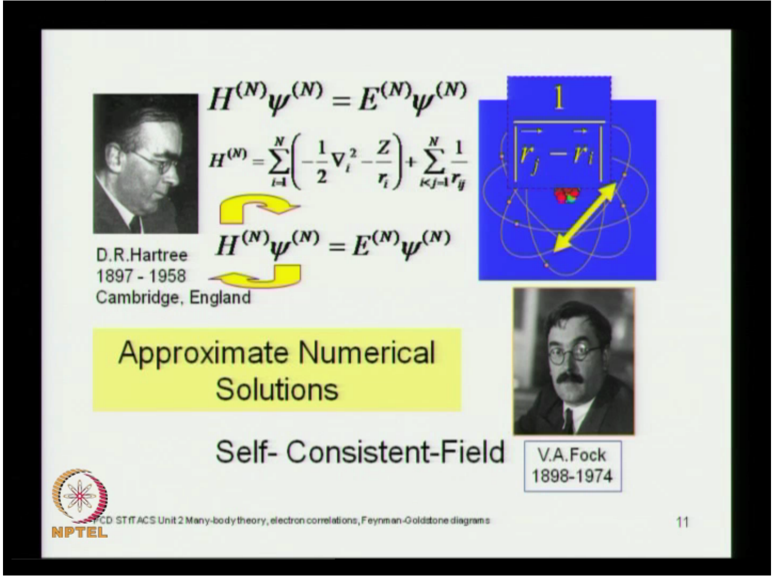

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

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

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

D.R.Hartree
1897 - 1958
Cambridge, England

Approximate Numerical Solutions

Self- Consistent-Field

V.A.Fock
1898-1974

And the main idea in this is the following that if you write the N electron Hamiltonian as the sum of these single particle operators. This is a single party kinetic energy; this is the kinetic energy of each electron in the field of the nucleus. But this is the electron-electron repulsion and the 1 over rij which is the electron-electron repulsion. So, this requires for your consideration the distance between these two electrons right.

And this distance can be specified only in terms of distance between the two probability densities because charges these are not classical point charges. So, you need the probability densities which can come only from the wave function. So, you need the wave function even to construct the Hamiltonian. And unless you have the Hamiltonian you cannot set up the differential equation at all, so this is the Catch-22 situation.

And to break it you follow Hartree's procedure and have approximate numerical solutions in which you obtain self consistent field solutions. So, some of these details we have discussed in our previous course I will not go through it now. This is just a quick reminder that these are the techniques which are used and then of course you go beyond Hartree you must include the spin and that is the Hartree Fock formalism okay.

(Question time: 17:57 – not audible) It is neglected here it is given an average effect; this is a nuclear part this is the single atomic system, so there is a single nucleus. For molecules of course you have the nuclear nuclear interaction, this is a single nucleus. So, we, I am developing the formalism in the context of a single atom. But of course in condensed matter where you have a molecule or a cluster, then you have the nuclear-nuclear term as well.

So, the contribution from the nucleus is not neglected it is Z over ri over here. For in molecule where there are more than one nucleus you can carry out the Born Oppenheimer approximation or you can do even better that but that is a matter of detail okay, (Question time: 18:45 – not audible) in field approximation yeah.

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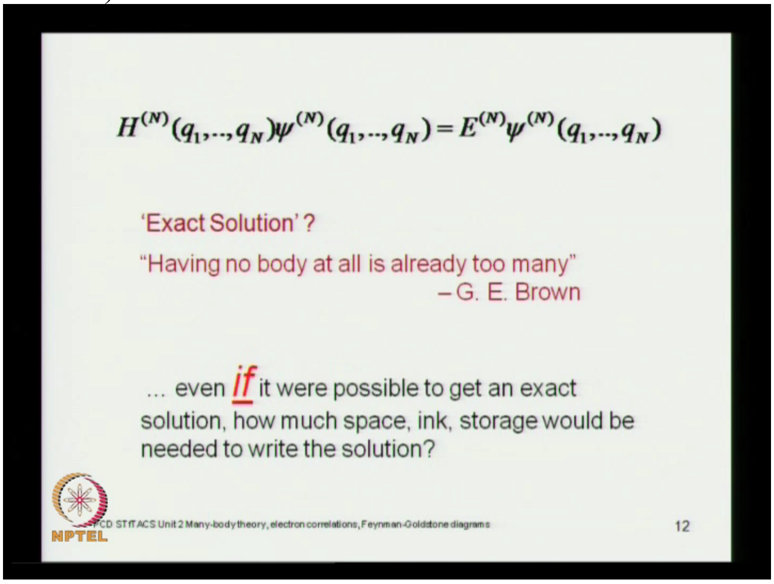

$$H^{(N)}(q_1,..,q_N)\psi^{(N)}(q_1,..,q_N)=E^{(N)}\psi^{(N)}(q_1,..,q_N)$$

'Exact Solution' ?

"Having no body at all is already too many"
– G. E. Brown

… even *if* it were possible to get an exact solution, how much space, ink, storage would be needed to write the solution?

So, essentially it is hopeless to look for an exact solution of a many body system okay. There is no chance that you can get an exact solution. It is not that it is difficult mushkil hi nahin na moonki me okay. So, it is absolutely hopeless that you can understand it only in those terms. So, it is impossible to get an exact solution.

And this is best stated in remark by Brown in his book where he says that having nobody at all is already too many if you are looking for an exact solution. So, you have to look for you know approximate solutions. And even to write down these solutions you have a very huge task because just how much of storage space would you need to write handle these Slater determinant. How many terms do you have in this Slater determinant.

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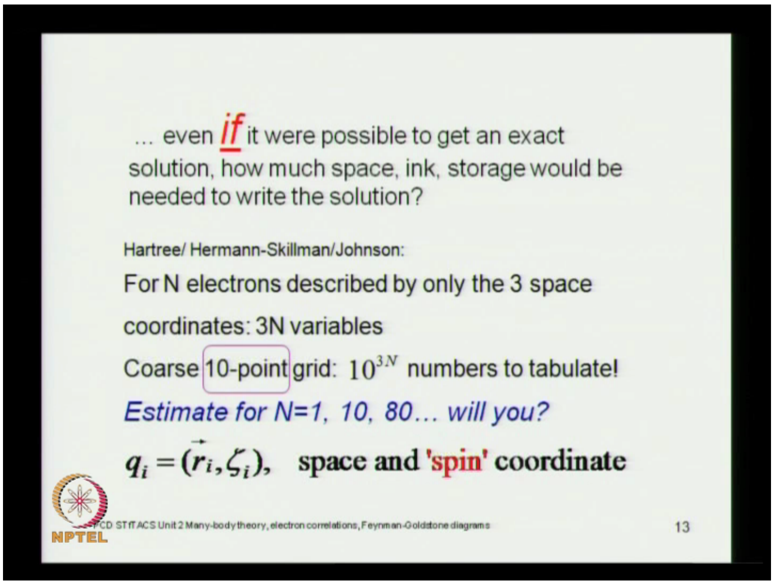

… even *if* it were possible to get an exact solution, how much space, ink, storage would be needed to write the solution?

Hartree/ Hermann-Skillman/Johnson:

For N electrons described by only the 3 space coordinates: 3N variables

Coarse 10-point grid: 10^{3N} numbers to tabulate!

Estimate for N=1, 10, 80… will you?

$q_i = (\vec{r}_i, \zeta_i)$, **space and 'spin' coordinate**

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If you just take a small atom like every electron has three degrees of freedom. So, it has got 3N variables right and if you write the wave function just on a 10-point grid actually it is more than 3 because you know that there is the spin also. So, just to simplify this I have taken 3, if you take a 10-point grid then you have 10 to the 3N numbers to tabulate.

And you will get a very bad wave function on a grid which has got only ten points. But even that you have 10 to the power 3N numbers and what kind of a number is it okay. For N = 1 it is already a thousand okay. And then for neon, for mercury atom these are huge numbers okay. So, you need techniques and the occupation number of formalism.

The second quantization methods that we are going to discuss in this unit will tell you very elegant ways of doing this. So, you have to deal with spin as well.

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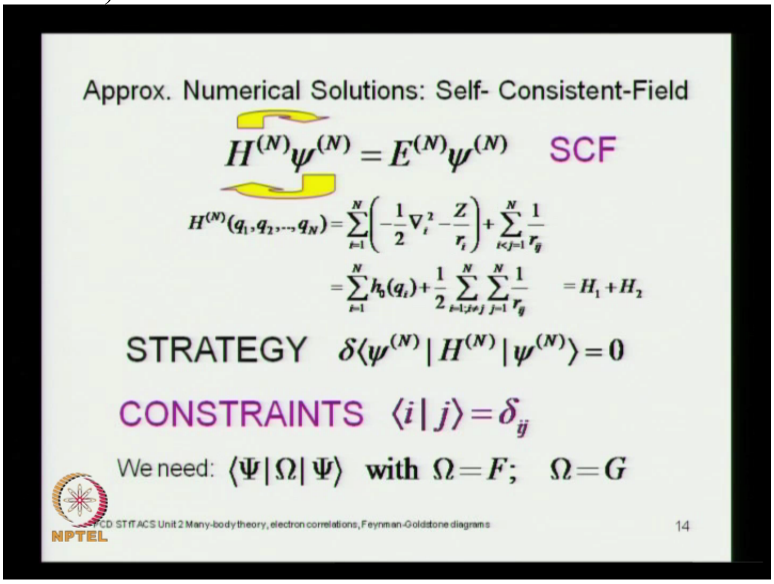

Approx. Numerical Solutions: Self- Consistent-Field

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)} \quad \text{SCF}$$

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

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

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

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

We need: $\langle\Psi|\Omega|\Psi\rangle$ **with** $\Omega = F$; $\Omega = G$

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And we know that self consistent field solutions are possible in the Hartree Fock formalism. And the main strategy of Hartree Fock is to get an extremum of the expectation value of the n electron Hamiltonian in the Slater determinant. This is a single Slater determinant mind you okay.

And in this you obtain this extremum subject to the condition of constraints of the orthogonality of the single particle wave functions and their normalization as well. So, you can determine the expectation value of the single particle and two particle operators and proceed and this is what we discussed in our previous course in atomic physics.

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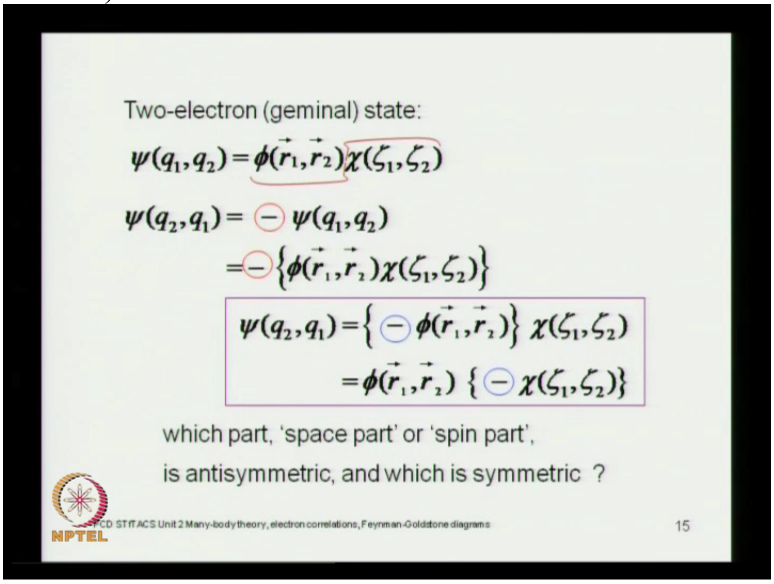

Two-electron (geminal) state:

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

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

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

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

which part, 'space part' or 'spin part',

is antisymmetric, and which is symmetric ?

The two-electron geminal state which is always nice to have some kind of handle on because all the two electron interactions are expressed in terms of these functions you can have the anti symmetry of the wave function that when you interchange q1 and q2, q1 is here in q2 here. When you interchange the first one is q2 and the second one is q1 the wave function must change its sign.

But this sign must be attributed either to the spin part or to the orbital part. And either of the two possibilities will give you an anti symmetric wave function. So, there are two possibilities here that the orbital part is anti symmetric and the spin part is symmetric or the orbital part is symmetric on the spin part is anti-symmetric.

So, you have two kinds of you know solutions and you must ask which part is symmetric and which part is anti-symmetric.

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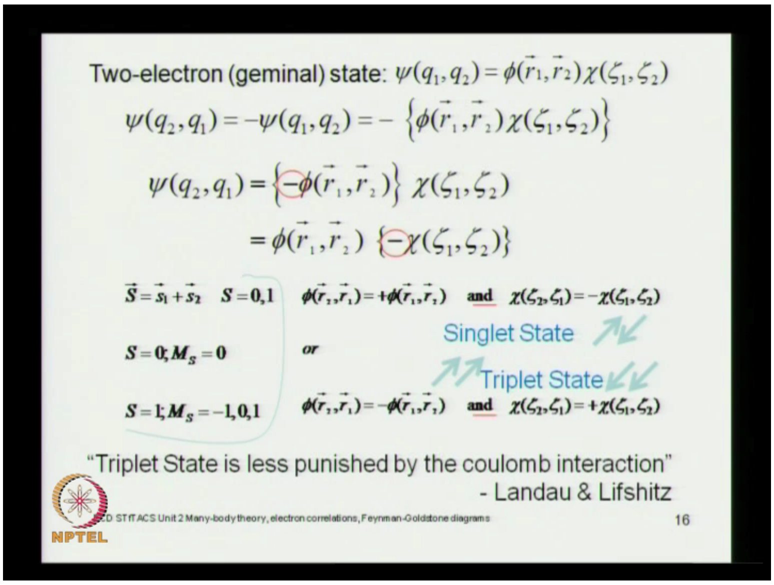

Two-electron (geminal) state: $\psi(q_1,q_2)=\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)$

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

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

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

$\vec{S}=\vec{s}_1+\vec{s}_2$ $S=0,1$ $\phi(\vec{r}_2,\vec{r}_1)=+\phi(\vec{r}_1,\vec{r}_2)$ **and** $\chi(\zeta_2,\zeta_1)=-\chi(\zeta_1,\zeta_2)$

Singlet State

$S=0; M_S=0$ *or*

Triplet State

$S=1; M_S=-1,0,1$ $\phi(\vec{r}_2,\vec{r}_1)=-\phi(\vec{r}_1,\vec{r}_2)$ **and** $\chi(\zeta_2,\zeta_1)=+\chi(\zeta_1,\zeta_2)$

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

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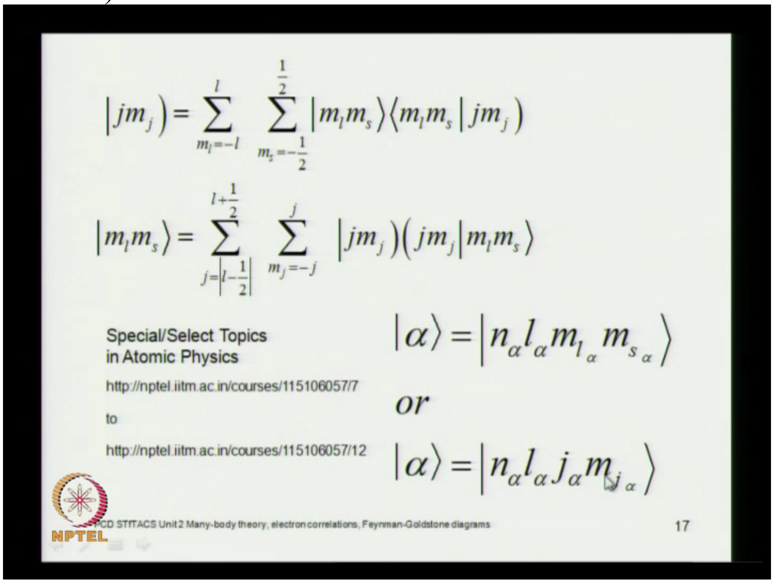
And depending on whether you are dealing with a symmetric orbital part or a symmetric spin part you get the triplet or the singlet states at this again I will not spend any time discussing this. We have had fairly extensive discussion in our previous course in atomic physics. So, you can certainly refer back to that.

And I will just like to remind you that if you consider the diagonalization of the Coulomb interaction in this you know that the triplet state is less punished as Landau and Lifshitz call it, it has got a lower energy than the singlet okay.
(Refer Slide Time: 23:33)



$$|jm_j)=\sum_{m_l=-l}^{l}\sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}}|m_lm_s\rangle\langle m_lm_s|jm_j)$$

$$|m_lm_s\rangle=\sum_{j=\left|l-\frac{1}{2}\right|}^{l+\frac{1}{2}}\sum_{m_j=-j}^{j}|jm_j)(jm_j|m_lm_s\rangle$$

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$$|\alpha\rangle=|n_\alpha l_\alpha m_{l_\alpha} m_{s_\alpha}\rangle$$

or

$$|\alpha\rangle=|n_\alpha l_\alpha j_\alpha m_{j_\alpha}\rangle$$

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So, now you can of course right the single particle quantum numbers either as n, l, ml, ms or as n, l, j, mj and you can write one in terms of the other by simply carrying out this rotation of the base vectors in the couple angular momentum space okay. You have got two sources of angular momentum for the electron one is orbital angular momentum, the other is spin angular momentum.

And you can have their uncoupled spaces or you can have the couple spaces and you can write both are equally valid. You can write the wave functions either in terms of one basis or the other, any basis is good all you need is a complete set of basis and some of these details again we have discussed at length in our previous course in atomic physics. And some of these video lectures are also available on the internet.

And you can refer to that if required but I just want to mention that you can use either of the two to designations.

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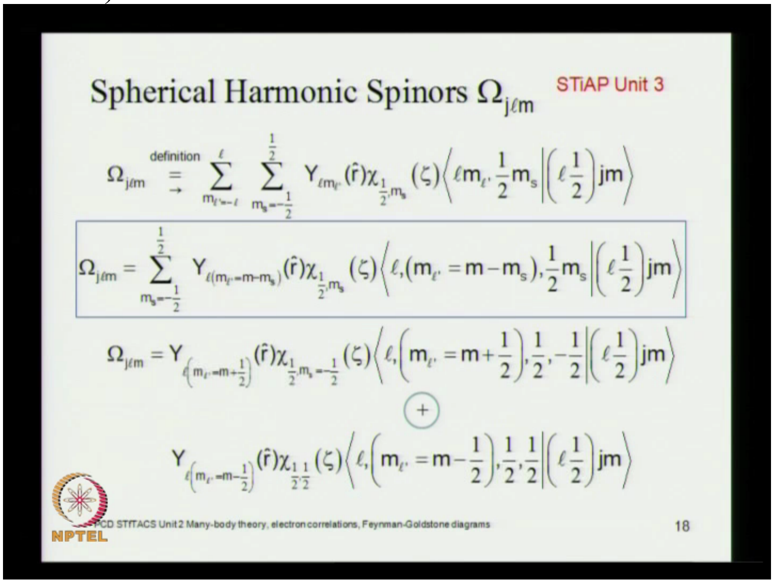

Spherical Harmonic Spinors $\Omega_{j\ell m}$

STiAP Unit 3

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

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

$$\Omega_{j\ell m} = Y_{\ell\left(m_{\ell}=m+\frac{1}{2}\right)}(\hat{r})\chi_{\frac{1}{2},m_s=-\frac{1}{2}}(\zeta)\left\langle \ell,\left(m_{\ell}=m+\frac{1}{2}\right),\frac{1}{2},-\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm\right\rangle$$

$$\oplus$$

$$Y_{\ell\left(m_{\ell}=m-\frac{1}{2}\right)}(\hat{r})\chi_{\frac{1}{2},\frac{1}{2}}(\zeta)\left\langle \ell,\left(m_{\ell}=m-\frac{1}{2}\right),\frac{1}{2},\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm\right\rangle$$

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And depending on the coupling scheme if you are coupling you know if the jm basis you have these spherical harmonics spinners which are you know which have two rows and one column. So, you can write these wave functions in terms of these spherical harmonics spinners, so instead of the ml, ms basis right.

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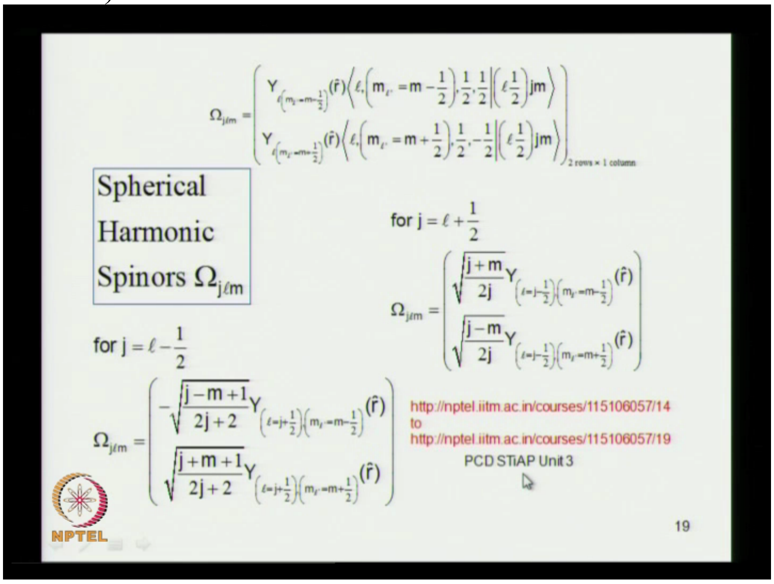

$$\Omega_{j\ell m} = \begin{pmatrix} Y_{\ell\left(m_{\ell}=m-\frac{1}{2}\right)}(\hat{r})\left\langle \ell,\left(m_{\ell}=m-\frac{1}{2}\right),\frac{1}{2},\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm\right\rangle \\ Y_{\ell\left(m_{\ell}=m+\frac{1}{2}\right)}(\hat{r})\left\langle \ell,\left(m_{\ell}=m+\frac{1}{2}\right),\frac{1}{2},-\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm\right\rangle \end{pmatrix}_{2\text{ rows}\times 1\text{ column}}$$

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

for $j=\ell+\frac{1}{2}$

$$\Omega_{j\ell m} = \begin{pmatrix} \sqrt{\frac{j+m}{2j}}\,Y_{\left(\ell=j-\frac{1}{2}\right)\left(m_{\ell}=m-\frac{1}{2}\right)}(\hat{r}) \\ \sqrt{\frac{j-m}{2j}}\,Y_{\left(\ell=j-\frac{1}{2}\right)\left(m_{\ell}=m+\frac{1}{2}\right)}(\hat{r}) \end{pmatrix}$$

for $j=\ell-\frac{1}{2}$

$$\Omega_{j\ell m} = \begin{pmatrix} -\sqrt{\frac{j-m+1}{2j+2}}\,Y_{\left(\ell=j+\frac{1}{2}\right)\left(m_{\ell}=m-\frac{1}{2}\right)}(\hat{r}) \\ \sqrt{\frac{j+m+1}{2j+2}}\,Y_{\left(\ell=j+\frac{1}{2}\right)\left(m_{\ell}=m+\frac{1}{2}\right)}(\hat{r}) \end{pmatrix}$$

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So, here again the details can be found in unit 3 of the previous course on atomic physics. But I want to quickly go over to the many-electron formalism which really requires us to go in for second quantization methods.

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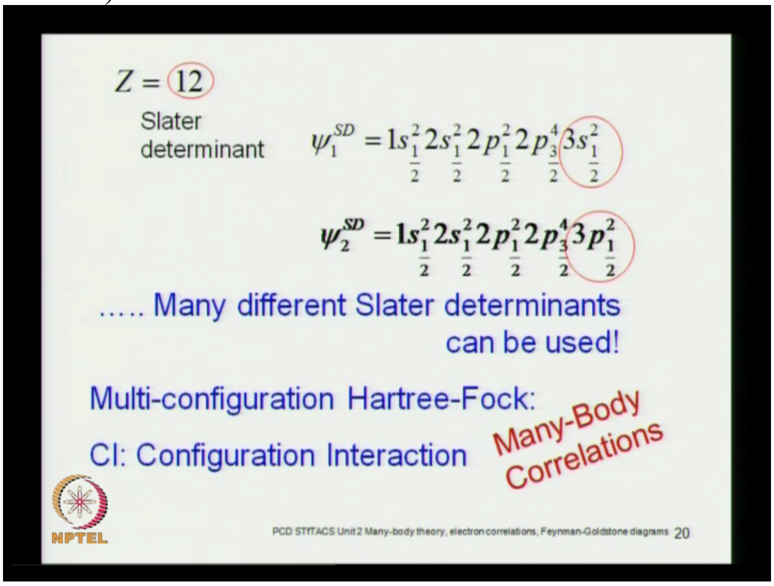

$Z = \boxed{12}$

Slater determinant $\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3s_{\frac{1}{2}}^2$

$\psi_2^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3p_{\frac{1}{2}}^2$

….. Many different Slater determinants can be used!

Multi-configuration Hartree-Fock:

CI: Configuration Interaction

Many-Body Correlations

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Now let us take a particular case a many electron system. Let us take the case of magnesium now magnesium has got 12 electrons the usual configuration is 1s2, 2s2, 2p6, 3s2 okay. The 2p is the spin orbit split right because of the relativistic effects. In the nonrelativistic quantum mechanics you will not have the spin at all right.

In relativistic quantum mechanics or in nonrelativistic quantum mechanics in which spin is plugged in on an ad hoc basis then also you can do some quantum mechanics with spin. Then you have j becomes a good quantum number and j is either half or 3 half for l = 1, for 2p l =1, s for the electron is half. So, you have two possibilities l + half and l - half right, from angular momentum coupling.

And the l + half gives you the j = 3 half state in which you can have 4 electrons because this has got a degeneracy which is fourfold for ej mj can take 4 values. So, for j = 3 half mj can take 3 half, 1 half, -half, -3 half, so it has got a fourfold degeneracy. And for j = half you have got a twofold degeneracy for j = half, mj can be plus or minus half. So, this is your configuration the superscript SD stands for the Slater determinant.

And this is the Slater determinant which I call as Slater determinant 1 which I write as a subscript. Which is an anticipation of the fact that we will have a Slater determinant 2, 3, 4 how far can you account, many right. So, you can have a number of Slater determinants. Let us consider this one, now instead of 3s2, I have got the first ten electrons go in the same states. But the 11th and the 12th electron instead of going in 3s go into 3p.

Now this is also magnesium atom you have got the same number of neutrons, the same number of protons, the same nucleus, the same number of electrons but the configuration is different. And if you were to write a Slater determinant for the first configuration compare it with the Slater determinant for the second configuration you obviously recognize the fact that the two Slater determinants must be different from each other okay.

In other words each Slater determinant corresponds to a particular configuration there is a one-to-one correspondence between the given configuration and the Slater determinant okay there is a one-to-one correspondence. And you can have many different Slater determinant you can have two electrons in 3p 3 half.

You can have two electrons in 3d 1 half, sorry 3d 3 half, 3d of course does not have one half, 3d has got either 5half or 3 half. So, you can have what else, 4s, 5p anything you have really infinite number of possible Slater determinant. And strictly speaking to have a complete basis you must include all of these.

And according to the fundamental consideration that we have in the expansion of an arbitrary wave function in a linearly independent complete set of basis you must have expand the magnesium wave function in terms of this complete set of basis. So, you really have infinite Slater determinant, yes the coefficients of most of them may go to 0.

But the coefficient of many may not go to 0 and how many really, you really do need to include depends on the nature of the correlation that is there in the system, in the 12 electron system. So, you have got a many body system which contains 12 electrons, this is your many body system, this is your many electron system and it is a correlated system. Now if you have more Slater determinant what happens to your Hartree Fock.

In the Hartree Fock you did an extremum of the Hamiltonian the expectation value of the Hamiltonian in a single Slater determinant right. But now you recognize the fact that you have more than one Slater determinant 2, 3, 4 maybe more a certain number of Slater determinant and all of these later determinants need to be considered. This is what is meant by saying that you must go beyond the Hartree Fock.

At what requires you to go beyond the Hartree Fock is the Coulomb correlation. So, this is the definition of Coulomb correlation. Coulomb correlation is what is left out of the Hartree Fock okay. In the single configuration Hartree Fock, you of course have the Coulomb interaction. All those two electron integrals that you did in your previous course okay, there are matrix elements of 1 over rij that is the Coulomb interaction right.

So, you had the one Coulomb interaction you also have the exchange how did he have the exchange because you had anti symmetric wave functions. So, you had the exchange you also have the Coulomb interaction but you restricted yourself to a single Slater determinant. So, the confinement to a single Slater determinant is the single particle model when you go beyond that you begins to include correlations.

It does not mean that there is no correlation in the Hartree Fock there is the exchange-correlation but there is no Coulomb correlation (Question time: 32:11- not audible) sorry because it is coming once again from the 1over r12 but the one over r12 is coupling not only states from a single configuration but also from this okay.

There are so many other configurations and all of these correlations they are coming because of the Coulomb interaction. But then coming from different configurations (Question time: 32:45- not audible) in the last two but they could refer in many others right that is the I mean I thought that is the Coulomb correlation; that is just another possible state of the 12 electron system.

And the reason you have this alternative state as an accessible state for the 12 electron system is because of the Coulomb correlation okay. They should all have the same angular momentum so finally they must couple to the same j that is a matter of detail but I am not getting into that at this point.

(Question time: 33:28- not audible) Coulomb correlation is because of the anti symmetry of the wave function and it is happening inside internal Slater determinant, it is it is there in each Slater determinant. So, this is one Slater determinant which is completely anti symmetric. So, if you interchange any two rows or any two columns the sign of the determinant will change okay. So, the sign of the determinant will change under any interchange.

So, the exchange correlation which is the anti symmetry of the wave function or the Pauli Exclusion Principle that is already built into this and this is a different Slater determinant. But the system wave function is a linear superposition of these two. So, you are then relayed to what is called as a multi configuration Hartree Fock.

So, now you cannot deal with just a single Slater determinant but a linear superposition of Slater determinant what is it coming, where is it coming from it is coming because you have to consider the interaction between the first configuration and the second configuration this is what is called as CI or the configuration interaction okay.

So, this is the configuration interaction and this requires you to go beyond the Hartree Fock and that is what many-body theory is about. So, even the Hartree Fock in a certain sense is a many-body theory. In a certain sense it also has the correlation but the correlation it has is only the exchange correlation.

But the name many-body theory is typically reserved for those formalisms in you go beyond the Hartree Fock. Consider the configuration interaction and include the Coulomb correlations not just the Fermi correlations not just the exchange correlations. So, these are what are typically called as many body correlations.

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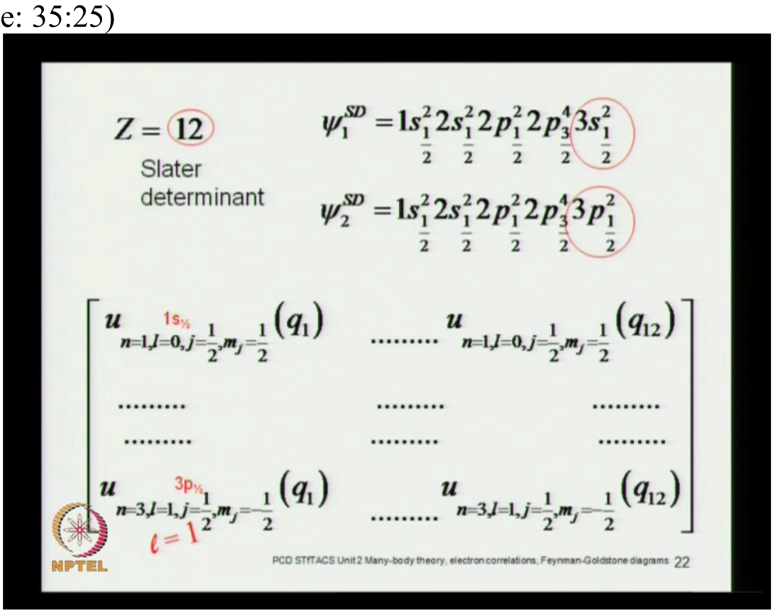

$Z = \boxed{12}$

Slater determinant

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 \boxed{3s_{\frac{1}{2}}^2}$$

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 \boxed{3p_{\frac{1}{2}}^2}$$

$$\begin{bmatrix} \overset{1s_{1/2}}{u}_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_1) & \cdots\cdots\cdots & u_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_{12}) \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ \overset{3p_{1/2}}{u}_{n=3,\underset{l=1}{l=1},j=\frac{1}{2},m_j=-\frac{1}{2}}(q_1) & \cdots\cdots\cdots & u_{n=3,l=1,j=\frac{1}{2},m_j=-\frac{1}{2}}(q_{12}) \end{bmatrix}$$

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And I will describe it once again for the magnesium atom so if it has this 2p6, 3s2 this is the usual configuration that one talks about. This is the default that one that comes to your mind and the Slater determinant for this will consist of 12 columns so q1 through q12 okay. So, as you go from left to right you are going from first column, to the second, the third until you get to the 12 column and when you go through the rows one to the next and so on.

You go from different quantum states this is nlj mj quantum numbers are what I have used okay. So, this is the one s up state right and then the last one will be the 3s down with mj = -1 okay. So, that is the 12th row okay. So you have got a 12 by 12 determinant this is the determinant wave function. And this is corresponding to different single particle states. Each row is labeled by a set of 4 quantum numbers.

All the 4 quantum numbers are the same in a given row. They change only from one row to the next in at least one quantum number okay. They may change in more than one quantum number like if you look at the first row and the last row, the first row has got mj = half, the last row has about mj = - half. But that is not the only difference the first row has got n = 1, the last row has got n = 3.

So, they may change in one or more quantum numbers. But there must be at least one quantum number which is different. If all of them are the same then you have two rows which are equal in a determinant, the determinant would vanish okay. So, this is where you have the Slater determinant corresponding to the 2p6, 3s2 configuration. But then we agreed that you have not only this configuration.

But you also have the possibility of the 3p2 configuration and not just this there are many more, well let us take this as an example. So, if you were to write a Slater determinant for this then you will have the first 10 rows will be the same but the 11th and 12th row will be different. And the 12th row will now have l = 1 here mind you okay. Because this is the 3p state, so you have got a 3p here and not a 3s anymore.

So, what you are going to do is you have these different single particle states and you can arrange them in some order. You can say that okay n = 1, l = 0, j = half, mg = half is my state number 1, n = 1, l = 0, j = half, mg = -half is my state number two. And you start giving numbers to each row okay, so the first 10 you have labeled then 11 and 12 you label according to the 3s2. Now these two rows you cannot label anymore as 11 and 12.

Because the label number 11 corresponds to the 3s up, so this will be your 13 and 14 okay. What is happening in this later determinant is that 11 and 12 are empty and 13 and 14 are occupied okay. The first 10 are the same but what was 11 and 12 in the previous configuration is now vacant and you have an occupancy of 2 in 3p so in other words these different Slater determinants which correspond to different configurations.

You can refer to them in terms of occupation numbers of single particle states. What is the occupation number of state number 1? What is occupation number of state number 2? What is the occupation number of state number 11? What is occupation number of state number 13? What is the occupation number of state number 20? Because you have got an infinite set of Slater determinant right.

So, you can write all of this in terms of these occupation numbers. Now that is the formalism which corresponds to the occupation number space and this is where we use second quantization methods. Which is what we are going to discuss yes and Amkur you have a question (Question time: 40:33) how many rows and how column you have this, you will always have 12 by 12 because you are describing a 12 electron system.

Then how can you say that the 11th and 12th row I mean not there we are using the , the 11th label is empty, the 11th label is empty, 11th row is occupied by what would be the 13th label. The 12th row will be occupied by what is the 14th label. (Question time: 41:11) here it is; you will always have each determinant for an N electron system will be an N by n determinant okay.

So it has to have 12 rows and 12 columns but which 12 rows that set is what we are talking about. And in this set the labels each label corresponds to a particular one electron state. And the last two labels in this are different from the last two of the previous. So, if you look at this you have got the 3p half is the last one. In the previous one you add this is you had the 3s okay. So, the 12th row was occupied by the 3s quantum numbers.

But now the 12th row is occupied by 3p one-half okay. So, you have 12 rows and 12 columns but which 12 rows is different in different Slater determinant. (Question time: 42:23)Previous case we are denoting by these two position is by q11th and q12th yeah and in this case whether we should use some q13, q14.

No, no you are talking about two electrons you are talking about 12 electrons what is the probability amplitude that a particular electron at coordinate qi is in the state alpha. So, here this is the probability amplitude that the electron at q1 is in this state okay. This probability amplitude is different from the probability amplitude that the electron at q1 is in the 3s state okay.

So, you have got 12 electrons they are where they are in the spin orbital space okay. But the probability amplitude that they are in different quantum state single particle quantum states is different. Which is why the rows are different okay, the coordinates of course will be from q1 to q2 all their only 12 electrons. (Question time: 43:40-not audible) 1 and 3p half and 1, It is certainly possible.

So, you have the levels 11 and 13th; you could have you can have that as a possible configuration. So, you will have infinite configurations of course there are some other constraints because the total angular momentum must be the same and so on. So, those are the details that we can talk about. But basically you will have many different kinds of possibilities. You can have two electrons going from first configuration to the other.

You can have one going from one state, the second going to a different state okay. So, here you have what we have done is we have elevated 3s2 to 3p2. You can elevate 3s2 to 3p2, you can elevate 3s2 1 going to nl and the other going to n prime l prime okay. So, there are all kinds of possibilities okay. And that is what makes many-body theory very challenging okay. And all this is happening because of the electron correlations.

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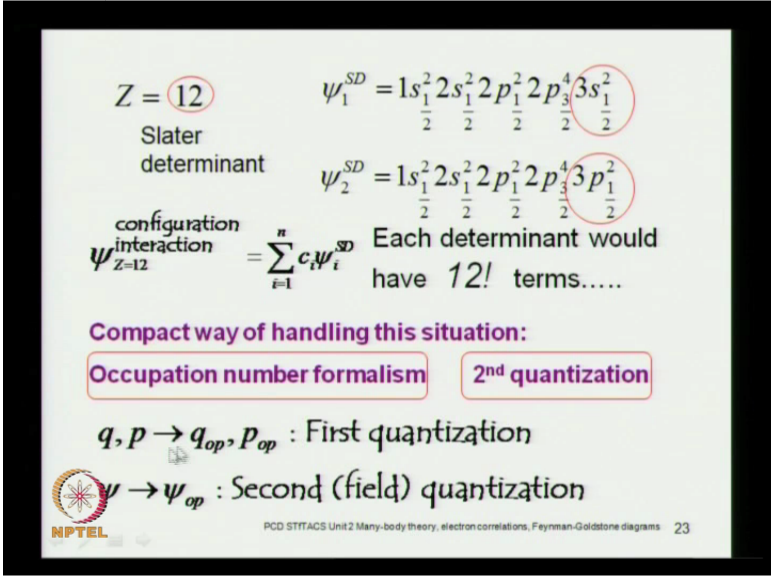

$Z = \boxed{12}$

Slater determinant

$\psi_1^{SD} = 1s^2_{\frac{1}{2}} 2s^2_{\frac{1}{2}} 2p^2_{\frac{1}{2}} 2p^4_{\frac{3}{2}} 3s^2_{\frac{1}{2}}$

$\psi_2^{SD} = 1s^2_{\frac{1}{2}} 2s^2_{\frac{1}{2}} 2p^2_{\frac{1}{2}} 2p^4_{\frac{3}{2}} 3p^2_{\frac{1}{2}}$

$\psi_{Z=12}^{\text{configuration interaction}} = \sum_{i=1}^{n} c_i \psi_i^{SD}$

Each determinant would have 12! terms.....

Compact way of handling this situation:

Occupation number formalism **2nd quantization**

$q, p \rightarrow q_{op}, p_{op}$: First quantization

$\psi \rightarrow \psi_{op}$: Second (field) quantization

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So, there are these possibilities and the configuration interaction wave function is now a linear superposition of all these Slater determinant. And depending on how many configurations need to be considered in this. This n can be either a small number like 2 or 3 or 4 or it can be quite large and people do calculations with hundreds sometimes even with thousands of configurations.

Now it is a mass because each determinant has got factorial 12 terms okay. We already felt like quiting when we were dealing with a single determinant. When we thought about a number like factorial 10 just for the neon atom which is a small atom right now you have factorial n terms and so many of them. So, there is a good way of handling this which is what makes use of the occupation number formalism.

This is where the second quantization methods come into the picture. So, the occupation number formalism is sometimes called as the second quantization why second because the first quantization was doing away with classical dynamical variables q and p position and momentum which were simultaneously measurable accurately in classical mechanics. Recognizing the fact that such a simultaneous accurate measurement is not possible.

And therefore replacing them by operators that was your quantization okay. Now what we are going to do is that the wave functions that you are talking about will also be treated as operators. In the first quantization methods the wave functions Psi was like a scalar function it was not treated like an operator. Now in the second quantization method, so it is a technique okay.

And because it is quantization of the scalar field it is sometimes also called as field quantization. But these are different expressions to talk about the same technique. The technique is essentially that of occupation number formalism also called a second quantization or field quantization, field theory.

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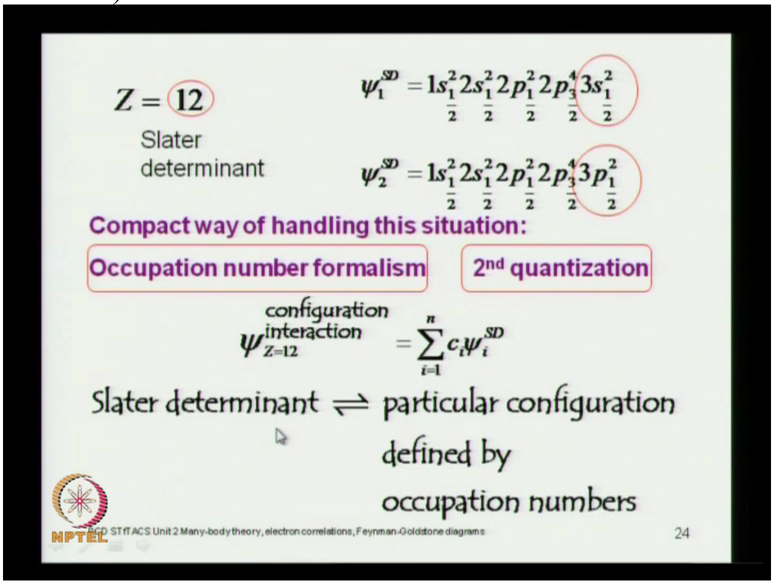

$Z = \boxed{12}$

Slater determinant

$$\psi_1^{SD} = 1s^2_{\frac{1}{2}} 2s^2_{\frac{1}{2}} 2p^2_{\frac{1}{2}} 2p^4_{\frac{3}{2}} \boxed{3s^2_{\frac{1}{2}}}$$

$$\psi_2^{SD} = 1s^2_{\frac{1}{2}} 2s^2_{\frac{1}{2}} 2p^2_{\frac{1}{2}} 2p^4_{\frac{3}{2}} \boxed{3p^2_{\frac{1}{2}}}$$

Compact way of handling this situation:

Occupation number formalism **2nd quantization**

$$\psi_{Z=12}^{\text{configuration interaction}} = \sum_{i=1}^{n} c_i \psi_i^{SD}$$

Slater determinant ⇌ particular configuration defined by occupation numbers

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And all of these are related terms depending on different context they do have different emphases contained in these alternate expressions. And they are inspired by the fact in the context of the fermions that each Slater determinant is decided by a particular configuration which means that which single particle states are occupied. In the first configuration other than the first ten these two are occupied are these two are empty.

But in this case the 3s are empty and the 3p are occupied right. So the occupation numbers are different and you can talk about going from one to the other by destroying two electrons in the first and creating two electrons in the other. So, you can begin to make use of operators which are called as creation and destruction.

Operators of creation and annihilation operators and the second quantization methods make use of these operators. And that is the formalism that we are going to learn in this unit.

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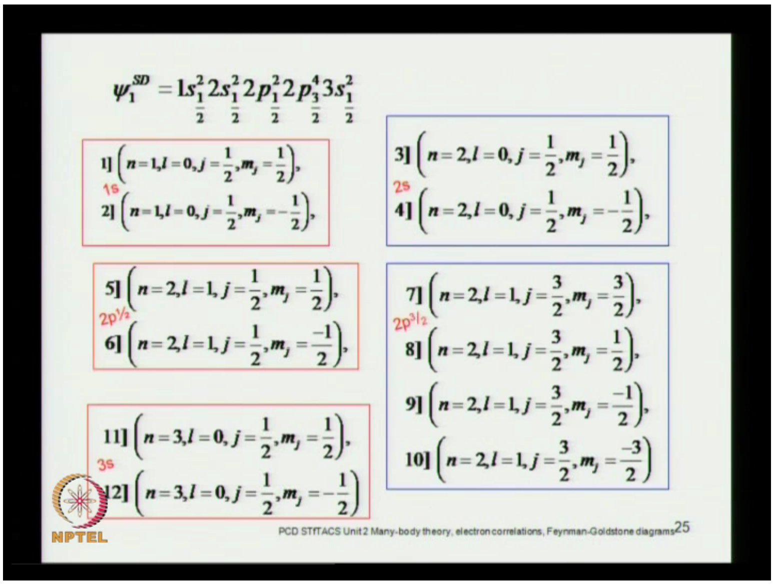

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3s_{\frac{1}{2}}^2$$

1s
1] $\left(n=1, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
2] $\left(n=1, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2s
3] $\left(n=2, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
4] $\left(n=2, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2p½
5] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
6] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{-1}{2}\right)$,

2p3/2
7] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{3}{2}\right)$,
8] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{1}{2}\right)$,
9] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-1}{2}\right)$,
10] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-3}{2}\right)$

3s
11] $\left(n=3, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
12] $\left(n=3, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$

NPTEL

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So, you are Slater determinant in the first configuration was made up of these states 1 and 2, 3 and 4 okay. Then you had the 2p 1 half you had the 2p 3 half and then you had two electrons in the 3s state. So, these are the 12 single particle states when you talk about the second configuration the 11th and 12th those two states, electrons in those two states are effectively destroyed.

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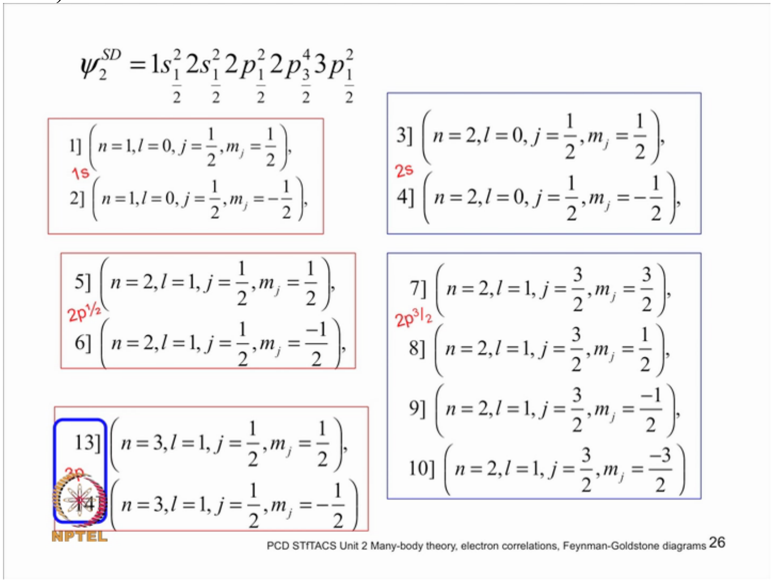

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3p_{\frac{1}{2}}^2$$

1s
1] $\left(n=1, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
2] $\left(n=1, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2s
3] $\left(n=2, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
4] $\left(n=2, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2p½
5] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
6] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{-1}{2}\right)$,

2p3/2
7] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{3}{2}\right)$,
8] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{1}{2}\right)$,
9] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-1}{2}\right)$,
10] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-3}{2}\right)$

3p
13] $\left(n=3, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,
14] $\left(n=3, l=1, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$

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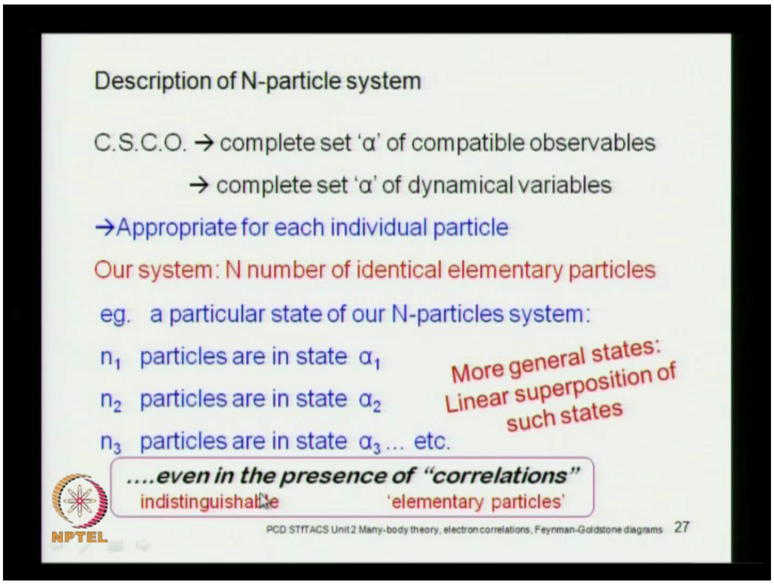

Description of N-particle system

C.S.C.O. → complete set 'α' of compatible observables

→ complete set 'α' of dynamical variables

→Appropriate for each individual particle

Our system: N number of identical elementary particles

eg. a particular state of our N-particles system:

n_1 particles are in state α_1

n_2 particles are in state α_2

n_3 particles are in state α_3 … etc.

More general states: Linear superposition of such states

….even in the presence of "correlations"

indistinguishable 'elementary particles'

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And you create 2 n3p 1 half okay. So, in the second configuration you have instead of the 11 and 12 you have 13 and 14 that is what I was referring to okay. And you can refer to these in terms of single particle operator's creation and destruction operators and these are the ones which are used to describe the N particle system. Essentially you are describing them in terms of a complete set of compatible observables okay.

Our Eigen values of complete set of commuting operators from Dirac's CSCO and you have N number of identical particles. So, the individuality of the particle that idea is carried over but so is the indistinguishability okay. So, is the statistics and so are now also the many body correlations. So, you use the single particle labels okay even in the presence of not just interactions.

But also in the presence of correlations and I have made a very clear distinction between the term interaction and correlation. So, correlation has got a specific connotation in the context in which we are discussing this. So, you describe a particular Slater determinant a particular configuration by spelling out how many particles are there Slater alpha one. Each alpha is a set of four quantum numbers.

How many particles are there in state alpha 2, now this number is either one or zero for Fermi particles. When it can be anything for Bose particles because there is no Pauli Exclusion Principle for bosons right, you can put any number of particles in a one Bose state as a matter of fact you can put all of them and get Bose Einstein condensation right.

So, there is no such restriction in that but the basic property of any configuration is of any many electron system is how many particles reside in these single particle states okay. And that number is the occupation number of that state. And this will give you one configuration but then of course the system wave function will contain many other configurations.

And you will have a linear superposition of such states. So, this is the idea behind indistinguishability, you take into account the correlations you recognize the elementary nature of these particles okay although they are indistinguishable.
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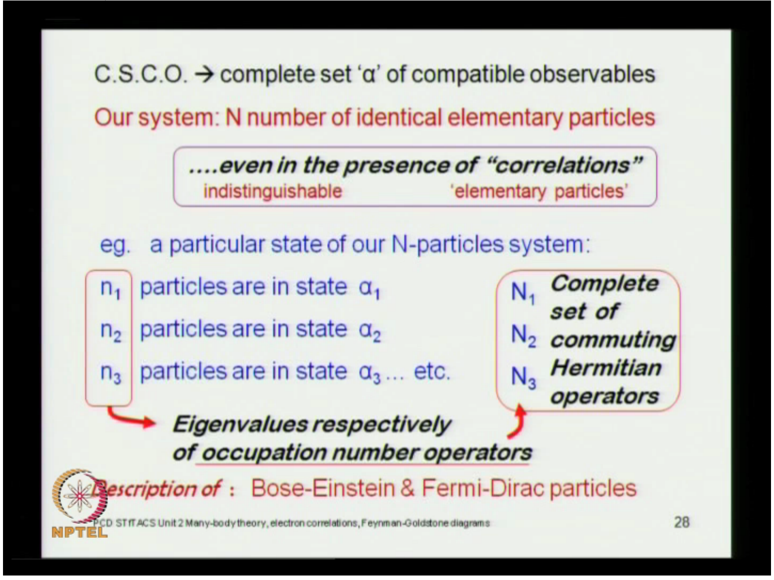

C.S.C.O. → complete set 'α' of compatible observables

Our system: N number of identical elementary particles

....even in the presence of "correlations"
indistinguishable 'elementary particles'

eg. a particular state of our N-particles system:

n_1 particles are in state α_1
n_2 particles are in state α_2
n_3 particles are in state α_3 ... etc.

N_1 N_2 N_3 ***Complete set of commuting Hermitian operators***

Eigenvalues respectively of occupation number operators

Description of : Bose-Einstein & Fermi-Dirac particles

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So you reconcile with that and essentially you can get these numbers as Eigen values of the occupation number operators which are a complete set of commuting hermitian operators. So, you define these occupation number operators and of course the description will be different in terms for Bose particles and for Fermi particles because if you have created a particle in one vacuum state and if that particle is a Fermi on you cannot create any more in that state.

But if it is the Bose particle the creation operator can operate twice or ten times or have a Bose Einstein condensation and pump everything into that okay. So, the properties the commutation properties of the creation and destruction operators for Fermi and Bose particles will be different. So the statistics will now be incorporated in the operators.
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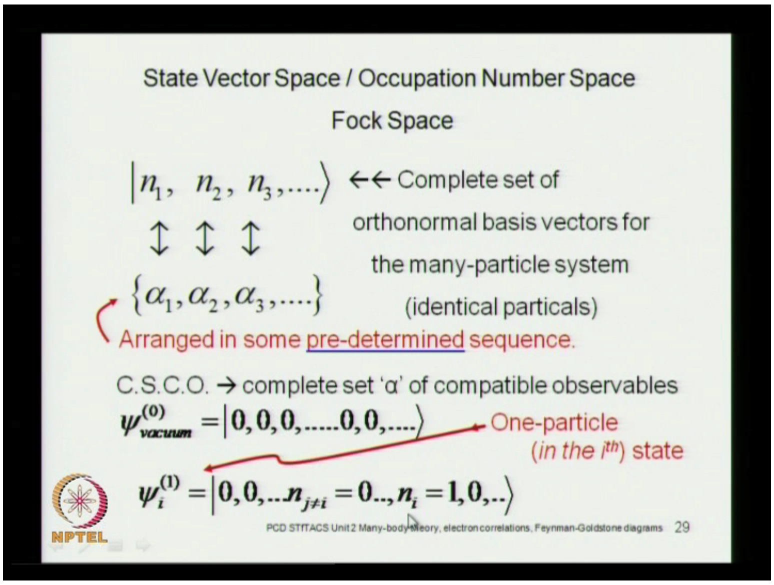

State Vector Space / Occupation Number Space

Fock Space

$|n_1,\ n_2,\ n_3,....\rangle$ ←← Complete set of orthonormal basis vectors for the many-particle system (identical particals)

$\updownarrow\ \updownarrow\ \updownarrow$

$\{\alpha_1, \alpha_2, \alpha_3, ...\}$

Arranged in some pre-determined sequence.

C.S.C.O. → complete set 'α' of compatible observables

$\psi^{(0)}_{vacuum} = |0,0,0,.....0,0,....\rangle$

One-particle (*in the i^{th}*) state

$\psi^{(1)}_i = |0,0,..n_{j\neq i} = 0..,n_i = 1,0,..\rangle$

So, you have some sort of an arrangement this alpha1, alpha2, alpha3 and is some predetermined sequence you decide what is in the your state number 11, you decide what is your state number 12, decide what is your state number 13, 14. And then you say that state number 11 and 12 is occupied in this and 13 and 14 is vacant.

And in the next configuration 11 and 12 are vacant and 13 and 14 but these numbers have to be pre assigned. So, you have some sort of a predetermined sequence and in this sequence you give the occupation numbers and then you have a vacuum state in which all of these particles, all of these states are vacant. You can have a single particle state in which there is only one particle in the state i.

So in the ith state ni = 1 and whenever j is not equal to i, this occupation number of only for the ith state the occupation number is equal to 1 whenever j is not equal to i the occupation number is 0. So, this is how you would describe a single particle state and depending on the number of particles you can write different occupation number states.

So, I will conclude my discussion today would be happy to take a few questions and we will go from here in the next class.

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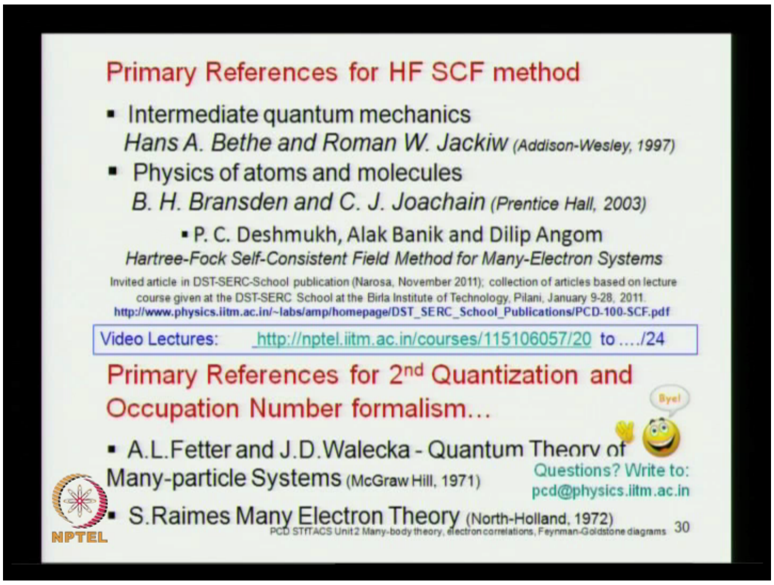

Primary References for HF SCF method

- Intermediate quantum mechanics
  Hans A. Bethe and Roman W. Jackiw (Addison-Wesley, 1997)
- Physics of atoms and molecules
  B. H. Bransden and C. J. Joachain (Prentice Hall, 2003)
- P. C. Deshmukh, Alak Banik and Dilip Angom
  Hartree-Fock Self-Consistent Field Method for Many-Electron Systems
  Invited article in DST-SERC-School publication (Narosa, November 2011); collection of articles based on lecture course given at the DST-SERC School at the Birla Institute of Technology, Pilani, January 9-28, 2011.
  http://www.physics.iitm.ac.in/~labs/amp/homepage/DST_SERC_School_Publications/PCD-100-SCF.pdf

Video Lectures: http://nptel.iitm.ac.in/courses/115106057/20 to …./24

Primary References for 2nd Quantization and Occupation Number formalism…

- A.L.Fetter and J.D.Walecka - Quantum Theory of Many-particle Systems (McGraw Hill, 1971)
- S.Raimes Many Electron Theory (North-Holland, 1972)

Questions? Write to:
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In the meantime there are some references which I would like to draw your attention to for Hartree Fock we have already given this reference in the previous course which is either Bethe and Jackiw or Bransden and Joachain these are the primary sources. And for second quantization and occupation number formalism I will primarily use Fetter and Walecka book or the book by Raimes called many-electron theory.

Questions(Question time: 54:55 – not audible)Given that magnesium two electron system the alpha's will be, the set of alpha you are referring to each configuration will be having 12 once and all other are zero's, so each of that kind of sets of configuration; yes, yes exactly. So out of the infinite numbers 12 will be occupied all the others will be 0.

But which 12 is going to be different for each configuration, a particular choice of 12 defines one Slater determinant okay. So there is one to one correspondence between a configuration at a Slater determinant and an occupation number state vector. So, these are state vectors in what is called as the occupation number space sometimes also called as a Fock's space.

(Question time: 55:48-not audible) where we are Raimes angulations right, so in our next class we will get into these second quantization operators the creation and destruction operators and the number operator and so on okay, all right. Thank you.