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MARZARI:**

OK, good morning. And welcome to lecture 6. We're still working on electronic structure methods. And today in particular, we'll finish up our introduction of the Hartree-Fock methods, if you want the cornerstone of quantum chemistry. Really developed in the late '20s, we have Douglas Hartree here from the University of Cambridge and Fock, I think, from the University of St. Petersburg.

And then we'll also go into Density-Functional theory that, in many ways, is a much more recent approach. The theory itself was developed in the '60s by Walter Kohn in collaboration with Pierre Hohenberg and in collaboration with Lu Sham. But really, I would say it's only in the mid '70s and then really in the mid '80s that it started to take off as actually a practical approach to study the electronic structure, especially of solids, and has become very popular, popular to the point that the Nobel Prize for chemistry in '98 was given to Walter Kohn for DFT and John Pople, a quantum chemist, for the development of quantum chemistry methods.

Let me remind you before we go on into the lecture of the two main conclusions of last class. The first one was the appropriate matrix formulation of the Schrodinger equation that is something that is very powerful and very useful when we actually need to solve a differential equation on a computer. And the hypothesis there was that we had chosen a basis set that I indicate here with ϕ . That would be the basis set in which I would expand my ground state wave function.

And so once the basis set is chosen-- it could be sines and cosines with different wavelengths. It could be localized wave functions like Gaussians. It could be just points on a discrete grid. But once my basis set is chosen, and once I know what is my electronic structure problem-- that is, once I know what is the potential in my Hamiltonian operator-- this here, these integrals, are just numbers. So solving the Schrodinger equation-- that is, finding the key E eigenvalues and the corresponding eigenvectors-- is nothing else than solving this linear algebra problem where, again, these coefficients here form a vector that really gives me what are the terms in the expansion of my wave function, in terms of orthonormal basis.

And so linear algebra problems, we have a matrix here. And it will have, if it's an order n matrix, n values for which the determinant is 0. And those are the eigenvalues for which we can find the solution. So this is important not only in electronic structure, but in a lot of applied computational approaches.

And the other very useful principle here that I have listed is the variational principle. That is, again, it is possible to define a functional-- that is, if you want an algorithm-- that takes as input a generic function and gives us output, a number. And the functional that we use is the functional that I've written here with the integral expectation value of the Hamiltonian on an arbitrary wave function divided by basically a normalization term.

And it can be proven-- and it was given to us an exercise-- that this quantity is always greater or equal than the ground state. And this is very powerful because, if we have no idea on what the solution for our ground state problem is, well, we can just try out a few. And our best solution-- although, we will never know if it's the exact one or not-- will be the one that gives the lowest expectation value for this term.

And here is an example on how we could actually go on and try to solve a very simple problem that is finding the eigenstates and eigenvalues for a hydrogen atom using the variational principle. And instead of trying actually different wave functions at a time, what we can do that is very meaningful is choose a parametric format for the wave function. So you see, I'm writing here a generic wave function that decays as an exponential as a function of the r distance from the nucleus from the center of the electron.

So if you wanted this parameter here, α determines how steep the decay of this wave function here. So by writing it in this way, I'm not considering any more just one way function. But I am considering an entire family of functions with different decays.

And so what I can do is try this family of wave functions. And so what I would do is stick this expression in this expectation value. And then actually, the constant, C , is what we call a normalization constant. It always cancels out, you see, from the integral below and the integral above. This C squared would just go away.

And so overall, the variational principle and expectation value is a parametric function of α . And the optimal α will be the α that gives me the minimum value for this number. Again, we can't go below the ground state for this expectation value. So the lower that we can go, the better. And if we use this particular choice of wave function-- and this is, again, a very simple analysis problem that you could actually work out by yourself. I've actually written here all the terms of the normalization integral. What is its value as a function of this parameter once you do it properly in spherical coordinates, considering that this is really the radial distance, and this is the expectation value of the kinetic energy, and this is the expectation value of-- you see minus 1 over r . That is the potential for the electron in the field of a proton.

And if you minimize this expression-- very easy-- what you obtain is α equal to 1 . So the optimal solution is then α equal to 1 . It turns out that, by solving directly the differential equation, the Schrodinger equation, we actually know that this exponential of minus r is actually the exact solution. And so what happens, in this case, is that this parametric family of wave functions is the right form. That is, it contains actually the exact the ground state among all its possible forms.

And that exact ground state is reached when α is equal to 1 . And the variational principle will give us α equal to 1 without having any need of solving the very complex radial Schrodinger equation that I've shown at a certain point in the class on Tuesday where we really need to solve for the spherical harmonics and find the Legendre polynomial, Laguerre terms in the radial part, and so on and so forth.

So this becomes very simple. And for this reason, the variational principle is very powerful. And we'll actually see how Hartree and Fock use that to find out a way to tackle the problem of many electrons interacting because, up to now, we have really only thought of the problem of one electron in a potential. But the problem of many interacting electrons increases its complexity very quickly.

So I'm just showing here what would be, say, the Schrodinger equation for a two-electron atom, say something typically like the atom of helium. You have a nucleus that has really two protons. And then you have two electrons around the nucleus, going around.

And so what is the Hamiltonian, the quantum mechanical Hamiltonian for this problem? Well, what we have is the kinetic energy terms here. So we have a Laplacian that is a second derivative in space for each one of the coordinates. So you see this is the wave function. The wave function is an amplitude that is a function of the combined position of r_1 describing the first electron and r_2 describing the second electron. So you have these two second derivatives.

And then there is the term that deals with the attraction between electron 1, say this electron here, and the nucleus. We have an attraction term here, Coulombic attraction, that goes basically as $2/r$ or as Z/r if we think of the nucleus as having charge Z . And so there is attraction here of the first electron to the nucleus and then attraction of the second electron to the nucleus. And then the last term is actually a repulsive term-- so there should be actually a plus sign here-- between the two electrons. And so you see it depends-- again, Coulombic comparison between the electrons-- on the distance between r_1 and r_2 , the instantaneous position.

So you see, this is how the Hamiltonian becomes, in the case of an atom that has two electrons and everything here, the final generalization still for one atom but with many electrons. So in the case where, again, you have a nucleus with many electrons orbiting around, what you will have is a wave function that is a combined amplitude of n different spatial variables. So if we have, say, an atom like iron that has 26 electrons, well, that wave function is a combined amplitude of 78 coordinates.

And the Hamiltonian operator, again, is our second derivative for each electron in there as an attractive term for each electron that is attracted to the nucleus that now has a charge Z equal to 26. And then each electron-- so this sum i goes over each electron. Each electron will be repelling each other electron. So there is an overall repulsive term.

And we actually call this term here-- this is the difficult term. We call this term here a two-body term because it depends on the simultaneous possession of two electrons. Well, if you want, the first the terms here are called one-body terms because they act only on one electron at a time, quantum kinetic energy and attraction.

And truly, this Schrodinger equation becomes overly complex already by the time when we have two electrons. So we can't solve analytically even the helium atom, OK? We can solve everything about the hydrogen atom. And we can solve the Schrodinger equation for a number of very simple problems. But already, for the helium atom, we can't do that.

And so in the '40s and '50s, people developed variational approaches. They were making an uncertain hypothesis on this wave function, expanding this wave function in a series of other functions, depending parametrically on a number of coefficients-- 2, 3, 5, 8, 200 coefficients. And the more coefficients there were, the more flexible that wave function was.

And so systematically, by adding more and more flexibility, you could go lower and lower. And hopefully, you were converging. And say for something like the helium atom, well, the total energy of two electrons in the helium atom is something like 5.8, 5.8 Rydbergs. And you could get very, very close, down to a fraction of hundreds of electron volts just by 3 or 5 parameters. But then as you go to more and more electrons, the problem really has a complexity that explodes.

And in all of this, I want to remind you, I'm not using any more the international system of units. So I'm not using meters and seconds. But I'm using what are called atomic units. And there is a handout on your Stellar web page reminding that the unit of energy is what we call the Hartree that corresponds to another set of unit that are often used. Say a Hartree corresponds to Rydberg. And the Rydberg is 13.6 electron volts. And electron volt is the energy of an electron that feels a potential difference of 1 volt. And 1 electron volt is often considered 23.5 kilocalories per mole.

In the electronic structure literature, you'll see all these numbers. Often, chemists use the kilocalorie per mole unit. Physicists tend to use the electron volts. And again, I remind you that the average kinetic energy of an atom at room temperature is 0.04 electron volts. And the binding of water dimer is 0.29 electron volts. So the electron volts is really the order of magnitude of the binding of weakly attached molecules.

OK. So now, the problem-- and that's where the Hartree and Hartree-Fock solution become important-- is to deal with a realistic system. That is, we need to deal with molecules or we need to deal with solids. So we need to deal in principle, with a Schrodinger equation in which we have a lot of nuclei. I'm denoting here with capital R the position of the nuclei. Again, if you want to find out what is the structure of benzene, if you want to find out what is the electron structure of silicon, you need to keep in mind that, say for benzene, you will have six Coulombic attractive centers that are the six carbon nuclei in a ring and also the six $1/r$ protons around.

So the position of those nuclei determines what is the potential acting on your electrons. So in principle, the Schrodinger equation will be something like I've written here. But we can make this fundamental simplification that will always be the case for the classes that follow. That is, we never treat the nuclei as quantum particles, OK?

In principle, also the nuclei are quantum particles. So they would have their own wavelength. They come in as variables into the wave function. And you would need to calculate, say, things like the quantum kinetic energy of the nucleus. That is the Laplacian, the second derivative of the overall wave function with respect to the nuclear coordinates.

In practice, remember the Bernoulli relation. The nuclei are so heavy that their wavelength is very, very small. So we can truly treat them as classical particles. And the electrons are so much faster than the nuclei that even if the nuclei move, the electrons can always, much faster than the nuclei, follow this movement and reorganize themselves as to be getting the lowest energy state possible.

Basically, you have to imagine this picture of the molecule vibrating at room temperature. And the nucleus then will have a kinetic energy. All the mass of the molecule is in the nuclei. So all the effects of temperature, if you want, are in the vibration of the nuclei. But these vibrations are very slow from the point of view of the electrons. So the electrons see that the nucleus is slowly moving and rearrange themselves as to being in the ground state for that instantaneous configuration of the nuclei.

Obviously, if the nucleus starts moving very, very fast by any chance, well, then the electrons can't do this. They can't follow any more. And so if you want, you can start having electronic excitation. That is the electrons are not anymore on the lowest energy state possible for that given configuration.

That doesn't really happen, especially if we are just considering a molecule a solid at room temperature. But it could happen, say, if we have an external potential that changes very fast. If we shine a laser light on a molecule, then light is nothing less than an electromagnetic field. And laser light will typically have a frequency that is fast and comparable to the frequency of the electrons. And so all these adiabatic approximations break down. And lo and behold, we can actually excite with the laser the electron in a higher energy state.

But for what you are seeing in this class, we'll always think of the electrons in a ground state. That this is what people call often the adiabatic or the Born-Oppenheimer approximation. These two terms, in most cases, are used in the same way. Although, chemists tend to make a subtle distinction about what adiabatic means and Born-Oppenheimer means.

And adiabatic really refers to the coupling between the different potential surfaces for the electrons, depending on the velocity of the nuclei. And Born-Oppenheimer implies that there is no influence of the ionic motion of one single electronic surface. But I mean, this is fairly technical. Just remember that sometimes these two terms actually mean something very different and very specific.

OK. So this has now become our most general expression for the Hamiltonian and also for the energy of a set of nuclei and a set of electrons. That is really our picture of a molecule or a solid. And again, we will have the nuclei generating Coulombic attractive potentials in every position where they are. So there is what we call an electron nucleus term. That is an attractive term in which we have a sum over each and every electron because each and every electron feels the potential of all the nuclei. And the sum of all the nuclei refers to a sum of Z/r terms.

So in whole space, wherever there is a nucleus, there is a $1/r$ term. And this sum over nuclei is the overall potential for the electronic system. And each electron feels this potential. And this is the fundamental attractive term. So electrons are attracted to the nuclei.

But also, electrons repel each other. And this is the other term. So you see each and every electron has a charge 1 in atomic units and has a Coulombic repulsion with each and every other electron. And then, of course, for each electron, we have the quantum kinetic energy here.

And so I listed here in the Hamiltonian all these terms. We have the quantum kinetic energy here. We have the electron-electron repulsion. And we have the electron-nucleus attraction. And then there is a last term that is truly a classical term because it involves only the nuclei. And so it's a repulsive term that is the nucleus-nucleus repulsion.

So if you want to think for a moment of a hydrogen molecule, say, what you would there is a nucleus, another nucleus, and then a wave function of all the electrons around. And there is a classic term that is the electrostatic repulsion between the two nuclei. And there is a quantum term of repulsion between the electrons and an attraction between the electron and the nuclei.

And basically, all these electrostatic terms-- nucleus-nucleus, electron-nucleus, and electron-electron-- almost balance themselves. Each and every one is very large. But then the combination of these three almost cancels itself out. And that's why actually the binding energy of a molecule is much, much smaller than any of the energy, say, of two charges at that distance repelling each other or even just the energy of a core electron very close to its nucleus.

And that's why also electronic structure calculations are very delicate because what you need to find out is a total energy that is the combination of terms that largely cancel each other out. And so you need to be very accurate in order to actually decide if something like a hydrogen molecule binds together or breaks apart.

OK. Now, this is truly a problem of greater computational complexity. And as I said over and over again, we can't really deal, even computationally, with an object that has all the information content of a wave function. So let me actually go through this into the next slide, in which I've written out explicitly the example of the iron atom.

So that has, again, 26 electrons. So the electromagnetic wave function will in itself have 78 variables. And if you think about how many numbers do we need to store this object with any kind of precision, well, suppose that we even limit ourselves to a very, very coarse sampling, only say 10 values around either nucleus. Well, even to give this wave function, to give this amplitude with this very coarse sampling, we would need 10 to the 78 numbers.

So basically, there is no way we can numerically deal with the complexity of the wave function. And this is where the power of the variational principle and the ideas of Hartree-Fock came together. And we'll first discuss the first idea of Hartree in dealing with this problem.

Remember, what we have is a set of interacting electrons. And I like to compare each one of you to an electron. So what you need to think, and what the complexity of this problem is, is that at every instant in time each one of you is interacting or actually repelling with each one else. So this is the complexity of a many-body problem.

In order to understand what's happening, each thing needs to know what everyone else is doing. And Hartree introduced the concept of independent particles and effective potential. This is something that comes over not only in electronic structure, but it comes over in a lot of problems where we actually need to deal with a very large number of interacting elements and interacting particles.

And the general idea is that we can approximate and try to solve this problem by not considering what each electron instantly does. But we can solve the problem by treating what one electron would do in a field that, on average, represents what all the other electrons would be doing. So if we want to think, say, what I would be doing-- I shouldn't try to find the solution that instantaneously knows about what each and everyone else is doing. But I could try to find a solution for myself interacting electrostatically with the average charge distribution that everyone else does.

So instead of having to know what is the instantaneous position of all the other interacting electrons, I could make an approximation that I could actually really just try to deal with the way I interact with an average distribution of everyone else. So this is, if you want, the concept of mean field or effective potential. We are averaging over all the variables.

And there is actually a mathematical way to do this that I'll introduce in this moment. But if you want, the Hartree solution really leads to this. It leads to a Schrodinger equation in which we are actually trying to solve the problem of a single electron at a time. But that electron feels the average electrostatic charge distribution of all the other electrons.

And one can actually obtain this directly from the variational principle. That is, one can make an answer for the wave function. What is written here is this most generic wave function. And one can make what turns out to be actually a fairly severe approximation.

That is, we can say that this many-body wave function can actually be written as a product of single particle orbitals. So you see, what's happening, when we are actually making this hypothesis, is that varying r_1 will change the amplitude of the wave function independently from what happens to r_2 and r_n . These have all become independent variables. There is no combined effect what r_2 and r_1 are doing-- so your any couple, any triplet, and so on and so forth.

So if you want, if we fix all the other variables, we can independently look at what each one of these orbitals is doing. And you can think just what would come from a Taylor expansion. This is an approximation. It's not a true solution, OK? Suppose that we were dealing with two variables.

Well, I mean, something like-- think of a generic wave function that could be written as, say, the exponential of the square root of r_1 plus r_2 that can't be decoupled in the product of two wave functions. So the product of two single-particle wave functions is something simple that doesn't capture the complexity of all the possible two-body wave functions. And so in this, it's an approximation.

And so Hartree made this approximation and then asked himself, what happens if I actually throw this approximation in the variational principle? Now, the difference is that, instead of having just a function that varies parametrically, now what we can really vary in our variational principle are the shapes of all these single-particle orbitals. So what we are asking ourselves is a function of this former throwing into the variational principle will give me a condition that each of these orbitals need to satisfy. So if you want, you really need to now calculate with functional analysis what are the differential equations that each of these orbitals, ϕ_1 to ϕ_n , needs to satisfy so that the overall expectation value of the energy is minimum for a wave function written in this restricted class of product of single-particle orbitals.

And so when you actually work out the fairly complex functional analysis of this problem-- that's actually described, if you're interested, in one of the references that we have given you, the Bransden and Joachain book on the physics of atoms and molecules-- what you obtain for the specific case, again of a Hamiltonian operator in which the potential is given by a linear combination of attractive Coulombic potential, is a set of equations. That is, what you obtain is a new set of differential equations.

Instead of having, if you want, one single Schrodinger equation for a many-body wave function-- what you obtain if you are dealing with n particles is n different differential equations, each one being a differential equation for only a single particle wave function. This is still fairly complex. But the complexity of this has gone from being a complexity of a wave function of 78 variables to, say, the complexity of 26 equations in three variables each, if we are working in three dimensions.

And actually, the form of this equation is very intriguing because this really looks like a Schrodinger equation for one electron. You see, here is the quantum kinetic energy term for this electron. And then there is the interaction between this single electron with the Coulombic distribution of nuclei. And then there is a term-- you see, this appropriately is called the Hartree term-- in which this electron, i , is actually feeling a Coulombic repulsion-- this is the Coulombic term-- of a charge density distribution.

Remember that if we take this square model of a wave function, we obtain the probability of finding an electron somewhere. And the charge density is nothing less than that. It's the probability of finding an electron somewhere. And so you see, what we have is, for the electron that we have denoted as i , the interaction between the wave function and a potential, as usual a potential, in which we have the Coulombic term. And the repulsion, the Coulombic repulsion is between the electron, i , and the charged density distribution of each and every other electron, j . So you see, this sum goes over all the other electrons.

So my many-body Schrodinger equation has become a series of equations that we call single-particle equations, a differential equation for each and every electron. And those differential equations, as I said, have been obtained formally just by applying this answer to the variational principle, are in the form of a Schrodinger-like equation with a kinetic energy, an attractive potential. And now, we have only a mean field interaction between the electrons because electron i doesn't instantaneously need to know what each and every other electron does. But it actually only interacts with the average charge density distribution that is given by the square model of j .

OK. So this is a great simplification. And it actually allowed some of the first calculations, say, on atoms. Actually, this was developed in the late '20s. And very quickly, it was realized what was wrong. And we'll see that in a moment. That is the lack of correlation because there is a specific role that electrons are fermions. But really, this was the first time in which we had a workable differential equation for our many-body system.

And the most important conclusion of this, and where the complexity of the many-body problem comes back in, is that this new operator, this new overall Hartree operator acting on the wave function, has become, as we say, self-consistent. That is, the operator itself depends on what the other electrons do. So it depends on what the solution to all the other differential equations are.

So if you want to know what electron i does in the mean field of all the other electrons, you need to know what is the wave function of each and every other electron. But in order to solve the wave function of each and every other electron, you will need to know also what electron i is doing.

And so really, this is very different. The Hamiltonian operator here is not anymore given at the beginning of the problem, but actually needs to be found because the operator-- the action on one electron depends on what the other electrons do. And in order to find out what the other electrons do, we need to solve the set. So this set of-- say, the case of iron again-- 26 differential equations needs to be solved simultaneously, OK? So we actually solve it iteratively. We start with a guess for what the wave function would be. And we try to find a combined solution. I'll describe in a moment what the algorithm is.

So this is how the many-body complexity comes in. That is, we need to solve a differential equation for which we don't even know, at the beginning, what is the operator acting on our single-particle wave function. And so the concept of self-consistency and of iterative solution will basically be always present in all the electronic structure approaches that we are going to see in this class.

And it's actually very simple to figure out what could be an actual algorithm to try to get to the solution. That is, we need to start with an arbitrary guess for all those 26 orbitals. And once we have that arbitrary guess, we can construct the charge density of every electron. And so we can construct what would be the operator acting on each one of the ψ_i . That is, we can construct this term here.

Once now we know what actually our differential equation is, we can solve it. So we find what are the ground states of each of those 26 differential equations. And now, with those ground states, we can construct again a charge density of each and every single electron. We put it together. We have a new Hartree operator. And we can solve these differential equations again. And we keep iterating this until what we obtain is a Hartree operator in each differential equation that doesn't change anymore. And so we have now a set of self-consistent orbitals.

In most cases, you actually don't get to convergence. So a lot of the algorithmic advances that has been done in the 20th century is actually to do with this problem. That is, we need to find ways to get this procedure to converge to an actually self-consistent point. But the concept is all here.

And if you want, the simplest thing that you can do to make sure that you're going to iterate to self-consistence is to move very slowly. That is, whenever you have a set of solutions, you don't want to construct your Hartree operator, this new charge density, with the solution. But you want just to modify a little bit your previous charge densities to go in the direction of the new charge density that you were calculating. So you somehow try to minimize the change in the operators from one iteration to the other. And that tends to be actually fairly functional in a lot of problems.

Now, Hartree was a very interesting character, again growing up in Cambridge at the turn of the century. He became an expert in differential equations during the First World War because basically people had the problem of sending cannonballs across the lines. So there was a lot of differential equations.

And so mid '20s, he developed this general idea of the Hartree equation that really what we call coupled integral differential equation because there are derivatives and there are integrals. And so what you need to do is now solve this equation that can't really be solved analytically.

And luckily, that was the time in which people were developing, if you want, the first computers. No electronic in there-- so computing machine, but mechanical. And one of the first computers was at MIT. This is actually a picture from the MIT archives. There was an electrical engineer named Vannevar Bush, to which Building 13 the Bush Building, is named that developed one of the first mechanical differential equation solvers. And so Hartree came at the end of the '20s to MIT to actually solve the Hartree equation, I guess, in some building here exactly on that machine, and then went back to Cambridge. And so this, I thought, was an interesting note.

So what do we obtain when we actually solve the Hartree equation? Well, the most fundamental concept is that we are losing some information on what's happening instantaneously to all the electrons. This is what we call, generically speaking, a correlation. And I'll give you the technical definition in a few slides.

But basically, this is what's happening. Let's consider the case of the helium atom. That is the simplest case in which you have more than one electron. So what you have is two electrons. What does the Hartree equation tell us about-- or what do the Hartree equations tell us about these two electrons?

Well, we have two equations. And in each of them, one electron is going to feel an average electrostatic repulsion from the other electron. So what we have is that this right electron here is attracted to the nucleus and is repelled by a spherically symmetrical average charge distribution. So this is what's happening. This is what Hartree tells us.

But in reality, electrons instantaneously try to keep themselves as far apart as possible because electrons repel each other. So in a simplified way, you could think of electron 1 and electron 2 trying to orbit the nucleus as much as possible in a position of phases. So the true two interacting electrons try to be as far as possible at every moment in time during their revolution around the helium nucleus.

But this instantaneous correlation-- that is, the fact that the wave functions tries to keep the electron as far away as possible-- is lost in the Hartree equations because what we do is we are really having one electron interacting with the average position of the other electron. And so in the Hartree equation, there are a lot of terms that have to do with our initial electron, red, being too close to the green charge density distribution.

So if you want, the wave function-- that is, the overall solution of the Hartree equation-- tends to have too much electrostatic repulsion between electron 1 and electron 2. And that's why ultimately the energy of this Hartree function is higher than the true solution. This is what is missing in the Hartree equation, the fact that what you want is a lot of correlation. That is, electrons want to keep each other apart as much as possible.

But that, if you want, is really an instantaneous solution. It's what people call dynamical correlation. Electrons want to keep apart from each other. But if you start looking at a mean field solution in which only one interacts with the average charge density, you have lost the possibility of having this instantaneous non-symmetric distribution. And so in general, this is what we call correlation. And this is what is missing in the Hartree picture.

There is another set of very fundamental concepts that I'll describe in a moment that the wave function-- the answer for the Hartree wave function-- doesn't satisfy a fundamental rule for wave functions. We say it's not anti-symmetric. And I'll show you in a moment what it is. That is, if you want, it doesn't respect a fundamental constraint on the shape of functions. And so that's, if you want, an error. And that's another source of error in our final estimate of the energy.

And in particular, what it doesn't do-- it does not remove what is the accidental degeneracy, the fact that there is the same energy for electrons that have the same principle quantum number n and the same angular momentum number l . But really, what is most important is this lack of a physical constraint and this lack of correlation.

Very soon, I mean probably the same year or a year later, Hartree, and independently Fock, realized that one could actually find a better solution to the problem satisfying one, again, of the fundamental rules of nature that had been discovered in the '20s during the development of quantum mechanics. And so one of these rules was what is called the spin-statistic correlation.

And this is really very general. First of all, there is a division in elementary particles that says that all elementary particles can be called either fermions or bosons. And so things like electrons are actually fermions. They have a half-integer spin. But there is a fundamental difference between fermions and bosons.

And in particular, they satisfy different statistical rules for an ensemble of many interacting electrons or for many bosons. And this rule-- so this is nothing else that-- again, another rule like in classical mechanics-- you have Newton's equation of motion. In quantum mechanics, you have a rule that wave functions that described fermions-- that is, a wave function that describes electrons needs to have this overall shape. That is, it needs to change sign when we invert two variables.

So we have this general form for the wave function. We exchange two variables. And what needs to happen is that the wave function needs to change sign. And this has something to do-- this can actually be demonstrated. But it's what people call quantum field theory. So it's an advanced concept. But it's a very simple rule. And it's a very simple symmetry of the wave functioning.

In the same way, if you want, you have in a crystal, you have physical symmetries for what could be some of your properties, like an elastic tensor or a piezoelectric coefficient. Well, what you have is a fundamental symmetry for a wave function describing electrons. It needs to change sign when you invert two coordinates.

And so what the Hartree solution didn't have was exactly this anti-symmetry requirement. Remember, the Hartree solution was just the product of single-particle orbitals. But Hartree very quickly realized that you can actually satisfy this symmetry requirement if instead of taking just the product of n orbitals, you take the sum of the product of n orbitals where you interchange the variables in all the possible ways-- putting a plus or minus sign in front, depending on how much interchanges you had.

And I think it's very simple to think of this problem if you have, say, only two electrons. So you have only two orbitals. And so we could call these two orbital, say, alpha and beta. And so what we would have is the Hartree solution that is the product of the alpha orbital function of the first r variable and the beta orbital function of the second variable. And this doesn't change sign if we exchange 1 with 2. It becomes a different function. It doesn't become the same function with the sign changed.

But you can see that what we can do, without increasing really the complexity of the problem-- that is, still dealing with just the need of describing two orbitals, what we could do is take as an ansatz for the wave function describing two electrons something that is actually $\alpha_1 \beta_2 - \beta_1 \alpha_2$, OK? So we have still two orbitals that we need to figure out. We need to figure out what is the shape of alpha and what is the shape of beta. But now, we are using as an ansatz for this two-electron wave function something that actually changes sign when you exchange 1 with 2.

So this is the trial wave function of Hartree. And this is the trial wave function of what we call the Hartree-Fock method that is basically a trial wave function that has built-in anti-symmetry constraint for exchange of particles. And this can be generalized to the case of n particles. And really, what we call a sum of n terms with all the possible permutations, with all the possible signs, is nothing less than a determinant.

If you think at what a determinant is, well, this determinant is going to have one element. It's going to have a sum of terms that each of them are rated as one term from each column. And we are taking all the possible permutations. And we are taking a plus sign or a minus sign in the sum of all these terms, depending on how many permutations they are. This is just the linear algebra definition of a determinant. And you see, again, a determinant of two functions is-- that's what I've written here in green, right here in the corner.

If we are asking what alpha 1 determinant beta 1 beta 2 and alpha and alpha-- so beta 1 and alpha 2. So this would be the specific expression of this determinant for the case of two particles. And if you just solved that determinant, you have only these two terms.

So we haven't increased, in going into the Hartree-Fock method, the complexity of the problem that we need to solve because we still need to find n functions, where n is the number of electrons. And we need to find out the appropriate differential equation that descend from the variational principle once we stick this determinant into the variational principle.

And again, it's not very complex functional analysis. And the Bransden Joachain describes that in detail. But with this new solution, with this ansatz, what we find is a new set of differential equations that look a lot like the Hartree equation that we had written before-- I'll go back to this in a moment-- but have an additional term. So what we find are, again, single-particle equations. So we have an integral differential equation for each single-particle orbital λ that is written in red.

And now, what we have is a set of additional terms. So we still have the quantum kinetic energy for that electron. And we still have the interaction between that electron and the collection of attractive Coulombic potentials. We still have the Hartree electrostatic term in which the electron λ interacts with the charge density ϕ_{μ} times ϕ_{μ} of every other electron μ . And I'll come to what goes into this sum in a moment. But basically, we have electron λ interacting with the charge density of electron μ . And obviously, it's a Coulombic electrostatic repulsion. So there is a $1/r$ term.

But now, there is a new term with a minus sign that comes out only from the anti-symmetry requirement. And that is what is called the exchange term and is the new player in the Hartree-Fock equation. And it's a little bit exotic because, if you want, now we don't have any more an operator that could be, say, a local operator, a charge density distribution acting on an orbital. But it's really become a known local operator because the orbital on which I'm acting has gone inside the orbital sign.

So this new term here that we call the exchange term is a purely quantum mechanical term that comes out exclusively by the anti symmetry requirements on what happens to a fermionic wave function when we invert coefficients. And there is another fundamental distinction between the Hartree and the Hartree-Fock equations.

This sum here-- you see this time over μ -- in the Hartree equation was running over all the electrons but the one that we were considering, OK? And now instead, this sum μ is running on all the possible electrons. So what you have in this term here is what is technically called self-interaction.

Suppose that for a moment you were trying to solve the hydrogen atom with just one electron. Well, what happens in the Hartree equation for the hydrogen atom-- there is obviously no exchange term. And there would be also no Hartree term because, in the Hartree equation that you've seen before, what you have is a sum over all the other electrons. But there are no other electrons. So this term is not there. And what you trivially recover is the single-particle Schrodinger equation for the hydrogen atom.

In the Hartree-Fock equations, now even for the hydrogen atom, what you have is that now you have this term. You have actually an unphysical self-interaction. That is, you have electron 1 interacting with itself. And that's really not interacting with itself in a local way. But it's interacting with its own charge distribution.

This is actually a sort of unphysical thing. But what happens exclusively in the Hartree-Fock formulation is that there is a second term. There is the exchange term. And the exchange term-- you see, there is a minus sign-- cancels for the hydrogen atom the self-interaction term exactly. If you just think-- if you have only one electron, you have that there is only one ϕ . So the λ goes away. The μ goes away.

So here, the electron is interacting with its charge distribution. But then this term here-- just remove all the sum and remove μ and λ -- is canceled out thanks to the minus sign by the exchange term. So Hartree-Fock formalism is actually what we call self-interaction corrected, OK? An electron, even if it's a mean field picture, doesn't interact with itself.

And that's actually a very beautiful symmetry property that other approaches like density functional theory do not satisfy. And truly, a lot of the problems that come out in density functional theory that otherwise perform really well have to do with this self-interaction problem. And so those problems are very significant, if you think for a moment, of problems like dissociation of a molecule in atoms.

So when you really consider how-- and we'll discuss this in detail-- how the energy changes along a process in which the electron needs to localize itself from a shared bonds to a localized bond and that self interaction problem kills density function theory and would actually not be present to begin with in Hartree-Fock. So this is actually very important.

There is another thing. Actually, the Hartree-Fock equation has a beauty in the fact that the operator acting on the single-particle orbitals does not depend on which orbital you are looking at because here we have a sum over all the states. So this does not depend on which electron you are looking at.

That's different from the Hartree equation. In the Hartree equation, there is a Hartree term where this sum would exclude the electron itself. So the Hartree equations are actually more complex to solve because the operator changes depending on which electron it's acting on, while the Hartree-Fock equation has the same operator. And so what we really need to find out, if we are solving the iron atom, what are the 26 lowest energy solutions for all the electrons in here.

So that's a very good thing. But there are terms-- there are integrals that are actually very expensive still to calculate. And ultimately, it's terms like this that give us the scaling cost of the equation. Often, what we saw in such a problem, we want to know what is its scaling cost. That is, how much our calculation becomes more expensive, say, if we double the size of the system because that basically tells us how large we can go.

And because of these integrals that involve three orbitals and the fact that then to calculate an energy of one more sum, really the scaling cost of the Hartree-Fock equations, in principle, goes as the fourth power. So if I'm starting a system with two electrons, and then I want to study a system with four electrons, well, the cost has gone up 16 times. And a fourth power, like any power, kills you very rapidly. So that's why we can't study a molecule like benzene with Hartree-Fock. But we can't study really something like DNA with Hartree-Fock or really none of the standard electronic structure methods. And a lot of effort that goes into developing a linear scaling methods, that is methods in which the computational cost of your calculation doubles if you double the number of electrons.

And at the end, nature is linear scaling because really you can imagine that the wave function of the electrons here doesn't have anything to do with the wave function of the electrons there. So there is really, when you go far away, no exchange of information between wave functions in different parts of space. And so there is ultimately a linear scaling nature. But our algorithms, in general, are not yet there. And we'll discuss a little bit in some of the later classes how to solve this problem.

Before going on, I wanted to show one set of very simple conclusions actually of having a wave function with the proper symmetry-- that is, having a wave function written as a Slater determinant-- because that form gives us automatically what is called the Pauli principle. If you remember what the Pauli principle is, it's that you can't have two fermions-- two electrons, in particular-- in the same quantum state.

So you can't have two electrons having, say, the same orbital. And that's obvious because, in a determinant, two electrons having the same orbital would mean that two columns in the determinant are identical. And when two columns in a determinant are identical, the determinant is linearly dependent. And so the solution is 0.

So a lot of good things came out Hartree-Fock. In particular, one could start solving atoms. And one would recover, say, the shell structure of atoms. So if you would obtain the Hartree-Fock solution for something like an argon atom, and then say plot the overall charge density of the system, well, it would start to look like this as we move from the center outwards. So it would clearly show the fundamentals of the periodic table nature of things. That is, it would show a 1s shell. And then it would show a 2s and a 2p shell. And this is something that some of the other approaches, like the Thomas Fermi approach that we'll see in a moment that were being developed at the time, didn't have.

In general, Hartree-Fock is very good to describe atomic properties. And what is most important is a well-defined approximation in the variational principle. Remember, one of the fundamental powers of the variational principle is that if we make our wave function ansatz, our [INAUDIBLE] wave function more and more flexible, we become better and better. So Hartree-Fock is a certain hypothesis and gives us certain energies.

But what we can do is make our wave functions more and more flexible-- write them not only just as a single determinant, but a single determinant plus something else. And the solution that we'll find will be computationally more expensive to find, but is going to be better. So Hartree-Fock, in principle, can be improved indefinitely. That is something very powerful conceptually. It's practically very complex because those costs that we are scaling already in a simple Hartree-Fock, like the fourth power, keep going up.

What you will see in this differential theory is that besides being a theory that tends to give more accurate results for a lot of physical properties, it's something that also scales a bit better. It scales as the third power of the size. But it's a theory that can't really be improved in any systematic way. One can find ingenious ways to make it better. But there isn't a brute force improvement strategy like there is in Hartree-Fock.

The Hartree-Fock operator included the last term that we have called the exchange term. And so for every possible atom, for every possible molecule, for every system, there is a well-defined Hartree-Fock energy. And this Hartree-Fock energy is going to be good, or very good, or sort of so-so. But it's always going to be higher than the true ground state energy of our system.

And actually, what is technically called the correlation energy is the difference between the true energy of your system and the Hartree-Fock energy. So when people talk about correlation energy, they refer to all the energy that is not captured by a Hartree-Fock approach. And in that sense, it's a well-defined quantity. Although, it involves a generic term correlation that can mean a lot of things. And I'll show you a few examples.

There is one more thing that we can do. We have never discussed up to now spin. But in reality, an electron is described by a wave function that doesn't have only space parts. So in order to describe an electron, we don't only describe what the distribution of its wave function is in space, but we also specify what is the spin of the electron. And that has to do basically with spin being an operator that can be simultaneously diagonalized with a set of-- well, it becomes complex. But it's another quantity. You can think of it as a color. We need to specify if our electron is red or blue. Or in particular, we need to specify what is its spin, what is its projection with respect to an axis.

And so in this, you need to think of a wave function of an electron not having only a spatial distribution. But it has another property besides the spatial variables that is called the spin. And you can make a sort of approximation-- that is what is called a restricted Hartree-Fock scheme-- in which you decide that an electron of spin up and an electron of spin down will have the same spatial part, so the same wave function in space. And their wave function differs only because you describe an electron with spin up and an electron with spin down.

Again, this corresponds to the classical periodic table picture. You are constructing the periodic table. You go, say, from hydrogen-- one electron in the 1s level-- to helium-- one electron in the 1s level with spin up and another electron in the same level with the spin down. Actually, if you think, the periodic table itself is not a truth. It's just a Hartree-Fock picture of electrons, OK?

In principle, you shouldn't be able to talk about single-particle quantities-- 1s, 2s quantities-- because, in reality, if you have iron, you have a many-body wave function that is an overall function of all the electrons. It's only when you enter into a Hartree-Fock picture that you can have a well-defined concept as a single orbital for an electron and what's the energy for that electron.

So if you want, what we think of this beautiful thing as the periodic table is nothing else than the Hartree-Fock solution of the atoms. And again, we can make the approximation in which we fill up every orbital, every spatial part with two electrons with the same spin. That tends to be a very good approximation for a lot of problems, say a lot of bound systems. And we'll see the case of the hydrogen molecule in a moment.

But you could actually make your wave function more flexible, saying that say orbitals don't need to be paired. That is, an electron with a spin up and an electron with a spin down, even if they are very close in energy, can have two wave functions in which the space part differs. And this is really an ansatz that contains this in itself. So an unrestricted Hartree-Fock solution will always give you a lower energy than a restricted solution. And we'll see in a moment an example. And this is the case of the dissociation of a hydrogen molecule.

So when we go back and try to understand what is the bonding between, say, two hydrogen atoms-- and we had seen in one of the first lectures, we discussed about potentials-- that is, what is the energy of a system as a function of the nuclear distances. And this is what we are doing here. We are trying to look at the energy of the system as a function of the hydrogen-hydrogen distance. And there will be an equilibrium distance that corresponds to the minimum of the energy.

And this is what classical potential tried to do. They tried to replicate what is the energy of a system as a function of the nuclear coordinates. And they tend to do very well, as Professor Ceder has told you, closer to the region where they have been fitted. If we have created a potential around here, we tend to be able to reproduce things very well. Obviously, it's very easy to even find out the potential that reproduced all these curves. But when you start to have more than two atoms interacting, there are all these problems of bond-breaking and bond-forming that can't really be given by classical potential and can be given by quantum mechanical calculations.

And so in principle, we have an ideal solution, that is if we were able. And nowadays, with numerical accuracy, we have basically been able to solve almost perfectly this problem. We are able to find out what is the total energy of the system as a function of the nuclear coordinates. And then for this specific problem, the Coulombic potentials at different distances, we can find a Hartree-Fock solution.

And with only two electrons, we can find a restricted Hartree-Fock solution in which we say, well, these two electrons are going to have the same orbital part in the wave function. They just differ in having a spin up and spin down term. And that makes them orthogonal. So certain things are going to happen in the exchange term. But then we plotted this energy as a function of the distance. And this is what we have.

And then we can release this condition. We can say these two electrons don't need to have the same orbital part for the wave functions. They can have different parts. And we can do that calculation. And what we obtain is the unrestricted Hartree-Fock solution.

And you see two fundamental things coming out from here. First of all is that all these Hartree-Fock approaches give you an energy that is obviously larger than the exact energy. It's the variational principle. We can get lower and lower. But we will never be able-- and that's very good-- to go below the true energy.

So the more flexible we make our wave function with both Hartree-Fock methods, the more we'll be able to recover this last electron volt of correlation energy. So this is all where our effort is going. But you see, Hartree-Fock is already doing extremely well in giving us the equilibrium distance. I mean, this is the Hartree-Fock equilibrium distance. And this is the exact equilibrium distance. So it's doing a good job.

What restricted Hartree-Fock is not doing well is giving us the dissociation energy. So restricted Hartree-Fock works very well around the minimum. Well, you really should have this sort of physical picture of your ground state being given by a bonding combination of 1s orbitals. Really, this is what the covalent bond for a hydrogen molecule is, is the two 1s orbitals covalently overlapping. And so restricted Hartree-Fock does very well here. And it's basically identical to unrestricted Hartree-Fock.

But formally, unrestricted will always be lower than restricted because it contains the restricted solution because, in order to have a restricted solution, you just need to have the orbital part for the two electrons to be identical. But because it can also be different, it will always be lower than the restricted Hartree-Fock.

And you see, when we break this system apart-- when we want to go from a bound hydrogen molecule to two atoms, the restricted Hartree-Fock is doing very poorly. You'll see, it'll give us an energy that is a very poor predictor of the dissociation energy. The dissociation energy-- the true disassociation energy of the system is the distance between the minimum here and the 0 value. That this is, it's the energy that we need to spend to break apart the molecule.

Unrestricted Hartree-Fock will do very well. I mean, obviously, it goes to 0 in this scale when we are far apart. And so we have this 1 electron volt error. But the restricted Hartree-Fock is doing very poorly. And why is that?

Well, basically because the restricted Hartree-Fock is really doubly occupying the same spatial part of the same bonding combination. And that's good when the system is bound. But when you break it apart, it's very poor because what you really want is-- in your solution, you want to mix in another determinant that is given by the anti-bonding combination because if you think of the bonding state as always a pile-up of charge in between the atoms. But when the molecule disassociates, you really want to have a solution that has zero charge density between the atoms. And that looks much more like the anti-bonding combination of 1s orbitals.

And so the restricted Hartree-Fock doesn't have this freedom. So it does it very poorly. And unrestricted has the freedom of having two orbitals that are different for the two electrons. And so it just puts one orbital on one atom and another orbital in another atom instead of having a single orbital doubly occupied. And so unrestricted Hartree-Fock is going to be much better, especially for problems like the bond-breaking reactions or for problems in which you have isolated spins, so you have atoms-- you have single electrons that are not paired.

There are actually a number of theorems that can be derived from the Hartree-Fock equation. I won't dwell on them. They are generically called Koopmans' theorems. And they have to do with calculations, say, of quantities like the ionization energy or the electron affinity. What is the ionization energy? It's the energy that you need to spend to remove an electron from an atom. Or the electron affinity is the energy that you gain when an electron captures-- sorry, when an atom captures an extra electron.

So how do you calculate them, say, in an electronic structure calculation? Say the ionization energy? Well, it'll just be given by the difference, say for the case of iron atoms, of the Hartree-Fock solution with 26 electrons and the Hartree-Fock solution with 25 electrons. So you do these two calculations. You take the difference. And that will be our ionization energy. And the affinity will be the difference between the calculation with 27 or 26 electrons.

But you can actually do very well without having to do two calculations, but having just one calculation, if you make the hypothesis that really your single-particle electrons do not change in the process. So if you make the hypothesis that in going from 26 to 25 the shape of electron 1, electron 2, electron 3 do not change-- and that's an approximation. They will change a little bit. But if you make this approximation, you can actually prove that the difference between the system with 26 electrons and the system with 25 electrons-- the difference in energy is just given by the eigenvalue of the 26th electron. So basically, a single calculation gives you already an estimate of ionization energies and electron affinities. Although, in principle, you could always do two calculations. But these, if you find them, are called the Koopmans' theorems.

What is missing in Hartree-Fock? What is this correlation that we are trying to recover? Well, often we think at it in two ways. We can think that part of it is dynamical correlation. It's what I described to you in the case of the helium atom. That is, when we have two electrons interacting, they like to keep each other as far away as possible from each other instantaneously. And because we have a mean field solution, we are actually overestimating the Hartree energy.

We tend to put electrons too close to each other because we have one electron interacting with the average field of the other. And so in that energy term, you have that there are a lot of configurations in which the electrons are too close to each other. That raises the energy of your system. So we call that dynamical correlation. And these are heuristic terms.

And then there is another class of errors that we are making that often are called static correlations. And those have to do more with the fact that a single determinant solution doesn't have the flexibility that you need. And this was the case of the breaking apart of the hydrogen molecule. You really want, when you you're breaking apart a molecule, to have a two determinant kind of flexibility with both bonding and anti-bonding combinations.

And all of this is missing. And we can systematically build it up, improving, say, the flexibility of the wave function. And one of the conceptually simplest way, but computationally more expensive ways, is actually to look at the wave function that now, instead of being given by a single determinant, is given by a combination of determinants with different coefficients in which, say, the determinants have been constructed with a number of orbitals that include also excited orbitals.

Our original Hartree-Fock determinant, say, for iron was given by the 26th lowest solution. And this is it. But then you could add a second term that contains 25 of those 26 lower solutions and then one excited state. Or you could do a number of things. But basically, you could increase the variation of flexibility of your problem. And the more flexible you become, the closer you get to the right solution. But you pay an enormous price for this. And this general approach would be called configuration interaction. That has actually this horrific scaling of n to the 7th. And so you can really do it for 10 electrons. But you can't do it for 11 electrons on your best computer. Probably now, we can get to 15 electrons or so.

And I think with this, I'll conclude. So this was a panorama on Hartree-Fock methods. One of the best books is the Jensen book of computational chemistry in the literature. And then with the next class, we'll start looking at density functional theory and again the Nobel Prize for chemistry in 1998.

Next Tuesday is-- being Monday Presidents' Day, we'll have on Tuesday Monday's schedule of classes. That means, in practice, that we have no class. So you have time until Thursday of next week to brood over this. I've posted a few readings on the website. If you are really wanting to more about the functional theory, one of those readings is the Kohanoff paper on fundamentals of density financial theory. And if you want to know more of Hartree-Fock, we won't really see any more in the rest of the class. You should go to one of the references. And otherwise, see you next Thursday.