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

Lecture - 19
Many-Electron Atoms
Hartree-Fock Self-Consistent Field Formalism

Greeting, we will begin unit 4 today, this will be on many electron systems, we did the hydrogen atom, the non relativistic hydrogen atom first and then the relativistic hydrogen atom, we did the Dirac formalism of the hydrogen atom as well. And we will be very fortunate dealing with this, because the one electron coulomb problem has exact solutions and we got the exact solutions for the hydrogen atom, both for the non relativistic case as well as the relativistic case.

So, atoms in general other than the hydrogen atom, they have more than one electrons and 2 3 4 and so on and you got the whole periodic table. So, we need to develop the quantum mechanics of many electrons systems and this is really important, because atoms in a certain sense, are the basic building blocks of condensed matter. So, when atoms come together, you have molecules, clusters and condense matter. So, in some general sense, you can even say that, the atom is like what elementary particle is, somewhat similar in a certain sense that, it is the elementary ingredient of condense matter. So, all properties of condensed matter are derived from the properties of atoms and from their collective behavior.

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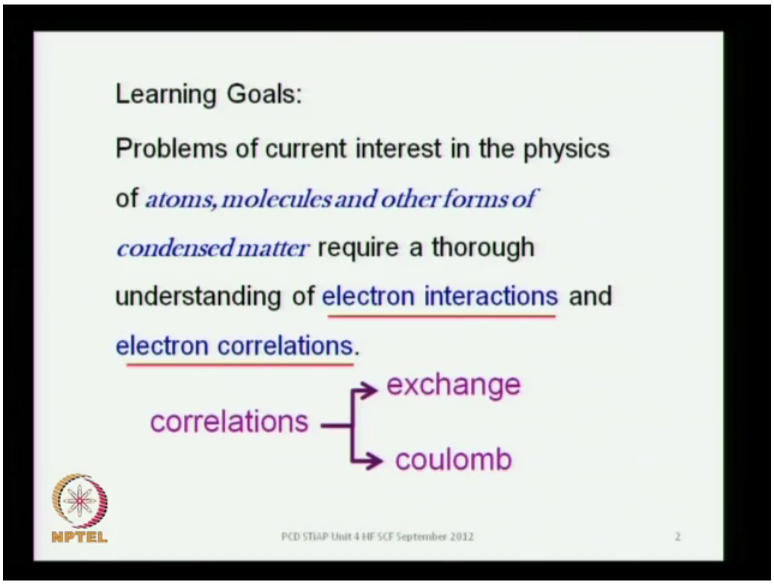

Learning Goals:

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 → exchange

correlations → coulomb

And we need to understand that, when you have more than one electron present then these electrons are going to interact with each other and we will talk about electron interactions with each other and also electron correlations. And I will make distinction between interactions and correlation, this difference will become clear, as the discussion progresses, that correlation has got a specific connotation, which will become very clear.

And in particular, I will talk about two different kinds of correlations, one which are known as exchange correlations and another kind of correlations, which are known as coulomb correlations, so we will talk about both of these in this unit. So, these are our primary learning goals and we will approach this from first principles as much as possible.

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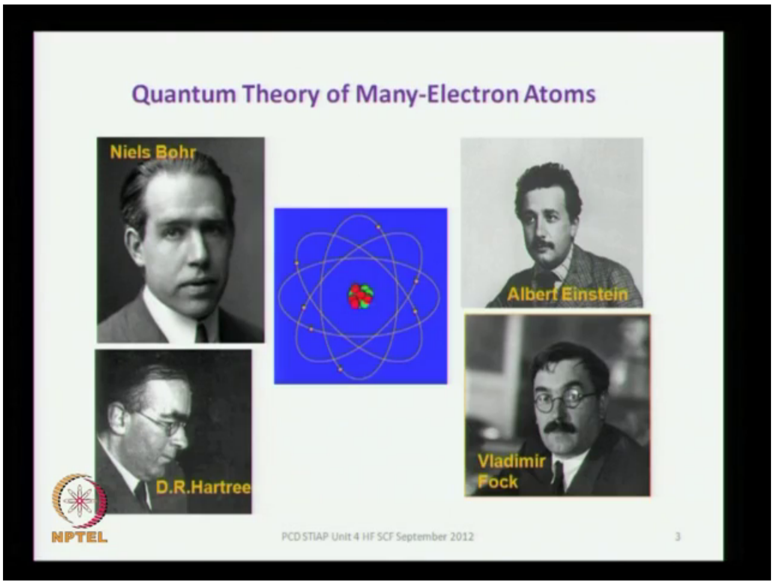

Quantum Theory of Many-Electron Atoms

And we will be extending quantum mechanics, which was developed by Einstein, Schrodinger, Isenberg and apply to atom atomic system by Niels Bohr. And then when it comes to the many electrons formalism, we will talk about the work of Hartree and Vladimir Fock, so this is our goal for this unit. I will be using Bethe and Jackiw's intermediate quantum mechanics, rather extensively for this unit. It is a book, which many of you would have used for the basic quantum mechanics.

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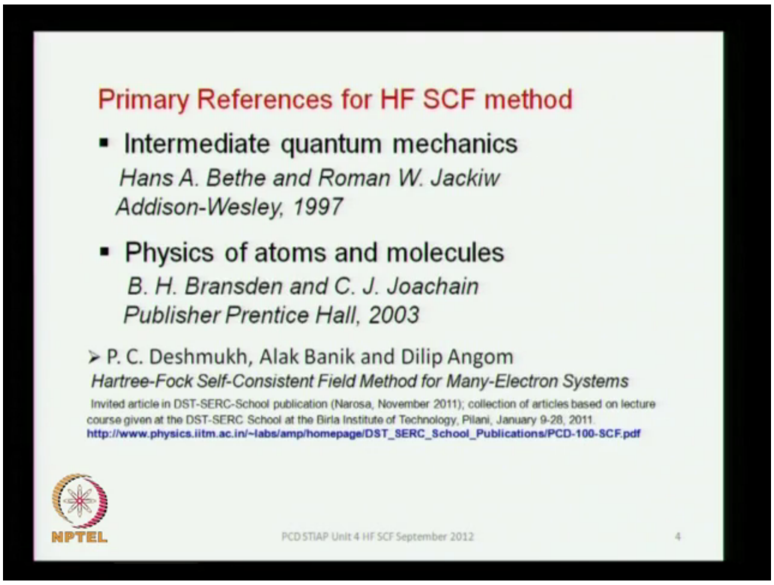

Primary References for HF SCF method

- 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
  Publisher 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

I will also use Bransden and Joachain books physics of atoms and molecules, and there is a small review on the Hartree-Fock method, which I have written with two of my colleagues, which is uploaded at the course web page, which also you can access, where some of the key features would be summarized. Now, this is the relationship that we have to address, so we will first work with the non relativistic many electron problem. And Schrodinger equation will read H psi equal to E psi for the N particle system, N being the number of electrons that we have in the system.

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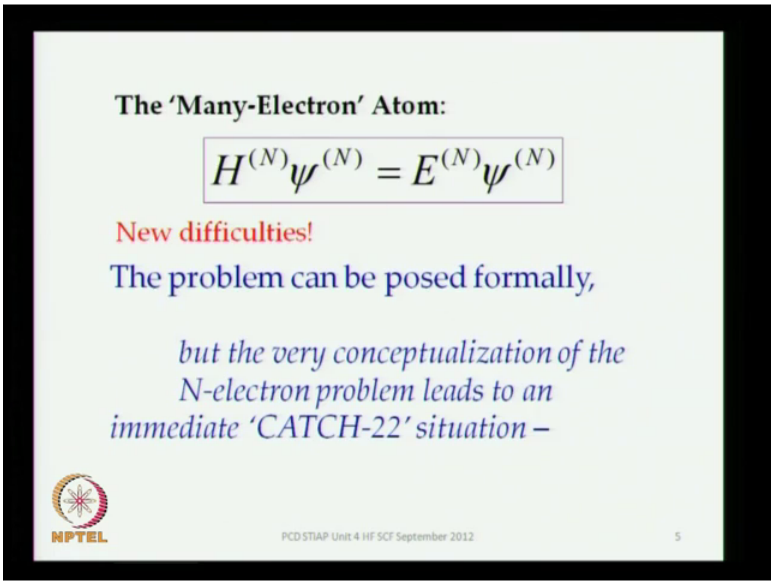

The 'Many-Electron' Atom:

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

New difficulties!

The problem can be posed formally,

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

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So far so good, but immediately we meet new difficulties and what are these new difficulties, what these new difficulties do, is to create a situation, which can perhaps we called as a CATCH-22 situation.

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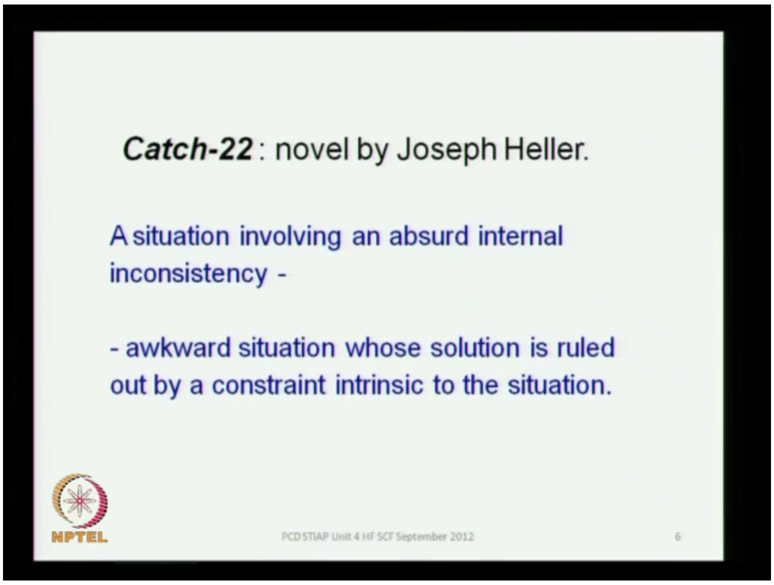

Catch-22 : novel by Joseph Heller.

A situation involving an absurd internal inconsistency -

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

And do you understand what CATCH-22 means, CATCH-22 actually this phrase comes from a novel by Joseph Heller and it meets so much impact on the English language, that it actually becomes accepted in the English language as a regular phrase. What it means is that, you have a situation, which has got some internal inconsistency, you can describe this situation. You can seek to solve that situation to address that situation and find some sort of solution, but the solution becomes impossible to be implemented, because of some internal constraints, which is intrinsic to the system.

It is a very fascinating novel and actually the situation in this novel is about an air force pilot, who does not want to go into the hazardous duties and he wants to escape from it. And he discovers that, he can escape from it on one ground that, if he is not physiologically fit, mentally fit to execute then he will relieve, so there was such a provision.

So, he applies, he asks to be relieved under that situation and then they say that, if he is sain enough to say that, he wants relive because of this reason then obviously, he is not mentally sick. So, it is a provision which is inbuilt to the situation and this is a CATCH-22, so there is a catch. And the many electron problem poses itself as a catch and I will tell you what the catch is.

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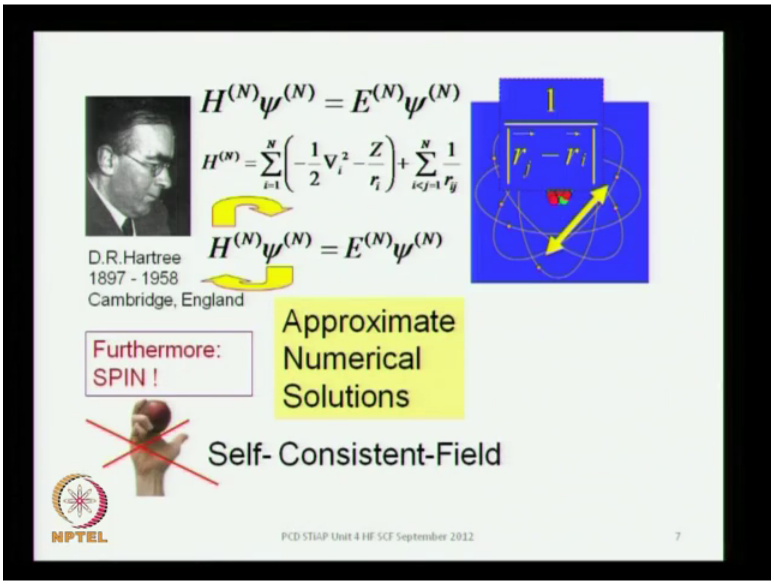

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

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

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

$$\frac{1}{\left|\vec{r}_j - \vec{r}_i\right|}$$

D.R.Hartree
1897 - 1958
Cambridge, England

Furthermore:
SPIN !

Approximate
Numerical
Solutions

Self- Consistent-Field

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So, let us look at the N electron Schrodinger equation, now you set up the Hamiltonian for N electron problem, which is a sum of the kinetic energy part. I have not written the mass which is natural units, put m equal to 1, H cross equal to 1, so this is the kinetic energy term. And then this is the potential energy of each electron on the field of the nucleus, there are Z protons on the nucleus. So, each electron would experience an attractive potential, which is Z over r and you would sum over i going from 1 to N and then each electron would repeal the other electrons.

So, between the i th and the j th electron, there would be the 1 over r i j coulomb repulsion and you must sum over all the i and j, i naught equal to j. So, this is the coulomb repulsion of between every pair of electrons, so this is your N electron Hamiltonian. Now, look at the system, if you have electrons in the atoms, so you have got the Z protons in the nucleus and then you have got this 1 over r i j term, which is between the i th and j th electron, between every pair.

Now, this is the distance between the i th and the j th electron, now the problem is that, electrons are not classical particles. So, they are not like point chargers and you cannot say that, this is where the i th electron is located, this is where the j th electron is located and this is the distance between them. So, that is how you would described the classical coulomb interaction between two classical charges. Now, the electrons are not like that, electrons are described by the waves in quantum mechanics.

So, they have a certain wave function associated with each electron, which is a probability amplitude function, as we know. Corresponding to this probability amplitude, there is a probability density and this multiplied by charged density is what would give you the charge in a certain volume. See, if you got a certain volume element over here, delta v and in this delta v, you find out what is the probability density integrated over the volume, that will give you the charge over here.

And then this charge would interact with the corresponding charge here, which is also be describe in terms of the probability density over here. And then these two charges would interact with each other, giving you the 1 over r i j term. So, that is precisely the catch, because to describe the charge density over here, do not you need the wave function for the electron you do. And how would you hoping to get this wave function, by solving the Schrodinger equation.

So, you set up the Hamiltonian, solve the Schrodinger equation and hope that. I will now get the wave function and use this wave function to describe the probability amplitude, the probability density and the charged density. But, you need the solution, even to pose the problem, that is a CATCH-22. So, you are caught up in a situation that, you need the Hamiltonian to get the wave function, but to constitute the Hamiltonian to formulate the Hamiltonian, you need the wave function.

And this is a vases circle and if you do not know how to deal with it, easiest thing to do is, is to quit physics and walkout or else, come up with some very nice innovative ideas and this is where self consistency comes in. What you can do is, I do not know the wave function and therefore, I cannot construct the Hamiltonian. So, let me make assumption on the wave function, I will make a guess, does not matter if it is wrong, let me make a guess.

And using this guessed wave function, I kick start the process, using this guess I construct the Hamiltonian and now using this Hamiltonian, which is based on a guessed wave function, I now solve the Schrodinger equation and get the solution. And now, I ask, is this solution the same as what I had guessed, if it was, I got lucky, if not, no problem I will change my guess. And then reconstruct the Hamiltonian with the new guessed wave function then solve the Schrodinger equation.

And then ask, is the new solution the same as my improved guess, it could be actually be worse, but it could be better. And you iterate on this process again and again and again and again, till you hit self consistency. Now, that is a trick and once you get the self consistency, you can then say that, now you know what the Hamiltonian is and now you know what the wave function is, you get the two together when you reach self consistency.

And then use that wave function to describe other properties of the atom and then do spectroscopy with these atoms or electrons structure analysis, collisions and so on. So, these solutions can be obtained numerically by carrying out this iterative process and this was a technique, which was developed by D. R. Hartree at Cambridge. And initially Hartree did not take to account the electrons spin but then there is the spin, which we know has to be taken into the account. And then the formalism of self consistency, which was developed inclusive of the electron spin, is what we called as a Hartree-Fock formalism, that is something to which Gardam Fock contributed significantly. So, that is the overall technique of Hartree-Fock.

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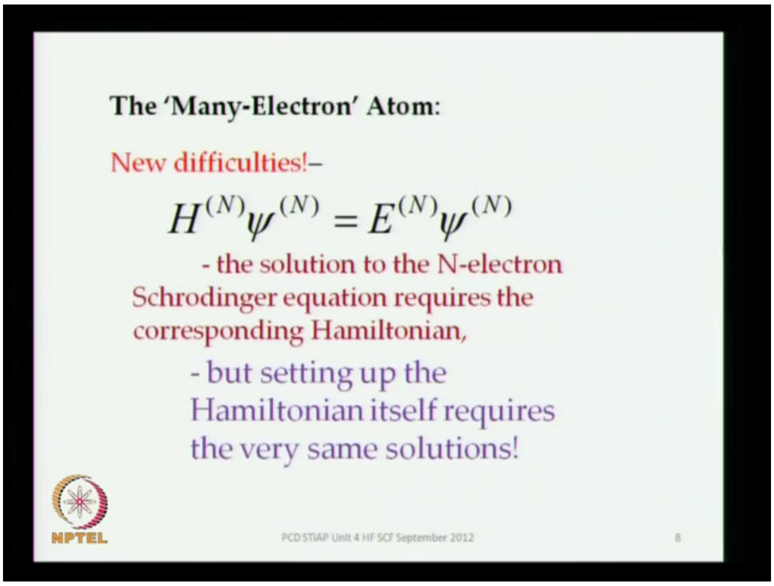

The 'Many-Electron' Atom:

New difficulties!–

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

- the solution to the N-electron Schrodinger equation requires the corresponding Hamiltonian,

- but setting up the Hamiltonian itself requires the very same solutions!

And essentially, the difficulty summarized on this slide, that setting up the Hamiltonian itself requires the very same solutions, which you hope to obtain by solving the Schrodinger equation. So, that is the difficulty that you are now going to address.

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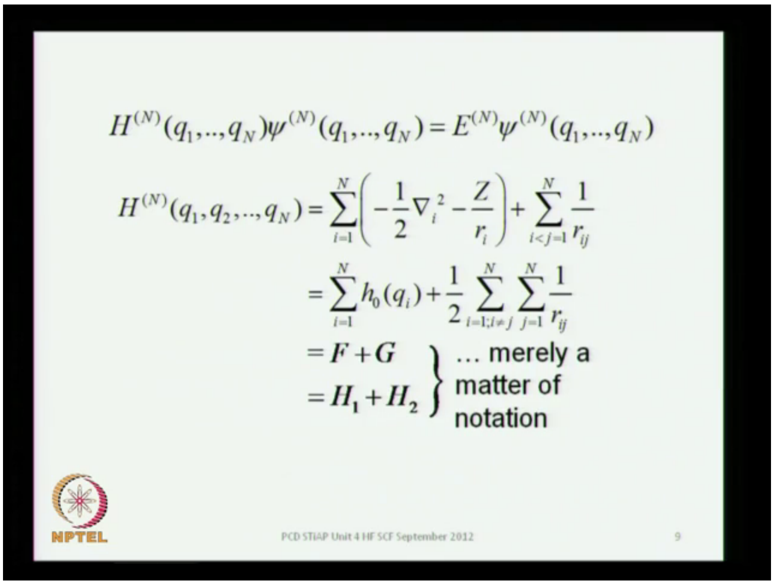

$$H^{(N)}(q_1,..,q_N)\psi^{(N)}(q_1,..,q_N)=E^{(N)}\psi^{(N)}(q_1,..,q_N)$$

$$\begin{aligned} H^{(N)}(q_1,q_2,..,q_N) &= \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}} \\ &= \sum_{i=1}^{N}h_0(q_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \\ &\left.\begin{aligned} &= F+G \\ &= H_1+H_2 \end{aligned}\right\} \text{... merely a matter of notation} \end{aligned}$$

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So, this is our many electron Hamiltonian, this is got a formal structure and the summation over the coulomb repulsion terms can be written either as this or half of this double summation with i and j going from 1 to N, but i naught equal to j. So, these two ways of writing this coulomb repulsion is completely equivalent, as you probably know. And this is got a part, which consist of only one electron coordinates and in this term, you have got two electron coordinates. So, this is usually call is a one electron Hamiltonian and this term as a two electron Hamiltonian. And sometime it is referred to as H 1, H 2 and sometime as F and G, that just a matter of notation, depending on which book you will be reading, so this the N electron Hamiltonian.

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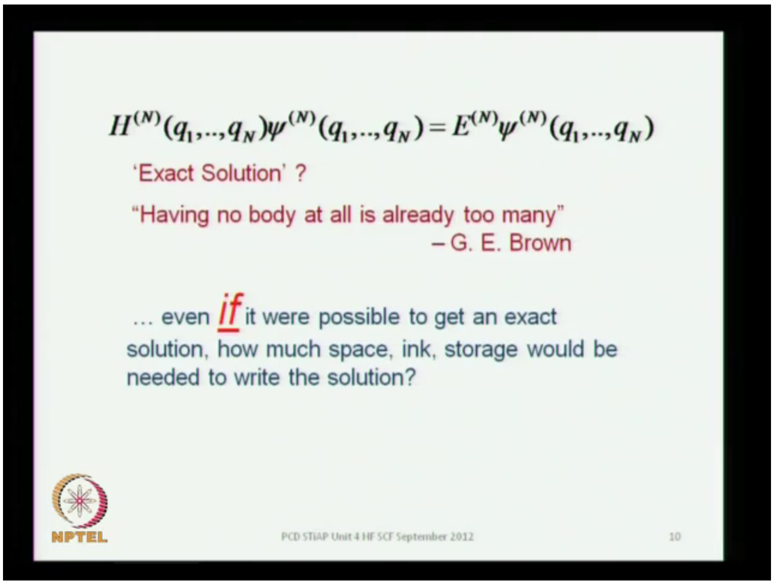

$$H^{(N)}(q_1,..,q_N)\psi^{(N)}(q_1,..,q_N)=E^{(N)}\psi^{(N)}(q_1,..,q_N)$$

'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?

And now, we are going to seek a solution and of course, we will be happy if we can get an exact solution and this problem was posed Tuponkare by the king of Sweden. If the three body classical system, the sun, earth and moon, does it have exact solutions and even in the classical mechanics, it does not have any exact solution, that is what leads to KIOS and other things.

Now, when it gets down to quantum mechanics and relativistic quantum mechanics, let alone three body problem, not even the two body problem, not even a one body problem, also that matter even the problem of vacuum state does not really have exact solution. It just does not, the solution does not exist and this is very nicely stated in Brown's book, where he says that, if you are looking for exact solution then having nobody at all is already too many, there is no any chance of getting an exact solution.

So now, what I am going to do, try to come up with the best approximation that you can and if you can make, come up with the good approximation then it is going to be a breakthrough and that is how science progresses. So, the Hartree-Fock method is not going to give you an exact solution to the N body problem, to the N electron problem, but it will give you an extremely good approximation.

Extremely good, again this is a really relative term, it really depends on what application you have in mind, what is extremely good at one level turns out to be completely unsatisfactory at another level and then you have to go beyond the Hartree-Fock. So, current studies in atomic physics do require you to go beyond the Hartree-Fock and I will tell you, what are the limitations of the Hartree-Fock and what is it that you need to go beyond the Hartree-Fock. But, before we get to talked about it, let us just make, let us at least make ourselves comfortable with the Hartree-Fock itself.

So, now there is a nice remark that I came across in Herman’s and Sherman's book on approximate Hartree-Fock solutions, in which they write that, let alone the fact that, you cannot get the exact solution, but suppose you did. Even if you could, how much space would it need to write down such a solution, how much ink would you need, how much storage space would you need.

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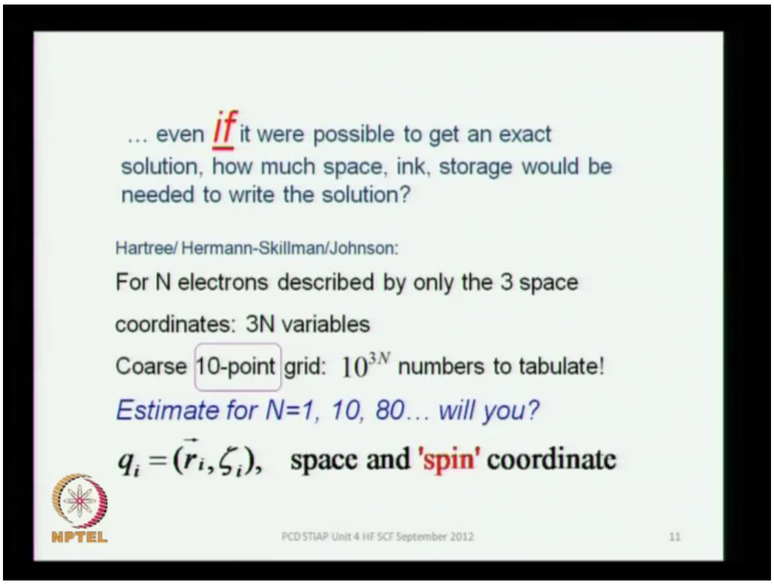

… even *if* it were possible to get an exact solution, how much space, ink, storage would be needed to write the solution?

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**

And just consider this problem that, if you have N electrons and each of described just by 3 parameters, 3 degrees of freedom then you have 3N variables, which you must specify. And you want to specify, what is the electron wave function amplitude over here and then here and then here and here, at least 10 points you need, if not infinite. So, a ten point grid would be a very coarse grid, nobody is going to satisfy with that. But, you will need 10 to the 3 N numbers and what is 10 to the 3 N for N equal to 1.

For N equal to 10, molecularly atom 80 electrons, can you punch this and find out from your calculators, what this number is, 10 into 300 for N equal to 80. And where are you going to write all these information, who is going to generate the ink for it and where is a storage space for it. So, you have to have some way of dealing with this problem in some practical manner and the Hartree-Fock method really let us you do that. So, in addition to do that of course, you have got the electron spin, which we know.

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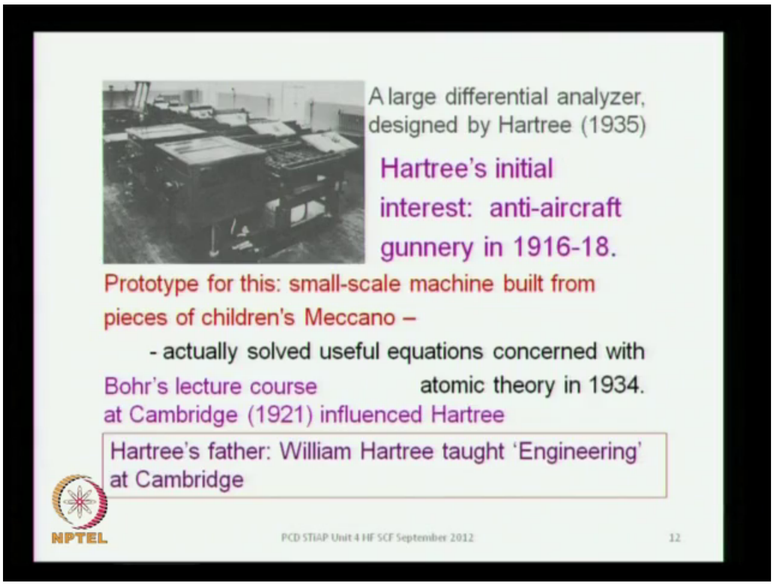

A large differential analyzer, designed by Hartree (1935)

Hartree's initial interest: anti-aircraft gunnery in 1916-18.

Prototype for this: small-scale machine built from pieces of children's Meccano –

- actually solved useful equations concerned with atomic theory in 1934.

Bohr's lecture course at Cambridge (1921) influenced Hartree

Hartree's father: William Hartree taught 'Engineering' at Cambridge

And the history of the development of the Hartree method is really very fascinating, I think it is worth reading. This was a differential analyzer, which was designed by Hartree in 1935 and Hartree played a big role in the development of computers. Initially, he was interested in anti aircraft gunnery, that was his initial interest but then there was, he also used children's Meccano, I do not know how many of you have played with it. And with these Meccano which are toys, are you could actually do some calculations.

And Hartree, he was invent it when after be able to use it and do some actually calculations at atomic physics. But then there was lecture posed by Niels Bohr at Cambridge and that what Hartree interested in atomic physics and then he started using his brains to come up with this formalism. And then he was helped by his father, who was a engineering professor, but he thought it was fun to do arithmetic and he helped his son, do all these numerical work to get, what we now called as Hartree self consistent field method. So, large number of computations have to be done and this was obviously, in the pre computer days and in fact, the first computer as you know is the ENIAC.

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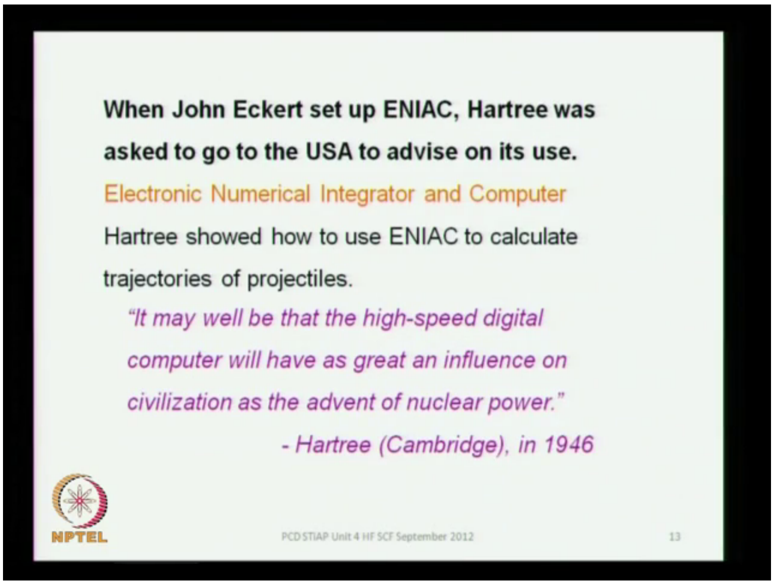

When John Eckert set up ENIAC, Hartree was asked to go to the USA to advise on its use.

Electronic Numerical Integrator and Computer

Hartree showed how to use ENIAC to calculate trajectories of projectiles.

> *"It may well be that the high-speed digital computer will have as great an influence on civilization as the advent of nuclear power."*
>
> \- Hartree (Cambridge), in 1946

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And when this was developed, Hartree was invited to advise, because unless there is somebody to use a good machine, you cannot really develop a good machine. So, all major computer companies IBM and so on, they do hire atomic physicist even today so that, they can develop their computers. So, Hartree was one of the first ones of this kind and Hartree said in 1946, that it may well be that the high speed digital computer will have as great an influence on civilization, as the advent of nuclear power and we do know, how through it is.

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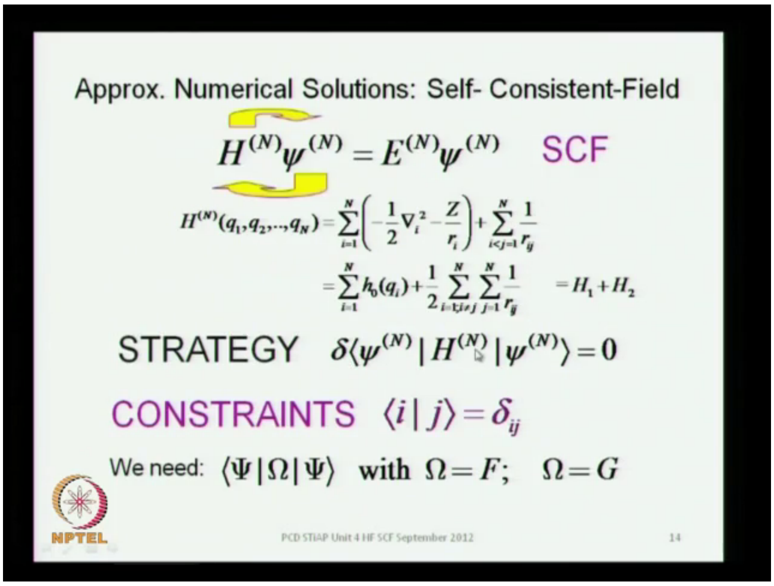

Approx. Numerical Solutions: Self- Consistent-Field

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

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

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

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 $\Omega = F; \quad \Omega = G$

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So, Hartree certainly made very important contribution to the development of the computers as well. And now, we discuss this problem further, this is the self consistency that we are seeking as I mentioned earlier. You got an electron Hamiltonia, which is made up of two parts, the one electron part H 1 and the two electron part H 2. So, these are the two parts of the Hamiltonian and the coulomb term 1 over r i j is the two electron part.

Now, what is going to be our strategy and this comes from our experience in physics, the variational methods are very powerful. You build the machinery of classical mechanics on the variational principle, Newton's causality principle is one pillar, on which you can build classical mechanics. But, you can also do so based on Hamiltonian variational principle and build the entire scheme of mechanics. You also know, you use a variational principle to explain, how light travels from mass principle and so on.

So, using the variational principle, you can set up a requirement that the variation in the expectation value of the Hamiltonian would be an extrema. What wave function would be the expectation value of the Hamiltonian an extrema. If you make this question, if you raise this question and find such a function then one could hope that, this would be the appropriate self consistent field solution to the problem. So, this is the variational approach and this is our strategy now, which is to seek that, the expectation value of the Hamiltonian is an extremum.

We certainly know how this works, because it does not necessarily mean that, it will be a minimum, because when you study only the first derivatives, you could have a minimum, you could also have a maximum, you could also have a shallow point. So, there are all kinds of possibilities that one has to be worry about and yes, these things are properly kept track off and we can get into these details, as the discussion progresses. But, this is a basic strategy, that the variation in the average value, the expectation value of the Hamiltonian, you seek that this would be an extremum.

But, when you vary these wave functions, you have got some wave function, it has got some profile and you change it. So, instead of certain profile, it becomes somewhat different, that is variation you have changed it. Now, when you change it, you have to make sure that, the new shape that the wave function would require under the variation that you are trying, still generates a normalized wave function, because if you integrate the probability density from 0 to infinity over the entire space, you should still get one charge per electron.

You would also expect this to be orthogonal to the remaining atomic orbital, so these are the constraints. So, you are seeking variation, but not arbitrary variation, a variation which will preserve the normalization of each one electron wave function and also it is orthogonality to the other single electron wave functions. So, these are the constraints and your problem is now posed as a problem in variational calculus. So, to get this variation in the expectation value of the Hamiltonian, this is the expectation value of a certain operator, which is N electron Hamiltonian.

But, the N electron Hamiltonian is made up of a two pieces, the one electron part and the two electron part, F and G or H 1 and H 2, however you call them. And you need to determine the expectation value of these two operators, the one electron operator and the two electron operator and then seek the variations. So, we first have to learn, how you are going to develop a formal structure of this term, which is the expectation value of this one electron operator and the two electron operator. So, this is going to be the first step in making progress on this problem.

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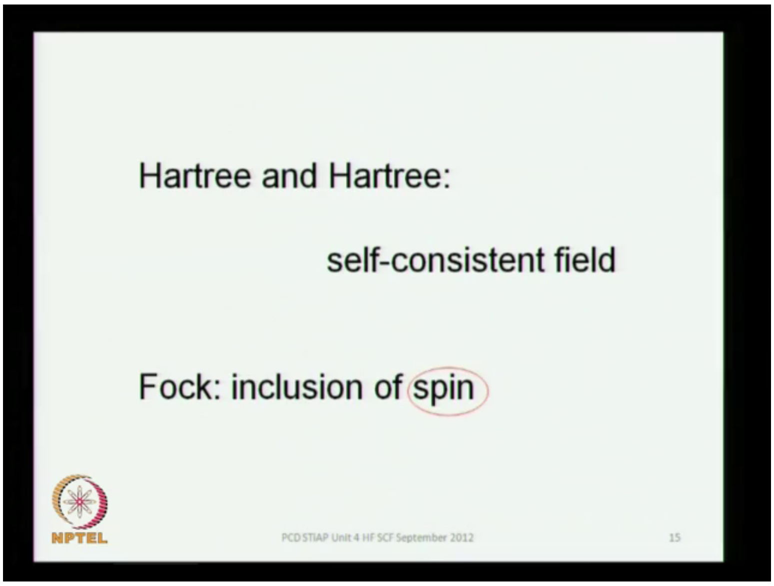

Hartree and Hartree:

self-consistent field

Fock: inclusion of spin

So, Hartree and the son Hartree and the dad Hartree, they developed the self consistent field for electrons, but they did not take into the account the electrons spin from the first principles. And then Fock included the spin as well and I will like to remind all of you once again that, spin is something which Uhlenbeck and Goudsmit hit upon accidently when they were interpreting certain experimental results in Paschen's laboratory.

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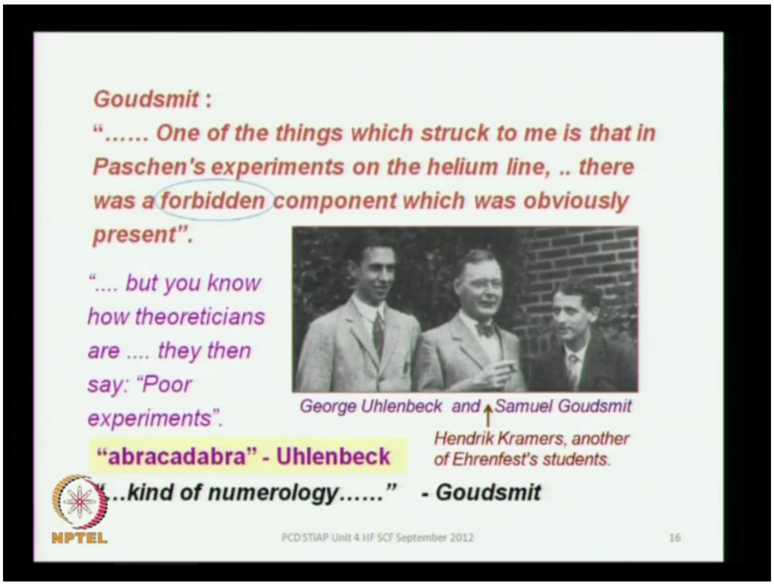

Goudsmit :

"...... One of the things which struck to me is that in Paschen's experiments on the helium line, .. there was a forbidden component which was obviously present".

".... but you know how theoreticians are .... they then say: "Poor experiments".

George Uhlenbeck and Samuel Goudsmit

Hendrik Kramers, another of Ehrenfest's students.

"abracadabra" - Uhlenbeck

"...kind of numerology......" - Goudsmit

And because they saw some transitions, which seem to be forbidden and then to explain those spectra, they made a guess and they said that, there has to be additional source of angular momentum and additional source of magnetic moment. And it just worked, but that is, it worked for no good reason, as was known at that time.

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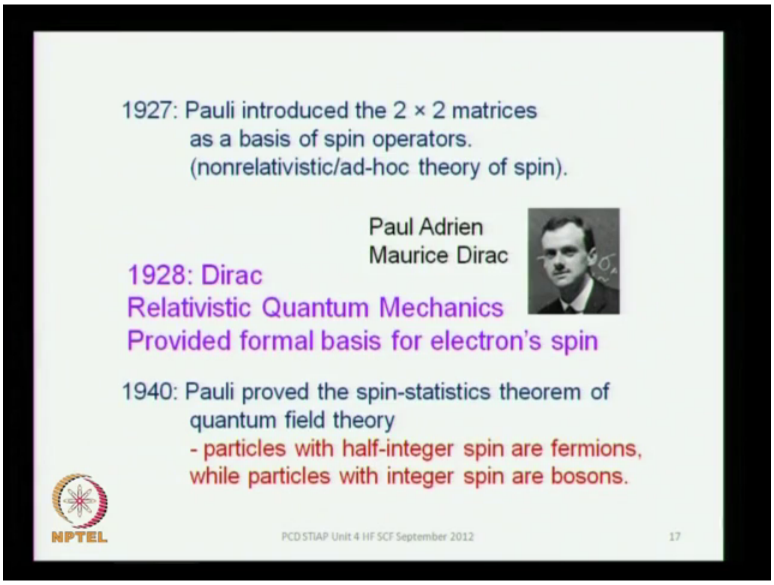

1927: Pauli introduced the 2 × 2 matrices
as a basis of spin operators.
(nonrelativistic/ad-hoc theory of spin).

Paul Adrien
Maurice Dirac

1928: Dirac
Relativistic Quantum Mechanics
Provided formal basis for electron's spin

1940: Pauli proved the spin-statistics theorem of
quantum field theory
- particles with half-integer spin are fermions,
while particles with integer spin are bosons.

But then we know that the reason is the formal existence of electron spin, as it comes out of the Dirac's relativistic quantum mechanics. So, spin is an integral property of the electron and then Pauli developed the spin statistics theorem, that particles with half integer spins observe the Fermi Dirac statistics and particles with integer spins, observe the bosons spin statistics. So, spin is an integral property of a electron, that it has to be taken into the account, as we know from relativistic quantum mechanics.

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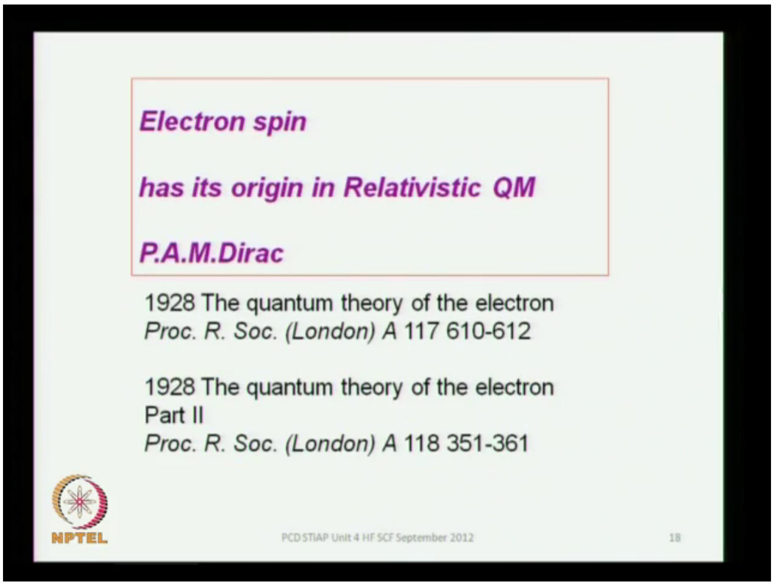

Electron spin

has its origin in Relativistic QM

P.A.M.Dirac

1928 The quantum theory of the electron
Proc. R. Soc. (London) A 117 610-612

1928 The quantum theory of the electron
Part II
Proc. R. Soc. (London) A 118 351-361

And these are the two classical papers in 1928 by the Dirac, when which he developed the relativistic quantum mechanics, which gave a formal basis to the idea of a electron spin.

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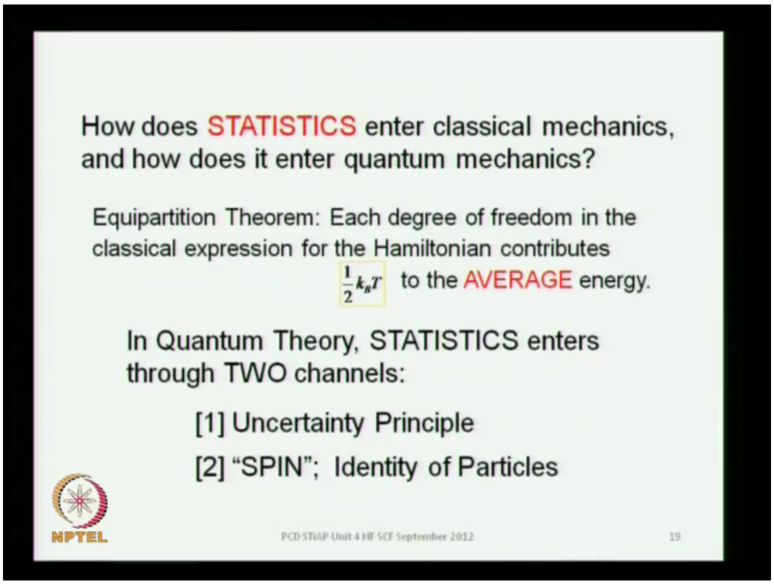

How does STATISTICS enter classical mechanics, and how does it enter quantum mechanics?

Equipartition Theorem: Each degree of freedom in the classical expression for the Hamiltonian contributes $\frac{1}{2}k_BT$ 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 it is interesting to ask this question, how does statistics, because now you are going to talk about many electron systems and electrons are Fermions. So, we will apply the Fermi Dirac statistics, so how does this statistics enter classical quantum mechanics at all, how does it enter classical mechanics and how does it enter quantum mechanics. So, in classical mechanics, basic laws of motion are deterministic, you know the initial condition, you can actually determined what the solution.

And you can do it for 1 particle, you can do it for 10, you can do it for 100, you can do it for 1000, that you may not need that much information it is a different matter. Because, when you want to talk about the average energy of some system then you know that each degree of freedom will contribute half K T to the average energy. But, this is a average kinetic energy, which we should described in terms of temperature. And it is coming from the kinetic energy, the half m v square kind of term, which gets added into what finally gives you the temperature of the system.

But, it is not the, you cannot determine that kinetic energy of each individual molecule, you can, in principle you can, you need to, because it is too much information, in which you are not interested and that is how, statistic entered classical mechanics. Because, you are dealing with the large number of particles and you really do not need all that information, it is not because you cannot get that information, you can, you do not need, these are two different situation altogether.

In quantum mechanics, statistics enters even for a single particle and even for a vacuum, because large of nature are increasingly quantum mechanical. And they are statistical, because quantum mechanics is a statistical theory, so it is not because there is a large number of particles that you are working with. Even for a single particle, you need statistics and then statistics enter also through the spin of the particle, because depending on the what spin is, you have to use a different form of statistics.

If the spin is half integer you would use Fermi Dirac, if the spin is integer you would use the bosons sign, so statistics and spin are very closely related and I will discuss this further. So, let me first deal with a two electrons system, you interchange this one electron, so there is one electron coordinate as q 1 and the other as q 2 and I is the interchange operator. It swaps them, the interchange operator swaps them, so you begin with the two electron system, apply the interchange operator.

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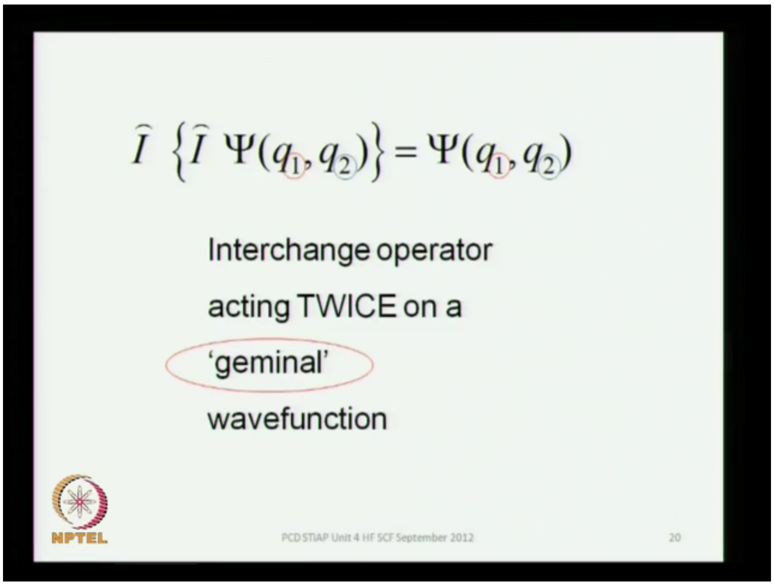

$$\hat{I}\ \{\hat{I}\ \Psi(q_1,q_2)\} = \Psi(q_1,q_2)$$

Interchange operator
acting TWICE on a
'geminal'
wavefunction

And now, you apply the interchange operator on this again, swap it one more time, you get this, you get what you started out with. So, two interchanges, I operating on psi q 1 and q 2 Aand then another interchange operator operating on the result would regenerate the original system that you begun with. Now, these two electrons are completely identical to each other, you cannot distinguish between them and that is the main difference between classical particles and quantum particles.

When you deal with the classical particles, you can sort of put a color on them or a number or some name and you can say that, this is particle a, this is particle b. But, that is not how particles in nature really are, elementary particles are indistinguishable from each other. You cannot really put a label on that and this is why, this two electron wave function is sometimes called as a geminal, do you know what geminal was.

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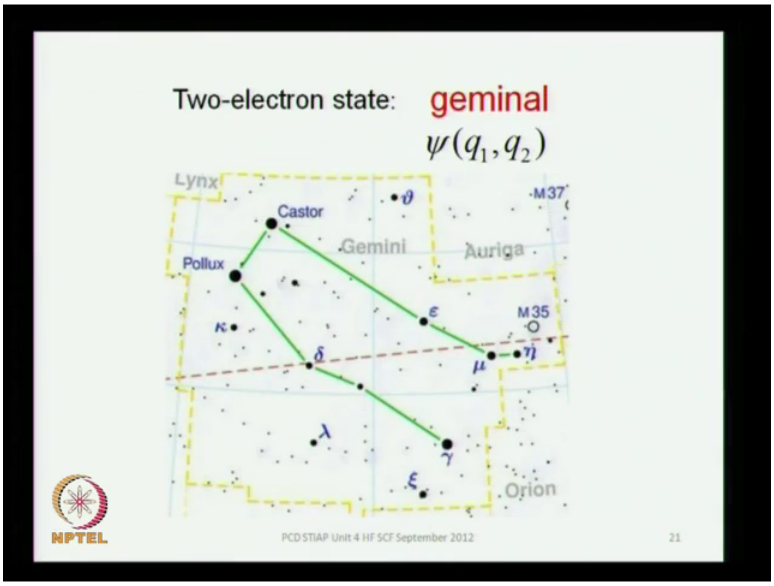

Two-electron state: geminal

$\psi(q_1,q_2)$

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Do you know what gemini is, have you seen the gemini constellation in the sky, so the beautiful part of the sky and there are two lovely stars Castor and Pollux in this consolation and they look so alike, so similar to each other. So, they look like a identical twins, which is why, this is called as gemini, so gemini refers to twins. And these two electrons that we are talking about psi q 1 q 2, these two electrons are completely identical to each other, they are completely indistinguishable from each other.

Castor and Pollux are actually you cannot distinguish between them, one is Castor and other is Pollux, you cannot do so with electrons. But, they are indistinguishable just like twins, which is why, a two electron wave function is sometime called as a geminal, not a very common usage, but not uncommon either.

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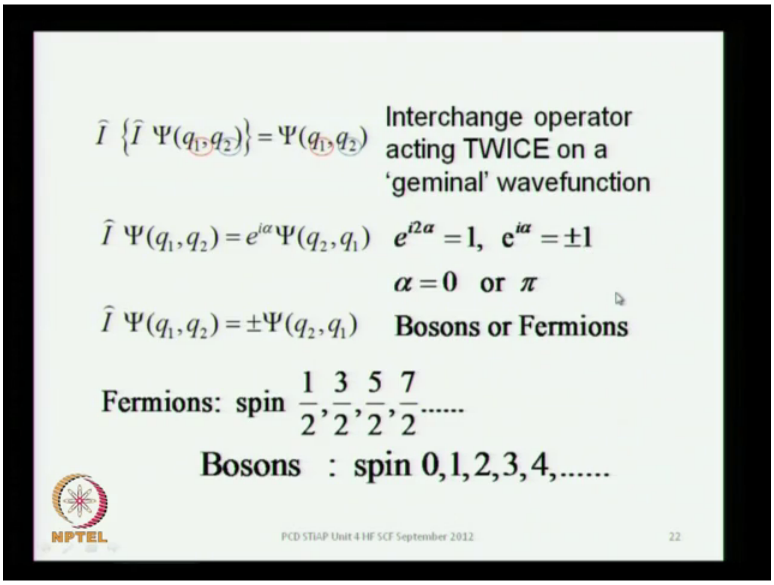

$\hat{I}\,\{\hat{I}\,\Psi(q_1,q_2)\}=\Psi(q_1,q_2)$ Interchange operator acting TWICE on a 'geminal' wavefunction

$\hat{I}\,\Psi(q_1,q_2)=e^{i\alpha}\Psi(q_2,q_1)$ $e^{i2\alpha}=1$, $e^{i\alpha}=\pm1$

$\alpha=0$ or π

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

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

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

So, you have a two electron system, you interchange twice, you recover the original configuration. What this means is that, a single interchange can only change the phase and it can give you a result when you interchange q 1 with q 2 by a single interchange operator. The result can be either plus or minus, because when you interchange it one more time, it will be the same as the previous one. So, this is what we have got, that two interchanges e to the i 2 alpha would give you 1, so e to the i alpha would be plus 1 or minus 1 and accordingly, this angle will be either 0 or pi.

So, there are two types of particles in nature, one are the Fermions which have got half integer spins, whose wave function would change sign under the interchange of two identical Fermions. But, if you interchange two identical bosons, the wave function will remain invariant, the sign will not change.

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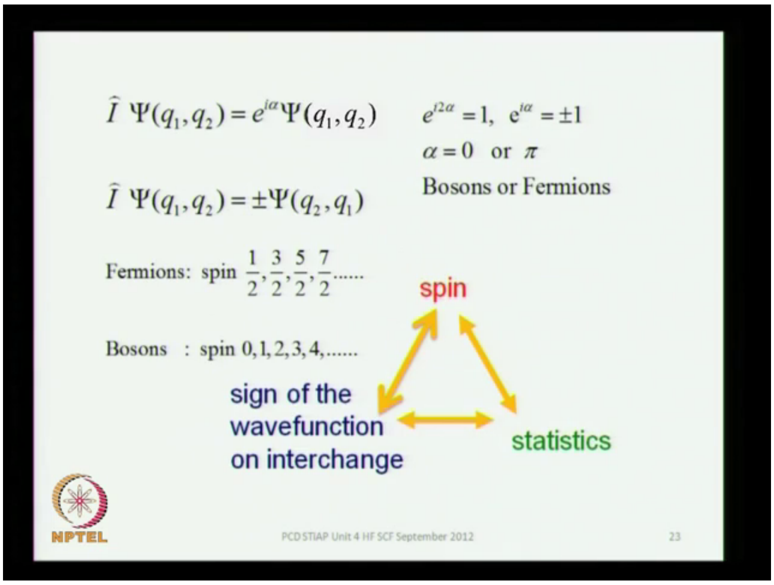

$$\hat{I}\,\Psi(q_1,q_2)=e^{i\alpha}\Psi(q_1,q_2)$$

$e^{i2\alpha}=1,\ \ e^{i\alpha}=\pm1$

$\alpha=0$ or π

Bosons or Fermions

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

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

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

spin

sign of the wavefunction on interchange

statistics

Now, there is this intimate relationship between spin, statistics and the sign of the wave function on interchange. These three things are intimately connected to each other, they all go together. The spin being half integer or integer goes with the statistics that particle would observe and this goes with, what would happened to the sign of the wave function and the interchange of two particles belonging into the system, these three things go hand in hand together.

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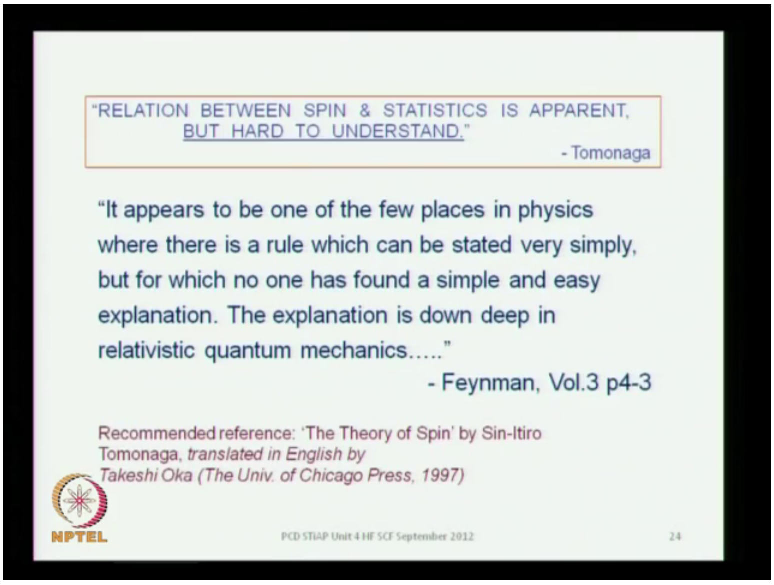

"RELATION BETWEEN SPIN & STATISTICS IS APPARENT, BUT HARD TO UNDERSTAND."

- Tomonaga

"It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is down deep in relativistic quantum mechanics….."

- Feynman, Vol.3 p4-3

Recommended reference: 'The Theory of Spin' by Sin-Itiro Tomonaga, *translated in English by Takeshi Oka (The Univ. of Chicago Press, 1997)*

Now, I code term Tomonaga's book, in which he points out the relation between spin and statistics is apparent, but hard to understand. And even more comprehensive code, which some of you might have come across is due to, perhaps one of the finest of physics teachers Richard Feynman. And he says in his volume 3, that it appears to be one of the few places in the physics, whether is a rule, which can be stated very simply, but for which, no one has found a simple and easy explanation.

The explanation is down deep in relativistic quantum mechanics, you can say very simply that, the particles are half integer spins, they observe Fermi Dirac statistics, if they are integer spins they observer bosons statistics. But, to get to the bottom of this issue, why this, one really needs to get it relativistic quantum mechanics in a fairly comprehensive way and that is a challenging topic by itself. But, I will recommend Tomonaga's book for this, the theory of spin, it is a very nice book, some of you might have come across or if you have not, you will enjoy reading it.

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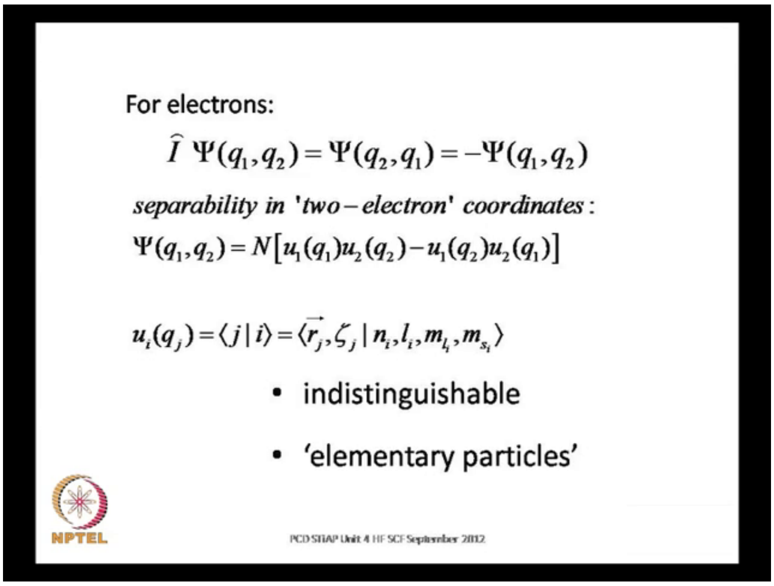

For electrons:

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

separability in 'two – electron' coordinates:

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

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

- indistinguishable
- 'elementary particles'

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So, anyhow, we accept that this is what it is and under one interchange, electron being Fermions the sign would change. And now, we talk about a two electron system, the two electron system is smallest many electron system and if we can develop the formalism for two electrons, we will know how to extend it to many electrons. So, we begin with the consideration of smallest many electron system, namely the two electron system. And we write the two electron geminal wave function psi q 1 q 2, which we know must change it is sign, when you interchange the two particles.

And obvious we have doing it, would be to write it as a product of these one particle wave functions, u 1 q 1 u 2 q 2 minus u 1 q 2 u 2 q 1, because if you interchange q 1 and q 2, this changes sign. So, it meets our essential requirement of an antisymmetric wave function, that is what an antisymmetric wave function means. Fermi Dirac wave functions are antisymmetric, because when you interchange particles, this sign changes.

So, this is an antisymmetric two electron wave function and it is written in terms of one electron wave function and I have written this one electron wave function more fully, because a wave function is the coordinate representation of state of vector. So, this is the coordinate representation of the state vector in the Dirac notation, which the wave function is. The state vector is described by a complete set of measurable physical properties, the four good quantum numbers, which are n, l, m l and m s for the electron.

And it is coordinate representation gives you the one electron wave function, this is inclusive of spin and there are therefore, 4 quantum numbers. Then, if you look at the de broglie Schrodinger notation, the u i q j, notice that the subscript here i represents the set of four quantum numbers and the argument of the wave function, which is q j represents the set of four degrees of freedom, the three space variables and one spin variable. So, the arguments q j are set of these four coordinates and the subscripts are the four good quantum numbers, that is the notation.

Now, it is important to recognize that, we are treating the two electron as indistinguishable, so you cannot separate one from the other, but the particles are still elementary particles. So, this is a very nice combinations of ideas, the elementary nature of the electron is not challenge here in this concern. But, you cannot distinguish one from the other, because normally when you talked about the elementary particle, you talked about the particle, as though it has got a complete separate identity, which is the fundamental identity of a fundamental particle.

But, that identity is lost when you are dealing with a pair of electrons, because you cannot say that, this is electron a, and the other is electron b, so whereas the identity. So, this is a combination of these two ideas, in distinguishability and the electrons being elementary particles and you have to use these two ideas without any contradiction in your mind. So, the electrons will be treated as elementary particles, but they will be considered indistinguishable from all the other electrons in the system.

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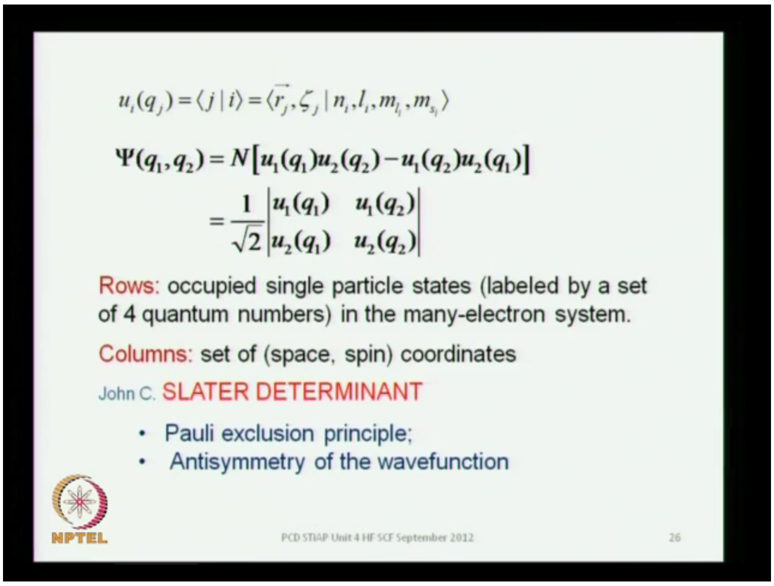

$$u_i(q_j) = \langle j | i \rangle = \langle \vec{r}_j, \zeta_j | n_i, l_i, m_{l_i}, m_{s_i} \rangle$$

$$\Psi(q_1, q_2) = N\left[u_1(q_1)u_2(q_2) - u_1(q_2)u_2(q_1)\right]$$
$$= \frac{1}{\sqrt{2}}\begin{vmatrix} u_1(q_1) & u_1(q_2) \\ u_2(q_1) & u_2(q_2) \end{vmatrix}$$

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

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And this is our representation of the electron coordinates and quantum numbers, you can write this easily as a determinant u 1 q 1 u 2 q 2 minus u 1 q 2 u 2 q 1. And if each of these one electron wave functions is normalize then you can see very easily that, you have a normalization 1 over root 2. So, you can easily write this as a determinant and in this determinant, the rows and columns, columns are labeled by q 1 the first column, the second column by q 2 and these are the coordinates.

The rows are labeled by the subscript, this is subscript 1 and this is subscript 2, so the rows correspond to the set of four quantum numbers, which are the occupied states of the electrons. So, this is called as the Slater determinant named after John Slater and you will see, that the Pauli’s exclusion principle is automatically built into it, because a determinant vanishes if two rows or two columns are the same. So, no two particles will have the same set of quantum numbers, which is Pauli’s exclusion principle. The antisymmetry of the wave function is also inbuilt into this representation, because if you interchange two rows, the sign of the determinant will change. So, it automatically takes into the account, the usual features of a many electron wave function.

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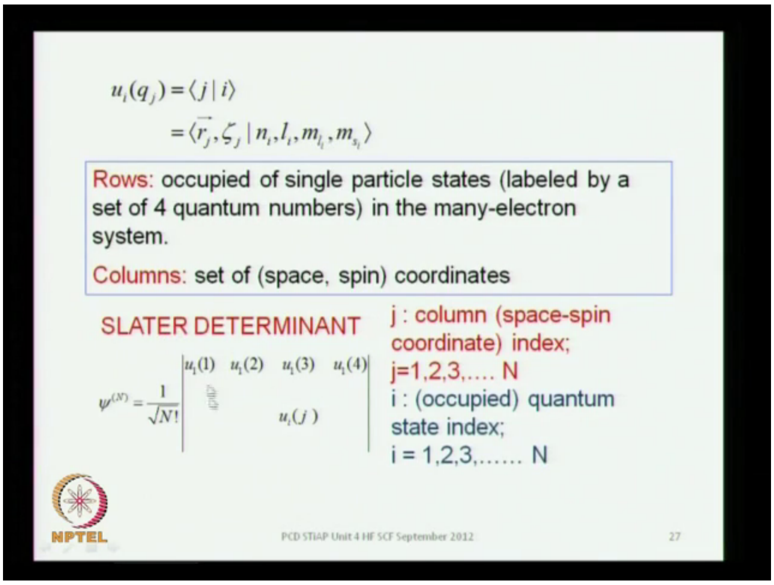

$$u_i(q_j) = \langle j \mid i \rangle$$
$$= \langle \vec{r}_j, \zeta_j \mid n_i, l_i, m_{l_i}, m_{s_i} \rangle$$

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

Columns: set of (space, spin) coordinates

SLATER DETERMINANT

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_1(2) & u_1(3) & u_1(4) \\ & & u_i(j) & \end{vmatrix}$$

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

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And you can easily extend this not just the two electrons, but to N electrons and then you have got N rows and N columns and a normalization of 1 over root factorial N. So, this is a straight forward extension from a two electron system to an N electron system, you can try to develop a determinant for a three electron wave function, do it by hand term by term. You will find that, there are factorial three ways of doing it, six ways of polling three electrons in three different systems.

So, the rows are designated by the one electron state, so the electron configuration is spelled out and this also spells out the occupancy of single particle states, that if you have got an energy spectrum, in which there are hundreds or even infinite set of single particle orbital which are solutions to the problem, not all of them are occupied. Say, if you have got a two electron system like the helium atom, you can have two electrons in the 1 s state, one with 1 s up and 1 s down.

But, you can also have one electron in the 1 s and other two in some excited states like 2 s, 3 s, 4 s and so on, so that will give you the different configuration. So, the first configuration had 2 electrons in 1 s, so occupation number of 1 s up was 1, 1 s down was also 1 and the occupation number of everything else was 0. Whereas, if you have one electron in 1 s and the other in 2 s then the occupation number of 2 s now becomes 1 and the rest become 0.

So, the occupation numbers and this is the language of second quantization, which also one uses in many electron theory. In second quantization, you deal with the occupation number states and you can see, how the Slater determinant expression can easily be adapted to the occupation number formalism. So, essentially what the Slater determinant does, is to spell out the occupancy of the single particle states and it incorporates the usual features of a many electron system, the Pauli exclusion principle, the antisymmetry of wave function.

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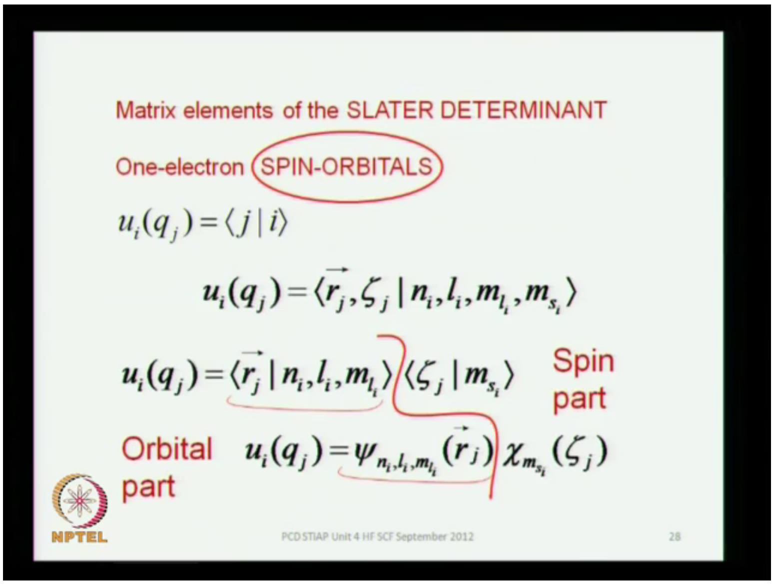

Matrix elements of the SLATER DETERMINANT

One-electron SPIN-ORBITALS

$$u_i(q_j) = \langle j | i \rangle$$

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

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

Spin part

Orbital part

$$u_i(q_j) = \psi_{n_i, l_i, m_{l_i}}(\vec{r}_j)\, \chi_{m_{s_i}}(\zeta_j)$$

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These are our designations and you can write the spin orbital, this is called as a spin orbital, this is a orbital part and this is a spin part and which is why, it is called as spin orbital. Because, you can factor this spin orbital u i q j into an orbital part and the spin part, so this is the spin part and this is the orbital part. So, the u i q j are typically called as spin orbitals.

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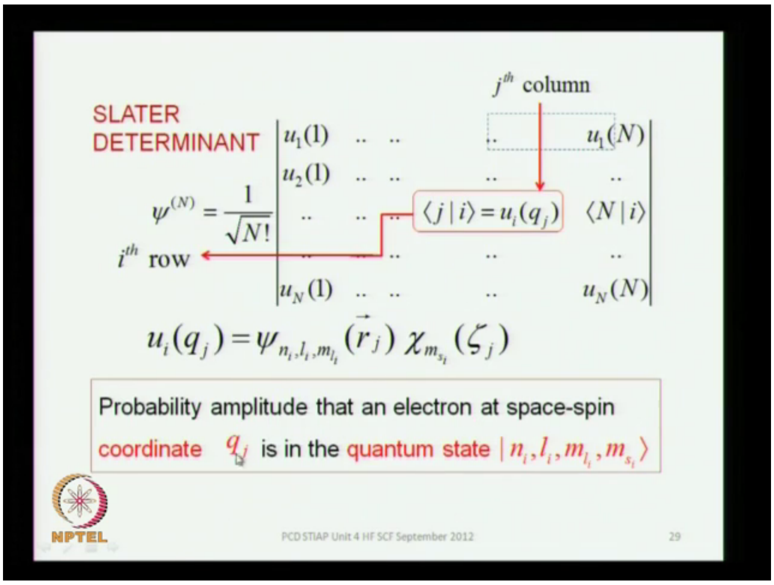

SLATER DETERMINANT

j^{th} column

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & .. & .. & .. & u_1(N) \\ u_2(1) & .. & .. & .. & .. \\ .. & .. & .. & \langle j \mid i \rangle = u_i(q_j) & \langle N \mid i \rangle \\ .. & .. & .. & .. & .. \\ u_N(1) & .. & .. & .. & u_N(N) \end{vmatrix}$$

i^{th} row

$$u_i(q_j) = \psi_{n_i,l_i,m_{l_i}}(\vec{r}_j)\,\chi_{m_{s_i}}(\zeta_j)$$

Probability amplitude that an electron at space-spin coordinate q_j is in the quantum state $|n_i, l_i, m_{l_i}, m_{s_i}\rangle$

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And the matrix elements of this letter determinant are essentially the spin orbitals, in which the columns are those which give, which correspond to the coordinates. And the rows correspond to the single particle states which are occupied and each spin orbital then is a measure of the probability amplitude, that in electron at space spin coordinate q j is in the quantum state n, l, m l, m s, corresponding to the i th row. So, that is the notation, that is the designation of the states.

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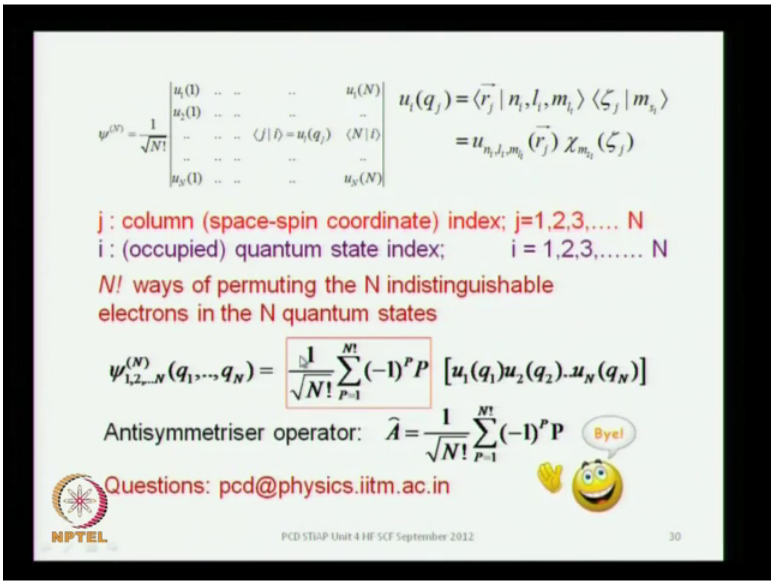

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & .. & .. & .. & u_1(N) \\ u_2(1) & .. & .. & .. & .. \\ .. & .. & .. & \langle j \mid i \rangle = u_i(q_j) & \langle N \mid i \rangle \\ .. & .. & .. & .. & .. \\ u_N(1) & .. & .. & .. & u_N(N) \end{vmatrix}$$

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

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

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

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

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

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

Bye!

Questions: pcd@physics.iitm.ac.in

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And this is how Slater determinant is written, you are of course aware, that there are factorial N ways of permuting the N indistinguishable electrons in N quantum states. So, you can also write this as, you can write all the elements along the diagonal u 1 q 1 u 2 q 2 u N q N and then begin permutations. And carry out all the permutations, but every time you permute, every time there is one interchange, you will have a change of sign. So, depending on a number of interchanges, which going to a permutation, you will have a minus 1 to the power p phase factor.

And you must sum over all the permutations, that there are factorial N of them, so you have to sum over all the permutations for p going from 1 to factorial N. So, you can write the Slater determinant equivalently also in this notation, it is a same as this Slater determinant. And this operator in this box is sometimes called as an antisymmetriser, because what it does, is to take this direct product of the diagonal elements and antisymmetrisers it.

So, this is sometimes called as an antisymmetrizer, so this is the antisymmetrizer operator, I will stop here for this class and we will begin from this point in the next class, questions.

Student: ((Refer Time: 50:07))

This spin orbit coupling does give you a net angular momentum, but these are distinguishable properties like, how do you define angular momentum. When I said that, angular momentum must be defined in a such a way that, when it is subjected to the rotations, it follows the certain law. And it is not going to follow that law, if you do not subject the orbital angular momentum and the spin angular momentum together, this is what we did in unit 2.

So, these are two separate sources of angular momentum, they are completely independent of each other. And they have though their Eigen functions, one is an Eigen function of l square l z, the other is an Eigen function of s square and s z. And together they give you l plus s equal to j and both Eigen function of l and s must be simultaneously subjected to a rotation. So, the separation comes from the fact that, these are two independent sources of the angular momentum.

Student: We have an non zero l dot s term then...

That is the matter, that you have a non zero l or s term, I understand your question, like s orbitals, s orbitals have got l equal to 0 and j will go from 0 minus half modulus to 0 plus half modulus, so there is only one state which is available. Now, that is only the Eigen value of l square, that does not prevent the electron from having the property of orbital angular momentum. It has a property of orbital angular momentum and it is in one of these states, corresponding to l equal to 0.

But, it is an independent property, which is completely independent of this spin, so these are two independent sources of angular momentum j 1 and j 2, which coupled to give you j 3 or the net j, which is l plus s equal to j. And their respective Eigen functions are the spin part and the orbital part, the net wave function is a product of these two, any other question. So, let me stop here and we will resume from this point tomorrow.