Quantum Chemistry of Atoms and Molecules

Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture 32
Atomic Orbitals and Orbital Approximation

We have discussed in detail the acceptable wave functions of hydrogen atom and we said that these are called orbitals. For the umpteenth time in this course orbitals are acceptable solutions for acceptable one electron wave functions; acceptable solutions for   equation for one electron for hydrogenic systems, so we have learnt how to plot them. We have learnt how to draw 3D and contour diagrams like this.

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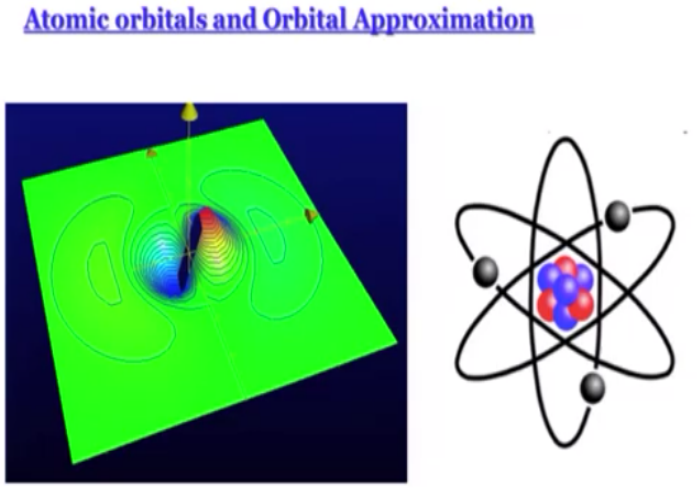

Atomic orbitals and Orbital Approximation

And we also said what happens when you draw with pen and paper qualitative sketches, that also we learnt. You draw the notes first and then every time we change the node; the sign must change. That is how it is. What you see here, I am sure you remember is a 3D depiction of a 3pz orbital along with the contours. Now the question that arises is, we have put in so much of time and effort to learn about atomic orbitals, of what use are they?

I mean, started as if you want to only study hydrogen. Hydrogen is the simplest atom. We want to talk about atoms with many electrons. We want to talk about molecules. Of what use are the simple one-electron wave functions? Are they of any use? As we will discover, they are of some use, a lot of use, at least at a starting point. Eventually, of course, when things get more complicated, we move on and we move on to more complex systems, more complex solutions.

But to start with, atomic orbitals actually have an important role to play and for a lot of chemists, orbitals actually make this very complicated quantum mechanical business, very simple, because they can be presented in the form of pictures and you can develop qualitative theories, just based on the symmetry of orbitals, what kind of distribution is there in space and so on and so forth. So orbitals are actually very, very important in chemistry.

So we start our discussion now about multi-electron atoms and then the first approach we will discuss is orbital approximation. So what we see here is very popular depiction of multi-electron atom with three electron and a nucleus; of course this very good looking picture is from Bohr-Sommerfeld model. So right now, it is not really state of the art, but it finds use in depiction of science in many, many platforms. I leave it to you to find out which major government agency has this picture or at least its adaptation in its logo.

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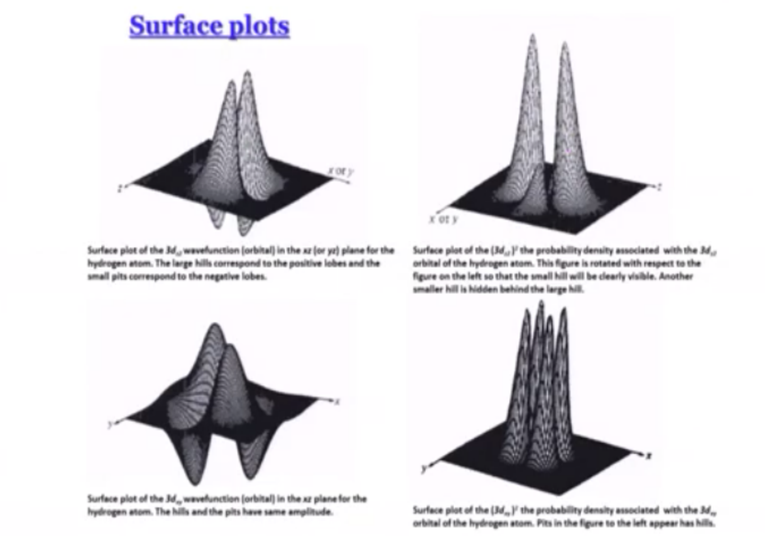

Surface plots

Surface plot of the $3d_{xz}$ wavefunction (orbital) in the xz (or yz) plane for the hydrogen atom. The large hills correspond to the positive lobes and the small pits correspond to the negative lobes.

Surface plot of the $(3d_{xz})^2$ the probability density associated with the $3d_{xz}$ orbital of the hydrogen atom. This figure is rotated with respect to the figure on the left so that the small hill will be clearly visible. Another smaller hill is hidden behind the large hill.

Surface plot of the $3d_{xy}$ wavefunction (orbital) in the xz plane for the hydrogen atom. The hills and the pits have same amplitude.

Surface plot of the $(3d_{xy})^2$ the probability density associated with the $3d_{xy}$ orbital of the hydrogen atom. Pits in the figure to the left appear has hills.

But to continue our discussion, we have learnt what sense to make up the surface plots.

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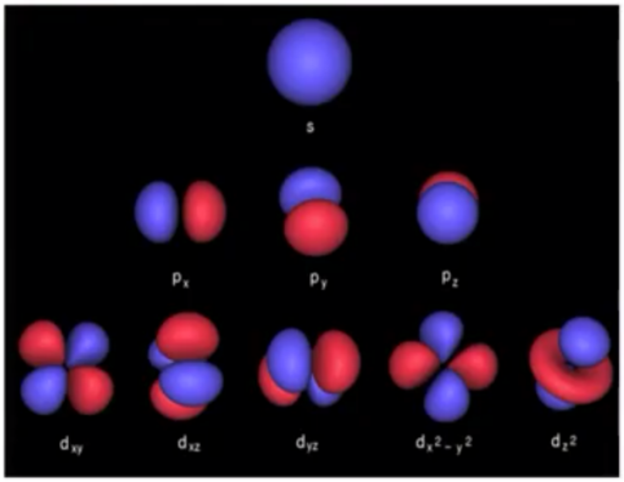
Orbitals: External Structure



And one thing I should say before moving out from this topic is that very often you see pictures like this and they are useful, as they say, because they present a qualitative picture, but please remember that what you see here most likely is the region of space, in which finding the probability is maximum. So you decide how much of probability you want to include. As we have discussed earlier, it is not only radius, theta also matters.

Phi does not matter because you get rid of phi when you generate real orbitals. So theta also matters and from theta and r, you can figure out at what r and what values of theta what kind of probabilities are there and you can construct the surfaces, which contain maybe 90%, 95% 99% of probability and additionally what you do is, you show the sign of the wave functions on the appropriate lobes. Please remember these are not really orbitals, even though they are called so. They are qualitatively similar looking, but these are regions of space. Orbitals, as you know are actually one electron wave function.

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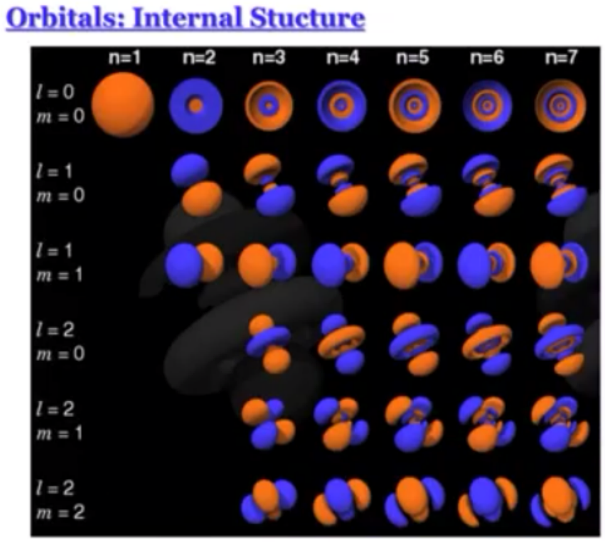

Orbitals: Internal Stucture

And one danger of this is that, very often you see popular figures like this, where earlier one was orbital outer structure, this one is inner structure. The purpose is to show the nodes and all. In fact, you can buy structures made of styrofoam using this. There is a general chemical equation paper, in which it says how you can cut open a styrofoam structure to actually see the nodes. The problem is, if you depict like this, l = 1, m = 1, one might think that m = 1 here.

That is not what the meaning is. The meaning is, these real pictures that are there for n = 2, 3 and so on and so forth, they are all generated by taking appropriate linear combinations of m = 1 and m = -1 orbitals, because as you understand e to the power im phi. There is a phi part. So you cannot really draw an imaginary function in real space. Same is true for l = 2, m = 1 and l = 2, m = 2. If you just take m = 1 or m = -1 or m = 2, m = -2, they are imaginary functions.

These are actually linear combinations that you get and that is how you generate them. So please remember that. I hope we will have no confusion about what orbitals really are and what these pictures really are from this point on.

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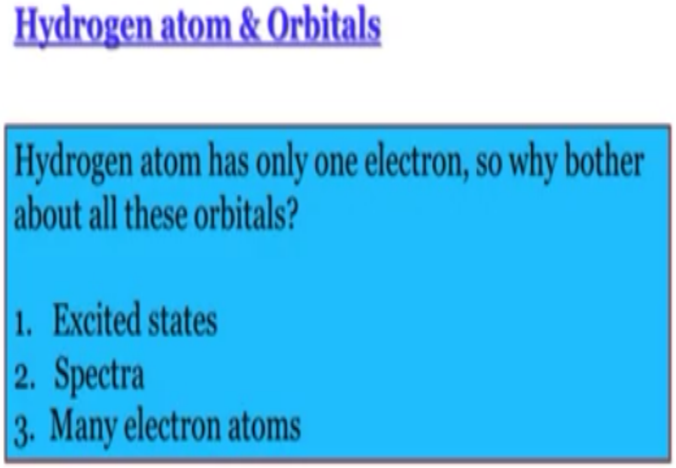

Hydrogen atom & Orbitals

Hydrogen atom has only one electron, so why bother about all these orbitals?

1. Excited states
2. Spectra
3. Many electron atoms

But now, we come back to our disturbing question. Hydrogen atom has one electron, fine. First of all, why we will even bother to spend three modules on so many orbitals? Of what use are they? And the answer is that hydrogen has one electron, true. It occupies only 1s orbital in the round shape, true, but do not forget one of the origins of quantum mechanics is hydrogen spectrum. The moment you talk about spectroscopy; you get involved with excited states.

This means, somehow you have to promote that electron from 1s to maybe whichever orbital the energy takes it to and then if it is emission spectroscopy, it has to come down. So if you want to talk about excited states, you better know about the wave functions that are involved in the excited states and without them, you cannot really talk about spectra and what we discussed now is, these orbitals with little bit of adaptation, can actually be used for many electron atoms as well to some extent.

You already know that, without me having to tell you so. What is the configuration of helium? You will say 1s2, how? 1s is an orbital, one electron wave function. So how is it that you are saying 1s2, lithium, beryllium, nitrogen, oxygen. If I just tell you the element, you will be able to rattle off the electron configuration like 1s2, 2s2, 2p3, so on and so forth. How is it that this is one is 2s2p, 3s3p, 3D, 4s?

How is it that these one electron wave functions are being used happily in talking about electron configuration of multi-electron atoms? How is it that we talk about sp hybrid orbitals when you talk about bonding? There are many, many electrons in molecules anyway. That is what we learnt slowly.

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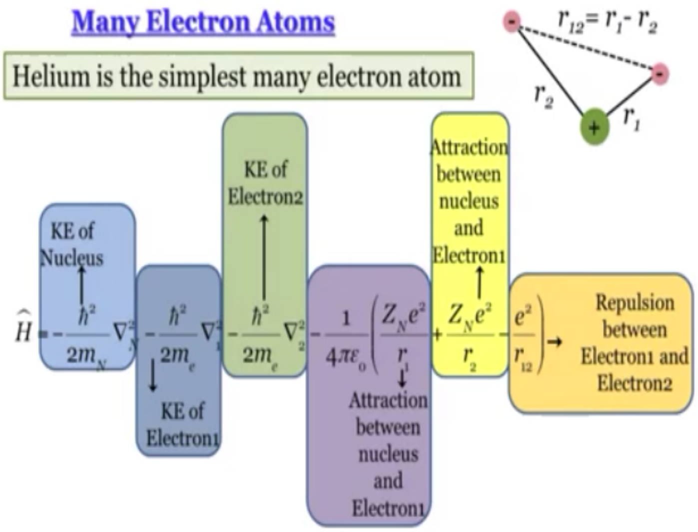

Many Electron Atoms

Helium is the simplest many electron atom

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\left(\frac{Z_N e^2}{r_1} + \frac{Z_N e^2}{r_2} - \frac{e^2}{r_{12}}\right)$$

KE of Nucleus

KE of Electron1

KE of Electron2

Attraction between nucleus and Electron1

Attraction between nucleus and Electron1

Repulsion between Electron1 and Electron2

To start with let us keep things as simple as possible. Let us start with helium. Helium is the simplest many electron atom that one can think of and if I draw a very rough model of helium. We always start from there. We draw simple pictures. Here we have the nucleus. This is electron number 1, this is electron number 2. Do the electrons know that they are number 1 or number 2? No, they do not. Electrons do not wear jerseys. Electrons do not have numbers written on them.

We are putting the numbers for our convenience, so that we can formulate the problem, but electrons are actually indistinguishable. We are going to come back to this point several times later in our discussion, but right for now, this is what you have. You have this position vector of electron number 1 r1, position vector of electron number 2 r2 or you can just think separation and separation between the two is the vector sum of r1 and r2. Here we have written r1 – r2.

Not really vector sum, we will subtract one vector from the other. So how do we write the Hamiltonian for a system like this? For any quantum mechanical problem, what you need to do is, you need to write the Hamiltonian, then you need to think if you can write the wave function in some way, then we can think of how we can solve it. So this is what the Hamiltonian is going to be. I have shown you the entire thing at one go, but every term is actually labeled with a different colour.

Let us go one by one. The first term we have written is –h cross square by 2mN del N square, N for nucleus. This is the term for the kinetic energy of the nucleus and as you can well imagine, understand that we can do separation of variables, so that we can express things in terms of center of mass coordinates and relative coordinates. This kinetic energy of nucleus will be expressed completely in center of mass coordinates and we will not worry about it.

The second term, of course, see I have written in this way. You can write it any order; it does not matter. Second one that I have written is –h cross square by 2me, me means mass of electron del e square. This is del 1 square. So this is the kinetic energy of electron number 1. Next one will be exactly the same thing, except for the fact that instead of 1, we have written 2. What about me? Does me change? No, they do not. The electrons weigh the same.

Mass is the same for both the electrons. you do not write me1 and me2, makes no sense, but you have to write del 1 and del 2 because x1 y1 z1 x2 y2 z2, these are distinct r1, r2 these are distinct. So far, we have kinetic energy of nucleus, kinetic energy of electrons, electron number 1, electron number 2. Then, you have to think of the attraction between nucleus and the electrons. First one, -1 by 4 pi epsilon 0 ZN nuclear charge, e square divided by r1,

This stands for attraction between nucleus and electron 1. Next term is exactly the same, once again 1 replaced by 2. This is attraction between nucleus and electron 2. There is a typo here, it is not electron 1, electron 2, please correct it yourself, so far so good. This is just an extension of what we did for hydrogen. Now comes the additional term. The term is e square divided by r12. This stands for repulsion between electron number 1 and electron number 2. As we will see, this becomes a major player and major headache in the subsequent discussion and a lot of our efforts go into how to account for this.

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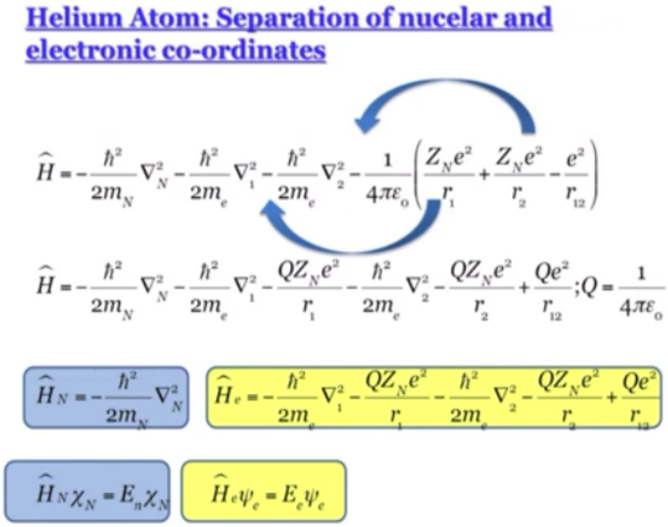

Helium Atom: Separation of nucelar and electronic co-ordinates

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\left(\frac{Z_N e^2}{r_1} + \frac{Z_N e^2}{r_2} - \frac{e^2}{r_{12}}\right)$$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2} + \frac{Qe^2}{r_{12}}; Q = \frac{1}{4\pi\varepsilon_0}$$

$$\hat{H}_N = -\frac{\hbar^2}{2m_N}\nabla_N^2 \qquad \hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2} + \frac{Qe^2}{r_{12}}$$

$$\hat{H}_N \chi_N = E_n \chi_N \qquad \hat{H}_e \psi_e = E_e \psi_e$$

So what you do is, first of all you separate the nuclei and electronic coordinates and while doing that, you write the terms in electron number 1 together, write the terms in electron number 2 together. So write instead of 1 by 4 pi epsilon 0, like what we did in hydrogen atom, we write Q and this is what we get. Out of this, the first term is basically the nuclear Hamiltonian; do not worry about it.

We only worry about the electronic part of the Hamiltonian and that is because the Hamiltonian for the nuclear part operates on the nuclear part of the wave function. Take the wave function to be a product of a nuclear part and electronic part like in hydrogen atom and you just do the separation, exactly same treatment as hydrogen atom, so we will not discuss it again.

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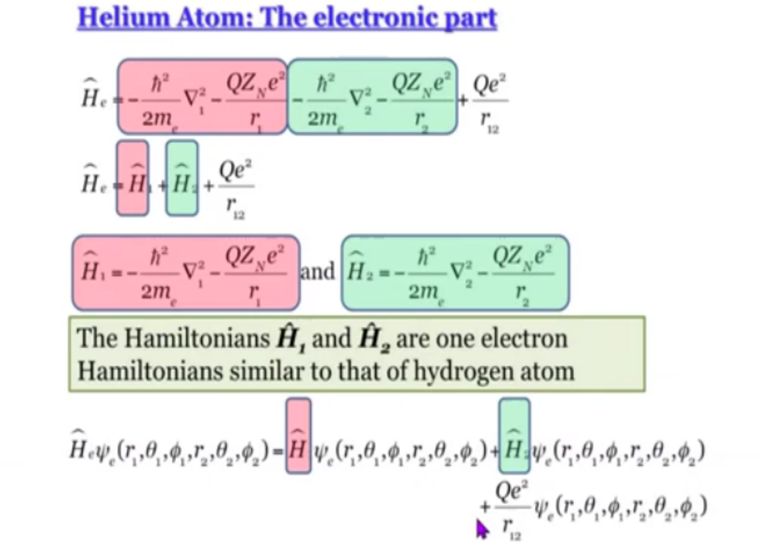

Helium Atom: The electronic part

$$\hat{H}_e = \boxed{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1}}\boxed{-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2}} + \frac{Qe^2}{r_{12}}$$

$$\hat{H}_e = \boxed{\hat{H}_1} + \boxed{\hat{H}_2} + \frac{Qe^2}{r_{12}}$$

$$\boxed{\hat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1}} \text{ and } \boxed{\hat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2}}$$

The Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ are one electron Hamiltonians similar to that of hydrogen atom

$$\hat{H}_e\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \boxed{\hat{H}}\,\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \boxed{\hat{H}_2}\,\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

What we now start worrying about is this electronic part of the Hamiltonian, for helium atom. How many terms do you have? 1, 2, 3, 4, 5. First term kinetic energy of electron 1, second term potential energy of electron 1 due to the nucleus, third term kinetic energy of electron 2, fourth term potential energy of electron 2 due to the nucleus. The last term is what you would not get in our electron system, the electron-electron repulsion.

So I have labeled the terms in one and those in 2. I cannot put a label here, I can, but it has to be a different colour, because this r12 involves coordinates of r1 as well as 2. So they cannot be separated so easily. So what you see is that first one, this one is essentially a one-electron Hamiltonian for electron number 1, is not it, -h cross square by 2me del 1 square – QZNe square divided by r1, exactly what we had encountered in hydrogen atom.

And the second one is also exactly the same as what we encountered in the hydrogen atom, but for electron number 2. One electron Hamiltonians, which is a sort of relief, but then what we need to also understand is that, see these Hamiltonians are all operating on wave functions that are more complex than what they were for hydrogen. Each wave function here say, let us take the first one psi e.

This is the function of not only r1 theta 1 phi 1; it is also a function of r2 theta 2 phi 2, because that electron-electron repulsion is there. Two electrons are there, same charge, they will repel each other. So we have more number of coordinates in these systems.

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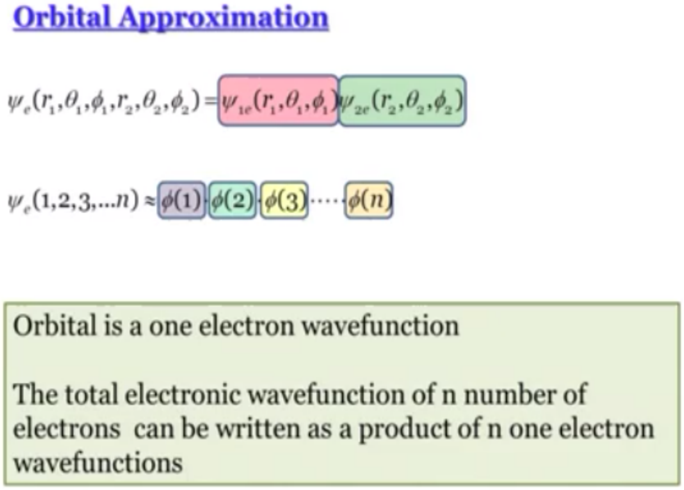

Orbital Approximation

$$\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \boxed{\psi_{1e}(r_1,\theta_1,\phi_1)}\boxed{\psi_{2e}(r_2,\theta_2,\phi_2)}$$

$$\psi_e(1,2,3,\dots n) \approx \boxed{\phi(1)}\boxed{\phi(2)}\boxed{\phi(3)}\cdots\boxed{\phi(n)}$$

Orbital is a one electron wavefunction

The total electronic wavefunction of n number of electrons can be written as a product of n one electron wavefunctions

To simplify, what we do is, to start with we invoke what is called orbital approximation. See we have learnt about atomic orbitals with so much of great effort. So it makes sense for us to try and retain them to the maximum extent possible. So what we do is, we write the wave function of any of these as a product of two one-electron wave functions, electron number 1 and electron number 2 and if you have n number of electrons here, we would have written it as product of phi 1, phi 2 and so on and so forth phi n.

We can always write products as we have discussed while talking about separation of variables earlier. these are in different dimensions, you cannot add them, but you can take products and the good thing is, since Hamiltonian is a derivative, Hamiltonian contains dQ2 kind of term, you take derivative, then derivative of products, as you know is a sum. So the Eigen value energy nicely separates into different parts also, but will it separate here; we will see. So this is where we are.

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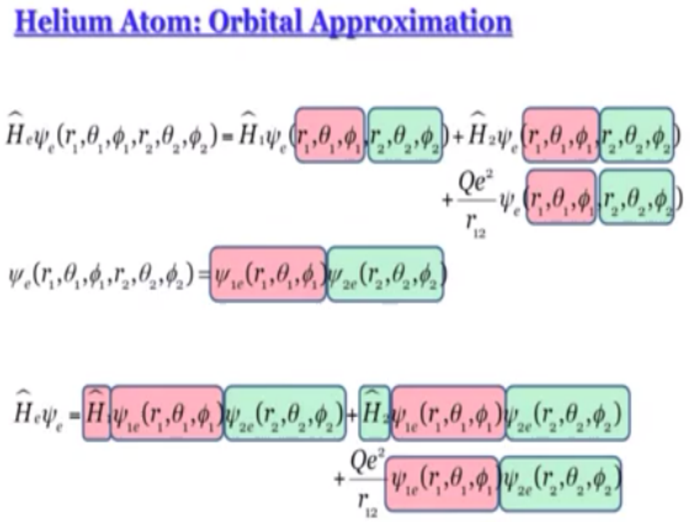

Helium Atom: Orbital Approximation

$$\hat{H}_e\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \hat{H}_1\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \hat{H}_2\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\hat{H}_e\psi_e = \hat{H}_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \hat{H}_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

Now what I have done is, I have collected everything in 1, collected everything in 2. So what we have is H1 operating on psi 1e multiplied by psi 2e + H2 operating on psi 1e multiplied by psi 2e + Qe square multiplied by the product is what you have.

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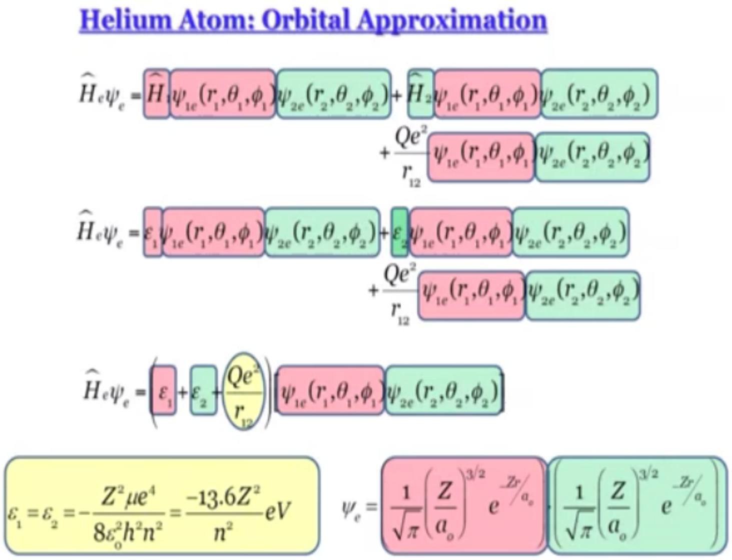

Helium Atom: Orbital Approximation

$$\hat{H}_e\psi_e = \hat{H}_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \hat{H}_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\hat{H}_e\psi_e = \varepsilon_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \varepsilon_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\hat{H}_e\psi_e = \left(\varepsilon_1 + \varepsilon_2 + \frac{Qe^2}{r_{12}}\right)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

$$\varepsilon_1 = \varepsilon_2 = -\frac{Z^2\mu e^4}{8\varepsilon_0^2h^2n^2} = \frac{-13.6Z^2}{n^2}eV$$

$$\psi_e = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}\,\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$$

Now what is H1 psi 1er1, psi 1 is a function of r1 theta 1 phi 1. Hi we know Schrodinger equation Hi = e psi, so this will be epsilon 1 where epsilon 1 is the energy associated with this wave function. When we are talking about helium remember, this wave function is essentially a 1s wave function. So we write epsilon 1. What about here and what about the second term psi 2e function of r2 theta 2, phi 2. It is going to be a constant as far as this H1 is concerned.

So it will come. Once we have got this epsilon 1 multiplied by this, we can rewrite it in this order, quite simple things, we have done many times. Second one also, for H2 this psi 1e is constant, it goes out, but H2 does operate on psi 2e to give you once again, we can write epsilon 2 psi 2e, but then epsilon 1 and epsilon 2 are actually, they have the same value -13.6 Z square by n square eV same energy as that of 1s electron of hydrogen.

Why do we get it, because we are operating an one-electron Hamiltonian on an one-electron wave function, where we write one or two how does it matter. So this is what we have got. Left hand side H psi, right hand side e psi. So this is your e. this is the energy of the system and we write the product as product of 2 1s orbitals, one in terms of electron number 1, one in terms of electron number 2. Everything looks hunky-dory so far. Then that is because we have so far not thought how the situation gets modified because of the presence of Qe square by r12.

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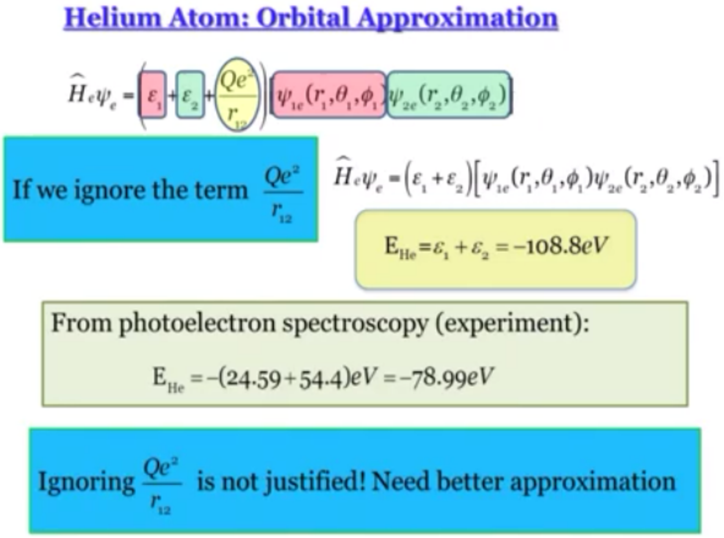

Helium Atom: Orbital Approximation

$$\widehat{H}_e\psi_e = \left(\boxed{\varepsilon_1} + \boxed{\varepsilon_2} + \frac{Qe^2}{r_{12}}\right)\left[\boxed{\psi_{1e}(r_1,\theta_1,\phi_1)}\boxed{\psi_{2e}(r_2,\theta_2,\phi_2)}\right]$$

If we ignore the term $\frac{Qe^2}{r_{12}}$

$$\widehat{H}_e\psi_e = (\varepsilon_1 + \varepsilon_2)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

$$E_{He} = \varepsilon_1 + \varepsilon_2 = -108.8eV$$

From photoelectron spectroscopy (experiment):

$$E_{He} = -(24.59 + 54.4)eV = -78.99eV$$

Ignoring $\frac{Qe^2}{r_{12}}$ is not justified! Need better approximation

That is the problematic part that we have conveniently kept aside until now, but we cannot do that any longer. We have to address it. To address it, the first thing we can do is, we can pretend that it is not there. We have a problem, we might know, the seven stages of acceptance of some bad news or seven stages of grief. The first stage is always denial. So right now we are in denial. We pretend as if that Q square by r12 term is not even there.

Knowing fully well that this is not going to hold water. If two electrons repel each other strongly, they are confined in a small place, still we have to start somewhere. Even if it is to prove that this approach is wrong, we have to start, so we do it. Let us set it to 0 for now. So this is a wave function. This is the equation you get, very nice He psi e = epsilon 1 + epsilon 2 multiplied by psi e, very nice. So this here is your Eigen function, Eigen value epsilon 1 + epsilon 2.

We know the values for hydrogen atom, so we expect -108.8 electron volt. This is the theoretical value that we get using orbital approximation and neglecting this electron-electron repulsion term. The problem is if you do an experiment, the experiment that is pertinent here is photoelectron spectroscopy. For now, we take a rain check on discussing photoelectron spectroscopy.

When you talk about molecules, we will have the scope to at least tell you how it works. For now, just believe me when I say that this is an experimental way of determining energy. The energy turns out to be -78.99 electron volt and the theoretical value that we get is -108.8 electron volt. Now again we are going to talk about it in a little more detail later on, but there is something called variation theorem, which says that your theoretically observed value can never be less.

This is negative value, stabilization. You can never go beyond the experimentally observed value, because experimental value is the truth. This is what Max Plank has said and I always end up coating this has become a cliché in my courses. The great Max Plank had said that experimental results are the only truth, everything else is poetry and imagination, not to undermine poetry and imagination. They set human beings apart from other animals, but then science is pursuit of truth.

To do that, you must do experiments properly and you must not make mistakes and you must have confidence in your experimental results, because they reflect what the situation actually is. Theory is a way of understanding it, reaching it, explaining it. So obviously, the theory that we have used is inadequate. We cannot wish this Qe square by r12 term away. We have to find a way of accommodating it somehow within the ambit of our theory. How do we do that?

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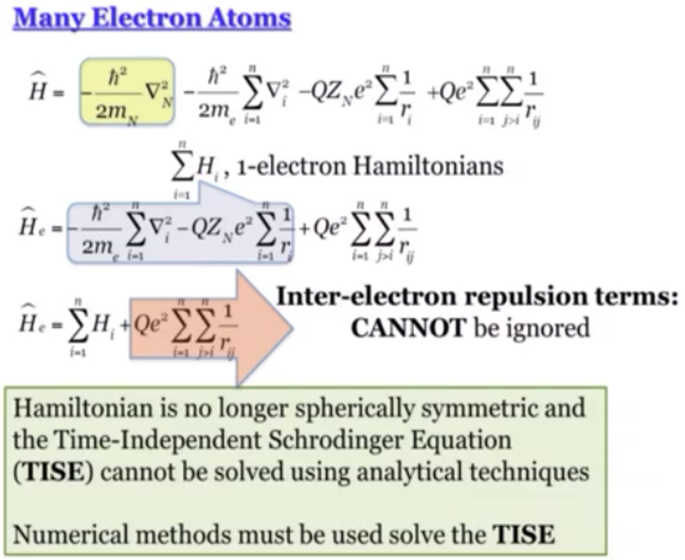

Many Electron Atoms

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$\sum_{i=1}^{n} H_i$, 1-electron Hamiltonians

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_Ne^2\sum_{i=1}^{n}\frac{1}{r_i} + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

$$\hat{H}_e = \sum_{i=1}^{n} H_i + Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

Inter-electron repulsion terms:
CANNOT be ignored

Hamiltonian is no longer spherically symmetric and the Time-Independent Schrodinger Equation (**TISE**) cannot be solved using analytical techniques

Numerical methods must be used solve the **TISE**

Before saying that, let me write this same problem in a little more general terms. For many electron atoms, what is Hamiltonian, -h cross square by 2mN, this is common. Next, we write it as a summation –h cross square by 2me sum over i = 1 to n, we are assuming n electron atom del i square. So this is the kinetic energy of each electron summed over all the electrons. Next we have –QZNe square sum over i = 1 to n 1 by ri. What is this?

This is the sum of potential energy of all the electrons due to their presence near the nucleus. So this term accounts for electron nucleus attraction. Finally, we have our problematic term and it has to be a double summation, because if you take i = 1, j can be 2, 3, 4 whatever. If you take i = 500, I mean there are 500 electrons, j can be 1, 2, 3, 4 so and so forth up to 499, then 501 onwards. So i = 1 to n, I would prefer to write j is not equal to i. This is the problematic part.

This one, as usual we do not worry about. That is a nuclear part. We worry about the electronic part of the Hamiltonian. I hope you see like we had discussed in the simple helium, what we have in the first terms, the first summations rather is a summation of n number of one-electron Hamiltonian and the term that are left over, the summation that are left over Q square, again double summation, 1 by rij. These are the electron-electron repulsion terms.

See when you have more than two electron, the situation is more complex. Suppose you have 3, then you have one-three repulsion, three-two repulsion, two-three repulsion, but then do not go back and say you also have three-one repulsion, three-two repulsion one-three repulsions so on and so forth. So you have to take combinations, not permutations. This is what it is. This is the simple form, in which I can write it. it cannot be ignored as we know.

These are the inter electron repulsion terms. So the only way to go ahead, hydrogen free electron particle in a box, these were all nice systems where we could exactly solve Schrodinger equation analytically. Now you cannot, you have to use numerical methods and we are going to spend considerable effort in understanding some of the numerical methods.

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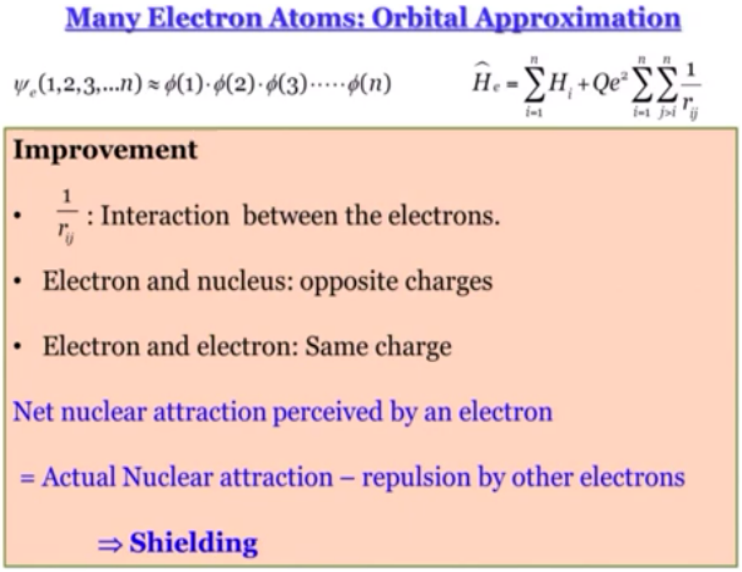

Many Electron Atoms: Orbital Approximation

$\psi_e(1,2,3,...n) \approx \phi(1)\cdot\phi(2)\cdot\phi(3)\cdots\phi(n)$ $\widehat{H}_e = \sum_{i=1}^{n} H_i + Qe^2 \sum_{i=1}^{n}\sum_{j>i}^{n} \frac{1}{r_{ij}}$

Improvement

- $\frac{1}{r_{ij}}$: Interaction between the electrons.
- Electron and nucleus: opposite charges
- Electron and electron: Same charge

Net nuclear attraction perceived by an electron

= Actual Nuclear attraction – repulsion by other electrons

$\Rightarrow$ **Shielding**

But for now, let us study the simplest one. We are working under the ambit of orbital approximation and this here is our Hamiltonian. What we do is this. We think in this way and well, this is nothing new for anybody, because this thought process is there from the very early days that you study atomic structure. The thought process is this, this 1 by rij this is basically repulsive interaction between the electrons.

Now what it does is that it offsets part of the attraction each electron feels with the nucleus. So what we are saying is that the actual nuclear attraction felt by the electron is a little less. Net nuclear attraction is actual nuclear attraction minus repulsion by other electrons. So this phenomenon is called shielding. Everybody know what a shield is, is not it? So well, when we were kids, star trek and all used to be very popular and there you would hear these people going out into outer space.

Screaming that the shield is down to 50%, shield is down to 20%, it is a protective layer. So what we are saying here is that the shield, each electron partially screens the nuclear charge for the other electron. So two electrons, due to presence of one electron, electron number 1 electron number 2 does not feel, suppose the nuclear charge is +3. It does not feel +3. It feels a nuclear charge of +2 or less or more, whatever, but each electron acts as a sort of an electrostatic shield or screen for the other one. Please remember for the other one. An electron does not shield itself from the nucleus. It shields the other ones. So that brings us to the concept of effective nuclear charge.

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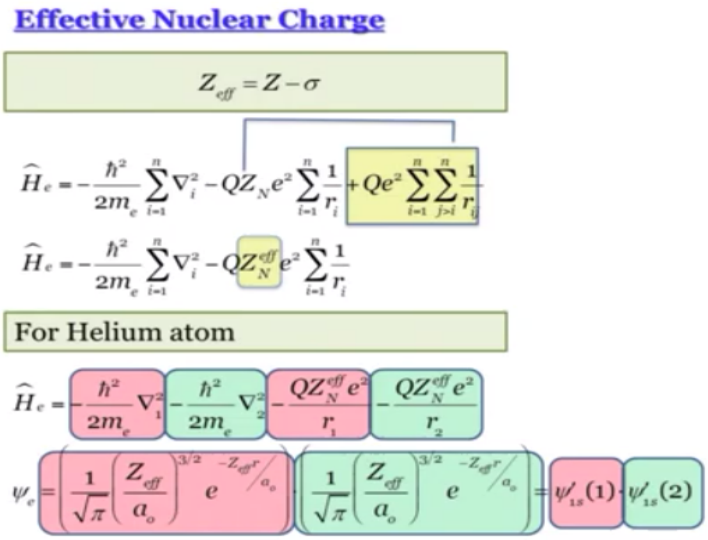

Effective Nuclear Charge

$$\boxed{Z_{eff} = Z - \sigma}$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - QZ_N e^2\sum_{i=1}^{n}\frac{1}{r_i} \boxed{+ Qe^2\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}}$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - Q\boxed{Z_N^{eff}}e^2\sum_{i=1}^{n}\frac{1}{r_i}$$

For Helium atom

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N^{eff}e^2}{r_1} - \frac{QZ_N^{eff}e^2}{r_2}$$

$$\psi_e = \left[\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right]\left[\frac{1}{\sqrt{\pi}}\left(\frac{Z_{eff}}{a_o}\right)^{3/2} e^{-Z_{eff}r/a_o}\right] = \psi'_{1s}(1)\cdot\psi'_{1s}(2)$$

I just said it without mentioning the name. I said that due to the presence of one electron, the other feels instead of 3, maybe nuclear charge of 2.5 or 2, or 1.5 or more or less. So we invoke the concept of effective nuclear charge, which is Z – sigma. Sigma is called the shielding constant. What are we doing here? This here is the Hamiltonian. First term no problem, second term no problem. Third term is a problematic part, which we are not being able to handle.

So we have conveniently shifted the effect of the third term into the second term itself, into Z itself. Then, we do not have to write the third term anymore. It is accounted for in this shielding constant. this is how you write it He = - h cross square by 2me sum over i = 1 to n del i square – Q into Z, effective nuclear charge e square sum over i = 1 to n, 1 by ri. So this rij, problematic rij vanishes. Have we neglected it, we have not actually.

We have accounted for it in sigma, but the good thing is that allows us to write our Hamiltonian in terms of n number of one electron Hamiltonians with the modification that screening does not differ. So for helium atom, this is going to be the Hamiltonian and your wave function is going to be something like this. So remember, wave function will also change. So these are 1s wave functions.

For helium 1s wave functions will be used, but look at this e to the power –Z effective r. Look at the constant Z effective by a0, what does that mean? If Z effective is less than Z, then this constant becomes smaller. So for any given value of r, psi becomes a little smaller. Also, the fall of is not as much as it could have been for full Z. Z effective is a smaller number. So the shape and size of orbitals, we should not put it that way. It is going to change because of effective nuclear charge.

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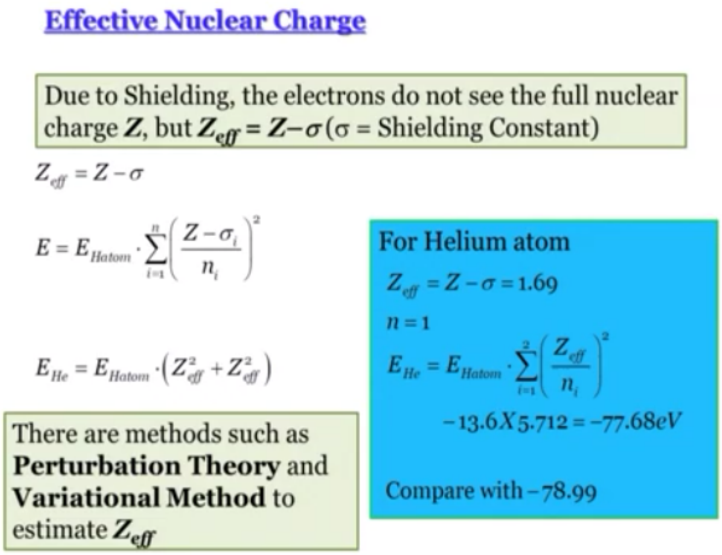

Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge **Z**, but $Z_{eff} = Z - \sigma$ (σ = Shielding Constant)

$$Z_{eff} = Z - \sigma$$

$$E = E_{Hatom} \cdot \sum_{i=1}^{n} \left(\frac{Z - \sigma_i}{n_i} \right)^2$$

$$E_{He} = E_{Hatom} \cdot \left(Z_{eff}^2 + Z_{eff}^2 \right)$$

There are methods such as **Perturbation Theory** and **Variational Method** to estimate Z_{eff}

For Helium atom

$$Z_{eff} = Z - \sigma = 1.69$$

$$n = 1$$

$$E_{He} = E_{Hatom} \cdot \sum_{i=1}^{2} \left(\frac{Z_{eff}}{n_i} \right)^2$$

$$-13.6 X 5.712 = -77.68 eV$$

Compare with −78.99

Now we will just demonstrate using a simple calculation. Let us say that we talk about helium atom, as usual. Z effective is 1.69, n = 1, so energy of helium accounting for your shielding turns out to be -77.68 whereas the experimental value is -78.99. So is that a good agreement or is that a good agreement? It is a good agreement. There is no scope of saying it is not good. Given the kind of approximation we have invoked, it is as good as it gets.

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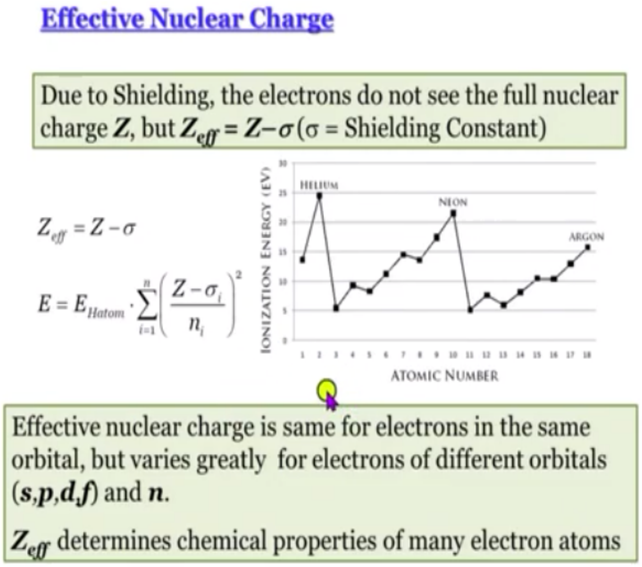

Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge **Z**, but **$Z_{eff} = Z - \sigma$** (σ = Shielding Constant)

$$Z_{eff} = Z - \sigma$$

$$E = E_{Hatom} \cdot \sum_{i=1}^{n} \left(\frac{Z - \sigma_i}{n_i} \right)^2$$

Effective nuclear charge is same for electrons in the same orbital, but varies greatly for electrons of different orbitals (***s*,*p*,*d*,*f***) and ***n***.

Z_{eff} determines chemical properties of many electron atoms

The effect of this effective nucleus charge is such that one thing that we need to remember, see for one electron systems, hydrogen atom, the 2s2p everything had the same energy. The moment you put in more electrons, the moment the system has more electrons than 1, 2s and 2p are no longer degenerated. They have different energies and that is because shielding of electrons in different orbitals, extent of shielding is actually different and that is why you have this.

You know this, very familiar with periodic properties and that is why ionization energy exhibits this kind of a saw-tooth variation, because it is not exactly like hydrogen. Electrons in different orbitals even if n is same, actually have different penetrations, different shielding.

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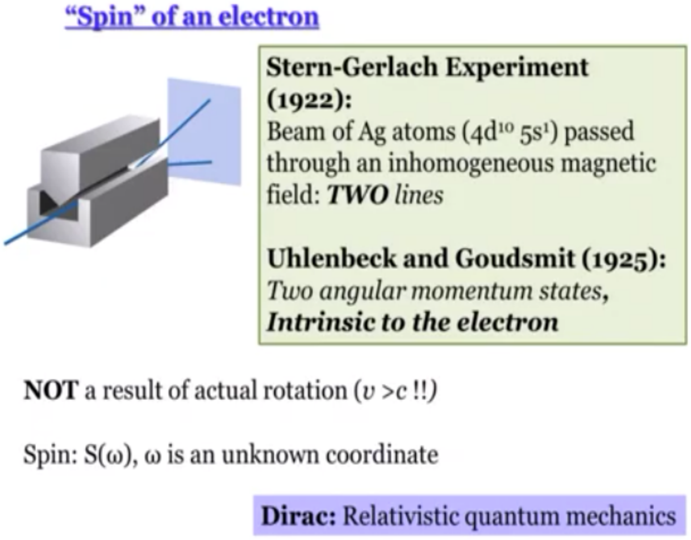

"Spin" of an electron

Stern-Gerlach Experiment (1922):
Beam of Ag atoms ($4d^{10}\ 5s^1$) passed through an inhomogeneous magnetic field: ***TWO** lines*

Uhlenbeck and Goudsmit (1925):
Two angular momentum states,
Intrinsic to the electron

NOT a result of actual rotation ($v > c$!!)

Spin: S(ω), ω is an unknown coordinate

Dirac: Relativistic quantum mechanics

That is one part of the story, electron-electron repulsion. The second part of the story, which at the moment I am in a little bit of dilemma about to what extent we will develop in this course, is that of spin. Spin is something that you have heard and many of us might have the idea that the spin quantum number arises out of the electron actually spinning on the axis. That is what people thought in the first place. That is why, it was given the name spin.

However, it is not. Origin of spin, one of the origins is Stern-Gerlach experiment of 1922 where the beam of silver atoms is passed through an inhomogeneous magnetic field showed two lines, which means that the ensemble splits into 2 kinds of atoms in the ensemble and the explanation was the presence of 2 angular momentum states. Remember angular momentum, we have talked about angular momentum at some length, but this angular momenta are different in the sense that they are intrinsic to the electron.

If you take an electron inside an atom, then you get an Lm and you get s. You just take a free electron, there is no n, no l, no m, s is still there, but one thing we will have to develop is what is the meaning of s and what is the meaning of ms. I think our earlier discussion of angular momentum, rigid rotor and hydrogen atom is going to help us big time. So very briefly we can say, there is not a result of actual rotation. It is written in an unknown coordinate, but interestingly, you can talk about its Z component.

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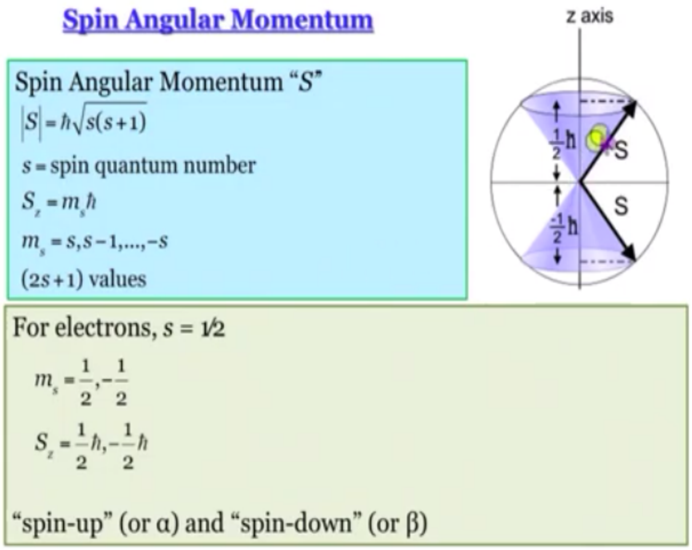

Spin Angular Momentum

Spin Angular Momentum "S"

$|S| = \hbar\sqrt{s(s+1)}$

s = spin quantum number

$S_z = m_s\hbar$

$m_s = s, s-1, \ldots, -s$

$(2s+1)$ values

For electrons, $s = 1/2$

$m_s = \frac{1}{2}, -\frac{1}{2}$

$S_z = \frac{1}{2}\hbar, -\frac{1}{2}\hbar$

"spin-up" (or α) and "spin-down" (or β)

It really arises out of relativistic quantum treatment that we have performed and many people still continue with it. So it is associated with spin angular momentum S and its magnitude as usual is h cross multiplied by root over s into s + 1, where s is a spin quantum number. You see the analogy between this and the Azimuthal quantum number or that rotational quantum number J of rigid rotor, l in hydrogen atom, S in spin quantum number, all have identical behavior.

And SZ is msh cross, ms as you know denotes the Z component of angular momentum, it has 2s + 1 values, as we have demonstrated earlier, same derivation as what we have done for J and m. Now for electrons, spin is half. This is another common source of error. Please remember for electrons, spin is not plus half and minus half; those are ms. Ms is plus half and minus half. Spin is half. What does spin designate? The length of the arrow. What do this plus, minus half designate? Whether the arrow is pointing up or down. We will talk about spin at a greater length in the next module.

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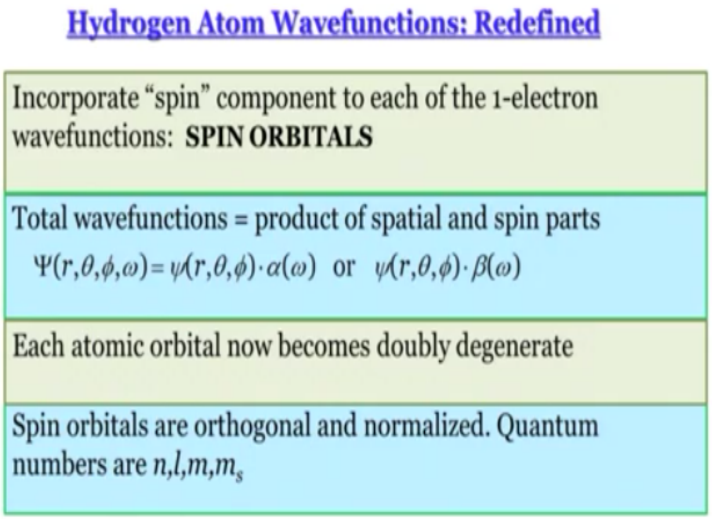

Hydrogen Atom Wavefunctions: Redefined

Incorporate "spin" component to each of the 1-electron wavefunctions: **SPIN ORBITALS**

Total wavefunctions = product of spatial and spin parts

$$\Psi(r,\theta,\phi,\omega)=\psi(r,\theta,\phi)\cdot\alpha(\omega) \quad \text{or} \quad \psi(r,\theta,\phi)\cdot\beta(\omega)$$

Each atomic orbital now becomes doubly degenerate

Spin orbitals are orthogonal and normalized. Quantum numbers are n,l,m,m_s

But for now, let us conclude here that you have to incorporate spin and you cannot just write these orbitals in terms spatial coordinates. When you include spin along with spatial coordinates, then you get modified orbitals that are called spin orbitals. So the total wave function is a product of spatial and spin parts. Each atomic orbitals now becomes a doubly degenerate, ms can be plus half or minus half.

That is why later on we come to this rule, where no more than 2 electrons can occupy each orbital, poly exclusion principle that comes because they have only two values of ms and then please remember spin orbitals are orthogonal and normalized, so total quantum numbers that we now have are n, l, m and ms. Please remember ms and not s. we went through this last portion a little hurriedly. It was meant to be only an introduction. We are going to develop the concept of spin in little more detail slowly. Then, we will continue with our discussion of atoms with more than one electron.