

NICOLA MARZARI: --for all our applications and for the lab sessions. I guess I keep using Albert Einstein. This is the 100th anniversary of his sort of famous year, 1905, so just a little celebration.

One slide of a reminder of what we have seen in the previous lecture, we have really developed the formalism leading to the Hartree-Fock equations. And the Hartree-Fock equation follow from a set of very simple and very beautiful path. We have the Schrodinger equation, and we have reformulated the Schrodinger equation in terms of the variational principle.

So we have a functional. And we know that we can throw into that functional any arbitrary wave function, and it'll give us an expectation value of the energy. And sort of the closer we get to the true ground state wave function, the lower that energy is going to be.

We are never going to go below the ground state energy. And so it's sort of a very powerful approach to try out sorts of possibilities and solution. And in particular, sort of Hartree and Fock took this approach.

They wrote sort of the most general many-body wave function that can be written as a product of single particle orbitals. That was actually the original Hartree solution. Wave functions written as data do not satisfy a fundamental symmetry of interacting fermions. That is they are not anti-symmetric.

And so what you do? You take this product of single particle orbitals, and you sum it with all the possible permutation, with all the possible signs in front, so that the overall wave function is anti-symmetric. And that can be sort of written compactly as what is called as later determinant here.

And basically, now our unknowns are the n orbitals ϕ . And so we need to determine the shape of this n single particle orbitals. And we want to determine them such that they minimize the expectation value of the variational principle.

And so that leads basically to a set of differential equation is just functional analysis. And when you ask yourself what are the conditions that those single particle orbitals need to satisfy in order to minimize the variational principle, well, this is it, the Hartree-Fock equation. So each single particle orbital ϕ of λ need to satisfy basically a Schrodinger-like equation.

Again, as always, there is a kinetic energy term here. There is the interaction with the external potential that is just the potential of the nuclei. And then come the so-called mean field terms.

So the electron λ here will interact with each and every other electron μ via an electrostatic interaction. You see $\phi^* \phi$ is the charge density coming from the orbital μ . And the field that the electron λ fills is the electrostatic average density.

And in these, we sum over all the electrons including the electron λ . So up to now, we have a system that is self-interacting. An electron λ fills the electrostatic interaction with itself. That, in principle, is not correct.

But luckily, this next term that is called the exchange term cancels that exactly. And the exchange term is the direct consequence of having written the trial wave function not just as a product of a single particle orbital, because up to now we would have sort of something closer to the Hartree equation, but written as a proper anti-symmetric wave function, summing on all the permutation with them appropriate signs.

And so, basically, we have Schrodinger-like equation. A great advantage with respect to the Hartree equation is now the operator doesn't change depending on the index λ because this sums if you want to go over all the electrons including λ . So our only constraint here is that we need to find the n lowest Eigen state of this single differential equation.

So if we have n electrons, if you want, it's not that we have n different differential equation, like it was the case of the Hartree equation. But we have an identical differential equation that is written here. And we need to find the n lowest energy states. And those will be our single-particle orbitals.

In all of this, we have started from a variational principle. So it's very easy to go beyond the Hartree-Fock. We can say, in large r variational cluster, we can add more Slater determinants with sort of different coefficients.

We can try to construct a more complex wave function. And that solution will become better and better. Or we can sort of use the perturbation theory. And so quantum chemistry has developed a number of techniques that are post-Hartree-Fock techniques that become systematically more and more accurate. They are also more and more expensive. And that's if you want, the main limitation of that direction.

What we'll see today is something, as they say in Monty Python, completely different. And that will be sort of density functional theory. That's, if you want a theory that starts from a very different set of hypotheses, the net result will be, again, a set of single-particle equations.

The concept are very similar actually, formally, to the Hartree-Fock equation, but they have been derived in a completely different spirit. Density functional theory tends to be less expensive than Hartree-Fock and, overall, tends to be more accurate. Especially for solid, it's much more accurate. You'll see when we discuss case studies the Hartree-Fock solution for, say, interacting electron gas or in general for metals tends to make them semiconducting or insulating-like.

So Hartree-Fock then works very poorly for solids. And that's why, if you want density functional theory, comes from the solid state community, while Hartree-Fock that tends to work very well for atoms comes from the quantum chemistry community. And all the theory was developed by Walter Kohn, and coworkers. So you'll see the Hohenberg and Kohn theorem, the Kohn [INAUDIBLE] mapping during the '60s.

But I would say it's only during the '70s that people started to be able to actually solve interesting cases using density functional theory. And it's really the beginning of the '80s-- you'll see some cases here today-- in which people started calculating something that had sort of a direct application. So we'll see the phase diagram of silicon as a function of pressure or volume and sort of the first principle prediction of properties of solids.

Walter Kohn, for the development of this eventual theory, got the Nobel Prize for chemistry in 1998 together with John Pople. That has been the person that's been fundamental in the development of Hartree-Fock and post-Hartree-Fock approaches in quantum chemistry. OK. So let's see sort of what is the general idea behind density functional theory.

And in many ways, we'll sort of start from ideas that had been developed at the end of the '20s and the beginning of the '30s, what is nowadays called the Thomas-Fermi approach. And again, the basic idea here is that the wave function of a many-body interacting problem is an object that is too complex to treat. And it would be very, very nice if we could instead try to deal with a simple object.

And sort of one of the choices could be the charge density. So if you want, Thomas and Fermi independently were asking themselves, well, could we try to solve not really a Schrodinger equation in the many-body wave function, but solve something else in which our only unknown is the charge density? If you think for a moment, the charge density is one of the sort of fundamental variables in the description of our interacting electron problem.

And so this was the question. Can we do something just with the charge density? And so what they did is writing out what we would call a heuristic function. That is trying to devise a set of terms that would give us the energy of a set of electrons in a potential just as a functional of their charge density.

And so, by now, you could sort of think that some of the relevant terms will be electron-electron interactions, electron interaction. And we could write a sort of electrostatic term, like the Hartree term in the Hartree or Hartree-Fock equation, that is just a functional of the charge density. So this is sort of fairly easy.

It's also very easy to sort of imagine what could be the interaction of the electrons with an external potential through the charge density. It will be just the integral of that external potential times the charge density. What becomes really critical is finding a functional that will give us the quantum kinetic energy.

If you think, in the Schrodinger equation, the quantum kinetic energy is really the second derivative of the wave function. And obtaining from a charge density only some insight into what could be the second derivative of the wave function is very complex. If you think for a moment at the extreme case of a plane wave, OK, so a sine and cosine sort of in space, if you remember, the charge density given by a plane wave is a constant.

We just multiply the imaginary exponential times its complex conjugate. That gives us a constant. So all plane waves lead to a constant, but obviously the quantum kinetic energy of a plane wave depends on the wavelength of that plane wave because the second derivative is what counts.

So what I'm trying to say is that, when we look at this as a possible wave function, a function, say, of r and the charge density that comes from this is going to be a constant, this wave function times this complex conjugate. But the kinetic energy of this object is going to be minus $1/2 k^2$ -- sorry, plus $1/2 k^2$.

And so there is really not a good way for this extreme case to correlate its charge density to its kinetic energy. It's an ill-defined problem. And this is really the difficulty.

So there isn't really a good way if you wanted to extract the information on the second derivative from just the charge density. Now, [INAUDIBLE] sort of this objection, they tried to find a reasonable functional, so without sort of trying to get the exact solution, but try to find a reasonable function that would give us a good estimate to the quantum kinetic energy starting from the charge density.

And the solution to this problem that is something very important is what we could call a local density approximation. So the problem here is that we have a non-homogeneous charge density everywhere in space. And we try to figure out what could be the quantum kinetic energy of this non-homogeneous problem.

And the approximation that Thomas and Fermi did was, well, dividing this non-homogeneous problem in a set of infinitesimal volume in space. So it's a bit difficult to draw, but suppose you have the charge density coming from some atom or some molecule. This is a non-homogeneous charge density distribution.

Now, what you do is you divide this in space and set a very small infinitesimal, if you want, volume. And inside each volume, the charge density can be approximated as a constant. And what Thomas and Fermi said is, well, the contribution coming from this infinitesimal volume, say, the first one to the overall quantum kinetic energy will be given by that volume times the kinetic energy density of the homogeneous electron gas at that density.

So if, again, we partition all space, we could have that the density in this little cube is 0.5. Here is 0.6. Here is 0.7. Outside, it goes to 0.

But we can actually calculate in some other way what would be the quantum kinetic energy of a homogeneous electron gas. That's a problem that we can solve if the homogeneous electron gas is not interacting.

And we can solve it numerically even if it is interacting. So we can know what is the quantum kinetic energy of a homogeneous gas with density 0.5, density 0.6, density 0.7. And so we can also know what would be the quantum kinetic energy per unit of volume of data.

And so we'll say that this non-homogeneous system in blue will have an overall quantum kinetic energy that is given really by the integral across space-- and it's written here-- of the quantum kinetic energy of the homogeneous electron gas integrated over space. And, say, for the non-interacting electron gas, it's actually very easy to do. So if you have a non-interacting electron gas at a density ρ , its quantum kinetic energy is just the ρ to the $2/3$ that then integrated times the unit volume gives us ρ to the $5/3$.

So by integrating this quantity, we would get an approximation. This approximation is basically exact in the limit of our homogeneous system, obviously. And it will be sort of quite good in the limit of our non-homogeneous system that has a very slowly changing charge density.

The more, if you want, inhomogeneous your system becomes, the less accurate this approximation is. And of course, something like an atom or a molecule is a very inhomogeneous system. You go with a charge density that goes from 0 to very high volumes close to the core of the nuclei.

So this is basically the overall answer for the overall expression that Thomas and Fermi postulated for the energy of an inhomogeneous system. They were saying, well, suppose that we have a system that has a certain distribution of charge ρ . Without trying to solve the Schrodinger equation finding out the wave function and sort of go through that the very complex many-body route, we can actually sort of postulate that the energy could be written, again, as an electrostatic energy. You see sort of each infinitesimal volume interacting with each other infinitesimal volume times via $1/R$ electrostatic interaction.

Then we have got an external potential. Again, it's usually the Coulombic field of the nuclei. And so the interaction between the electron and that external potential is just trivial given by ρ times v .

And the difficult term, the quantum kinetic energy, has been calculated with a local density approximation. And this is the term that's not going to be very good, again, because it's very difficult to figure out what could be the curvature of our wave function just from the density that that wave function produces.

But anyhow, this is a very simple expression to deal with. So for any external potential v , we can try to find out the ρ that minimizes this expression. And this will be our Thomas-Fermi solution.

There are obviously a number of problems. I'll show you in a moment an example of what the Thomas-Fermi solution would give to an atom. First of all, I mean, there is really no theoretical basis to this. It's what we call a heuristic derivation.

Thomas and Fermi just wrote out what could be a reasonable energy functional, and then tried to sort of see what results it would give. But there hasn't been any kind of formal derivation of that functional. It's not like the Hartree-Fock equation that sort of derive just with some analysis from the variational principle.

Another problem is that, again, it doesn't really sort of introduce the concept of anti-symmetry that fermions need to have, the fact that the many-body wave function needs to be anti-symmetric upon exchange. But you know, there is no conceptual problem in adding an exchange energy to the previous functional. Using the same concept, the same idea of local density approximation, suppose that we want to add an exchange term.

Well, we could look at what is the exchange energy coming from the Hartree-Fock equation, say, for a homogeneous electron gas. And that gives us ρ to the $1/3$ term. And that's basically the exchange energy density.

And so for an inhomogeneous system, we are going to sort of approximate its overall exchange energy just by taking the integral of that energy density that is $1/3$ times the sort of local value of the charge density. And so we have a ρ to the $4/3$. And so, again, it's a local density approximation.

The great consequence of having this energy functional that depends only on r is that it is absolutely inexpensive from the computational point of view. The only variable that we need to be concerned with is just the a scalar as a function of three coordinates. That is the density as a function of ρ .

And it's what we call a linear scaling system. If you double the size of your system, the computational complexity just becomes double. So it has a lot of very good things, but it's got a fundamental defect. Because of that approximation in the kinetic energy, it actually does a very poor job in describing a non-homogeneous system.

So it would work reasonably well for something like a metal. Suppose that you want to describe sodium, or suppose you want to describe aluminum. Those are system in which the valence electron produce a charge density that is very homogeneous.

So a Thomas-Fermi approach could actually work well. And it's actually been used even very recently sort of quite successfully to describe problems like the surfaces of lithium, the surfaces of aluminum. What happens, say, when these simple metals melt? What happens to the sort of formation of defects in aluminum?

So there are a number of successes. But sort of clear example of what goes wrong is, say, if we study an inhomogeneous systems like the argon atom. And again, if we think at the charge density of the argon atom as a function, say, of the radial distance from the center from the nucleus, well, it will look something like this.

We have first 1s, and then we have the 2s, and the 2p shells. This is somewhat a poor depiction of that charge density. If we try to solve the argon atom with a Thomas-Fermi approach, all these sort of fine structure of the core shells in the atoms is completely washed out.

OK. So it gives you a reasonable approximation and sort of an appropriate decay of the charge density as we move far away, but a lot of those details have completely disappeared. And for this reason really the Thomas-Fermi approach wasn't developed beyond the '30s apart from some of these recent applications for the very specific case of solids that have a very homogeneous charge density.

The reason why we describe it here is that because, in many ways, it's the grandfather of the ideas that were developed in the '60s in density functional theory and, in particular, the idea that for a moment that we should focus not on the wave function, but on the charge density of the system as the key ingredient.

The great difference between the Thomas-Fermi approach and density functional theory is that density functional theory actually is a theory. It starts with some theorems that are proven. And then it shows what are the form of the equations that, say, a charge density need to satisfy in order to solve exactly the problem.

So in many way, density functional theory is, in principle at least, an exact theory. It's sort of writes out what are the equation that the charge density needs to satisfy. And those are absolutely equivalent to a Schrodinger equation for the wave function.

There are some difficulties. And this is what we are going to sort of go into right now. But let me first give you the conceptual framework of density functional theory and how it was derived. And as usual, we start from the Schrodinger equation. OK. So we start from the idea that, in quantum mechanics, for any given external potential, you have a well-defined differential equation. OK. It's sort of very complex. It describes a many-body wave function. So in most practical cases, we might not be able to solve it, but everything is well-defined.

You have an external potential. You have the differential equation that the many-body wave function needs to satisfy. And so, in principle, you have the solution. And so in that sense, sort of the first statement here is summarized.

For a given external potential and knowing how many electrons are going to fill this potential, our quantum problem is formally completely defined. In principle, the solution exists unique. We might not be able to calculate it, but it exists. And once we know the many-body wave function, that solution, we know everything about our quantum system.

OK. So this is, if you want, the trivial part of the conclusion. That is, given an external potential, we find, by the Schrodinger equation, the wave function. The wave function determine all the properties of our system and, in particular, determine the ground state charge density.

So there is a unique pathway that starts from the external potential and leads us to the charge density, the ground state charge density. Once you have defined the potential, you, in principle, have uniquely defined what is the ground state's charge density of your system. And so in that sense, we say that the ground state charge density, the ground state energy, and all the properties of our system are, in some complex way, a functional of our external potential and the number of electrons.

Functional, again, can be anything. And in this case, it goes through the Schrodinger equation, nothing sort of complex at this point. The sort of remarkable result that no one had sort of figured out between 1964 and 1965 is that the opposite is also true and is not trivial at all. So what Hohenberg and Kohn stated first, actually, in 1964, was this, that the ground state charge density is a fundamental quantity, as fundamental as the external potential.

And in particular, not only the external potential, the terms uniquely the ground state's charge density of your system, but also the vice versa is true. That is, given a ground state charge density, in principle, one can prove that there is a unique external potential for which that ground state's charge density is the ground state solution for that external potential.

So if you have the external potential, conceptually it's trivial to go through the Schrodinger equation and its solution to the charge density. What Hohenberg and Kohn are telling us-- and I'll just show you a sketch of the proof in a moment-- is that in principle, if someone is giving you a charge density and is telling you this charge density is the ground state's charge density of a number of electrons and electrons in an external potential, in principle, what is that external potential is an information that is completely contained into the charged density.

And it's not contained in a trivial way. It's not that you can look at the ground state charge density and guess what the external potential is. And that's where all the complexity of practical density functional theory comes.

But from the conceptual and mathematical point of view, these two quantities are absolutely equivalent. From one, you get the other and vice versa. And this sort of vice versa was not trivial. And that is sort of what is contained in the so-called first Hohenberg and Kohn problem.

I won't go through the derivation. It's actually very simple. I've printed it here in case you sort of want to read it.

But it's basically is a derivation ad absurdum. What they are saying there is that, if that external potential were not unique, if there were two external potential that were different and would give the same ground state energy, we would get to absurdum. So typical mathematical demonstration, we suppose that there are two different external potential that give the same ground states as density and we show that we arrive to a conclusion that doesn't make sense.

So there can be only a single external potential. And that's the proof. And again, it wasn't trivial.

I mean, if you want, this is a very basic statement. But it took 40 years to be formulated. And it's actually not true in other cases that to first glance look very similar.

Suppose that for a moment we want to discuss excited states. You could say, well, if I have a charge density and I say this is the charge density of an excited electronic state, maybe I could also recover the potential that has generated there. And that's not true, actually.

So there are sort of a number of cases in which this is not true. But for this fundamental sort of relation between the charge density of the ground state and the external potential, this is true. So we have sort of moved away now our attention.

It's not any more the many-body wave function that we want to focus, but is the charge density. The charge density is as much a fundamental variable of our problem. It's not a derived variable. It's not something that comes from the wave function, but is something that we can actually focus all our attention into.

And now, we need to find the equivalent of the Schrodinger equation for the charged density. This is what Schrodinger had done in the '20s, in 1925. He said, this is the equation that quantum objects satisfy. And I'll call it the Schrodinger equation.

Now, Hohenberg and Kohn has shown that we don't need to think in terms of the wave function. We can think in terms of the charge density as being the fundamental descriptor of our quantum system. What is left?

They need to show me that there is an equivalent of the Schrodinger equation. That is we can write a density equation that is sort of what will give me the ground state and sort of all the properties of the system. And that's really the second Hohenberg and Kohn theorem.

That is really writing out the equivalent concept of the Schrodinger equation for the charge density. And now, sort of, it becomes fairly conceptual. OK. So this is the procedure.

And all of this in the next few slides is still a conceptual procedure. It will describe objects that are well-defined in principle, that are conceptually well-defined, but we still don't have a clue on what they look like in practice. And all the sort of density functional application goes through a procedure that we'll see later on that is the sort of [INAUDIBLE] mapping that gives a hint of what these objects look like.

But up to now, we are going to introduce objects that are well-defined in principle, but we don't know how they look like. And so that's why somehow density functional theory is a much less intuitive theory than something like Hartree-Fock. OK. So this is going towards the second Hohenberg and Kohn theorem, defining the fundamental equation for the charge density. And this is the step.

For any charge density ρ , so someone gives you, someone draws you, an arbitrary charge density. Well, we know that there is an external potential of which that charge density is the ground state. We don't know what it is, honestly, but we have proven that there is a unique external potential.

OK. So because there is a unique external potential, there is a many-body Schrodinger equation with that potential in there. And there is a wave function that is going to be the ground state wave function of that many-body Schrodinger equation. So given a certain ρ , we know that an external potential exists.

And it's unique. It determines a Schrodinger equation. And that Schrodinger equation determines our ground state wave function that we call ψ .

So what we are saying is that, given a ρ , in principle that ψ , the ground state wave function of the Schrodinger equation in the external potential that is uniquely defined by the ρ , is also a well-defined object. Again, we don't know what it is, but it is well-defined. And because it's a well-defined object, we can calculate the expectation value of that well-defined object of the quantum kinetic energy minus $1/2$ sum over all i of the second derivatives and the electron-electron interaction, just the $1/r_i - r_j$ term.

So again, this term is, in principle, well-defined. And we call this term the universal density functional. That is for any given arbitrary ρ , i , in principle, can define a number that is this number here. I have the ρ . In principle, from the ρ , I have the external potential. From the external potential, I have the Schrodinger equation.

In principle, I'm able to solve that Schrodinger equation found in principle the many-body ground state wave function. That will be ψ . And I can calculate the expectation value of ψ of the quantum kinetic energy and of the electron-electron interaction term, all well-defined.

We have really no clue on how to calculate because we can't really do in practice any of the steps, but this universal function of the density is well-defined. So with this universal functional that is now well-defined, we can write out something. We can write to an energy for any given external potential and for any given charge density. And we write it as this.

So for any given charge density, there will be a well-defined number that is this universal density functional of ρ . And then we add another term that is just trivially the integral of this v , this external potential, times the charge density ρ . So again, this new expression that we written is well-defined. For any ρ and for any external potential, we can calculate trivially this term. And in principle, we know what this number is.

And this is, if you want, 1964, 1965, the reformulation of quantum mechanics. Because, now, Hohenberg and Kohn are able to prove that there is a variational principle. That is, for this expression written here, for this functional of ρ , we can prove that for any ρ that we can throw in the overall numerical value of this expression is always going to be either greater or equal to the ground state energy that we would obtain from the Schrodinger equation in the presence of this external potential.

So now, we have a well-defined density functional. So if you have an external potential, the z over r of your atom, you can try out now not wave functions that are very difficult, but you can try out charge density. And the charged density that gives you the lowest expectation value, the lowest value for this functional, will be the ground state, the charge density.

Small problem, we have no clue what this looks like as a function of ρ . But if we knew, we would have a wonderfully simple approach to quantum mechanics. Now, we don't need to deal with the many-body complexity. We just minimize this expression as a function of ρ .

And again, it's sort of fairly easy to prove this variational principle. But one needs probably to sit-- I've given you some reading. So you're welcome, if you are really interested in this, to go back and read the first Hohenberg and Kohn theorem and read the second Hohenberg and Kohn theorem.

But in many ways, the proof of this second Hohenberg and Kohn theorem can be done again through the variational principle. That is, if we have a certain ρ , well, that, again, uniquely determines the ground state wave function. ρ will determine an external potential that, in principle, is different from this. But ρ will determine an external potential and will determine our wave function that is the solution of the many-body Schrodinger equation.

And if we take the expectation value of our Hamiltonian with this external potential in this, but evaluated on the wave function of c prime that comes from this charge density ρ prime, well, we can show that this expectation value here is just identical to functional that I have just written. And for the variational principle, then it needs to be greater or equal than E_0 .

I won't sort of dwell into that. And again, you can look at the sort of detailed description and in sort of some of the many references that I've given or that I've also posted on the website. But what is conceptually important is that we have a new equation. OK. So 1964, '65, quantum mechanics turned around. We don't have to think at many-body wave functions. We can think just at charge density.

And all would be well apart from this detail, that we don't know what that functional f of ρ is. And so we have a conceptual approach, but we don't have a practical approach to solve the density functional reformulation of quantum mechanics. And this is, if you wanted, true to this day.

We don't know what is the exact form of f of ρ . If we knew it, sort of most of our sort of quantum mechanical computational problems would be trivially solved. Because solving that variational principle in the charge density would be most likely a trivial thing to do.

The issue is that not only we don't know, but we have understood a lot of what that exchange correlation-- of what that universal density functional is. And it's very complex. So it's unlikely that there is a simple analytical expression of it as a function of the charge density only.

But, you know, the other great piece of, if you want, quantum engineering by Walter Kohn was finding out a very good approximation to that density functional. We don't know what the exact one is. But now, what they are doing is, well, finding out one that is going to be very, very closely similar to the exact one.

And so they are going to throw in some physical intuition to this problem that up to now, if you want, has been a mathematical problem. It's another layer of complexity in this discussion, so I hope I'm not losing you. But sort of what Walter Kohn did-- I think he had a young postdoc arriving from Cambridge. Lu Sham had just done his PhD in England and came there.

And sort of, you know, he told him, I have this new variational principle. Let's see what we can do to make it into a practical solution. I think they were in Santa Barbara, in San Diego probably, at that time.

OK. So this is what they are going to do. Remember, sort of, what is the problem. We need to figure out what is a reasonable approximation to this functional here.

So what they say is, well, suppose that someone has given us this charge density. So we need, in principle, to find out what would be the many-body wave function that is solution of this external potential that corresponds to this charge density. This is going to be very complex.

Let's invent a problem in which electrons do not interact between each other. OK. So electrons-- so that's the sort of main problem in the Schrodinger equation, that electrons interacting with each other introduce the two-body electrostatic repulsion in the Schrodinger equation. And that's what makes it difficult.

Well, what Kohn and Sham say is let's for a moment suppose that there is a system of electrons that don't interact. So the only thing that those so-called Kohn and Sham electrons fill is the external potential. OK. So those Kohn and Sham electrons will solve, will satisfy, a Schrodinger equation that is much simpler.

Because there is no electron-electron interaction. Those Kohn and Sham electron, the only thing that they fill is a new potential. And they will have their own quantum kinetic energy.

So what they are saying is, for any given charge density ρ , there is going to be a non-interacting set of electrons who's ground state charge density is identical to ρ . So we have said, if we have a charge density ρ , you can all go through, find out the external potential that comes from ρ , the Schrodinger equation, the many-body interacting electrons solution.

But now, what we are going to say is we can also think at a system of non-interacting electrons. And we want those non-interacting electrons to fill a potential that is such that their ground state is going to give us a charge density that is identical to the charge density I'm dealing with. OK. And we call that external potential the Kohn-Sham potential. OK. So now, for a charge density, you don't only have to think at all the complexity that I've discussed up to now.

But you have also to think that, for a charge density, there is going to be this set of Kohn and Sham known interacting electrons. And there is going to be a potential that is called the Kohn and Sham potential that is such that the ground state of the Schrodinger equation for non-interacting electron, that is without electron-electron interaction, in that Kohn and Sham potential will give us a wave function and a ground state that leads to a charge density identical to the charge density I'm sort of dealing with.

OK. What do we do with this? Well, at this stage, there is a sort of great simplification that, for the Schrodinger equation of non-interacting electron, we actually know what is the exact solution. So it's actually very simple to solve a Schrodinger equation in which the electrons do not interact. Because, now, this later determinant is actually the exact solution.

So if you have a set of non-interacting electrons, you don't have the electron-electron term in that Schrodinger equation, this later determinant is not only a good approximation, but it's actually the exact solution. So for this non-interactive set of electrons, we can solve everything exactly. And in particular, we can calculate, say, what is the kinetic energy of this set of non-interacting electrons.

OK. So now, we can sort of have a somehow pseudo-physical way of decompose this mysterious density functional into different terms. So what we are actually doing via the Kohn and Sham mapping is extracting from here terms that are very large and that we know how to write, we know how to calculate.

And then, hopefully, once we have extracted all these terms that we know how to define, we remain with something that is very small and that we'll find another numerical approximation for it. So Kohn and Sham say, well, we have this well-defined density functional. We extract two terms that are well-defined.

And these two terms that's sort of the great achievement actually contain most of the physics of our problem. And the sort of small term that is left over, we are going to approximate in some simple way. And actually, the approximation that they found worked very well. And that's why some of this functional theory became a practical theory.

And so in this sort of density functional, the first physical large term that they extract is the quantum kinetic energy that we call T_s not of the real system. Because, again, even if it's well-defined, we don't know how to do that. But what they were able to write is the quantum kinetic energy of this non-interacting problem.

So for a given charge density, there is this set of Kohn and Sham non-interacting electrons that lives in a potential, such that they have the same ground state charge density. And their kinetic energy is trivial because it's going to be just the kinetic energy of this later determinant, just the sum of a single particle term.

So for a charged density now, there is a well-defined quantum kinetic energy that is not the true quantum kinetic energy of the system, but is the quantum kinetic energy of this sort of associated system of non-interacting electrons. But this term is now well-defined. They say, well, let's extract another term that is well-defined that is just a Hartree electrostatic energy of a charge density distribution.

OK. So if we look at the charge density distribution in which each infinitesimal volume interacts with each other infinitesimal volume with an electrostatic interaction, that's going to be the term. And you know, what we are left is now something that they call the exchange correlation term. That is everything else.

OK. So F , in principle, is an exact quantity. We are now able to define our quantum kinetic energy term. That is an exact quantity, but is not really the quantum kinetic energy of the true system.

But we sort of say, you know, this is going to be equal to a well-defined term plus another well-defined term plus a third term that we don't know. So we have sort of decomposed a quantity that we have no clue what it is into three terms of which two terms are well-defined. And all our cluelessness is contained in the third term. And we call this third term the exchange correlation, but the sort of physical advantage of having done this is that it turns out that these two terms capture a lot of the complexity of your problem. And this term tends to be fairly small.

OK. So that's all, actually. That's why it works very well because somehow they manage to capture the complexity of our system. And so once that exchange correlation term is defined and it's approximated in some way that we'll see in a moment, our problem is now well-defined because we really have a variational principle.

Remember, the universal density functional plus the external potential plus the charge density in the field of the external potential minimizes the sort of new variational principle that comes from the Hohenberg and Kohn theorem. And so we can write it, our variational principle. That is this quantity with the constraint that the number of electrons should be equal to n should be minimum.

And as usual, when you sort of write a variational principle, you are saying that sort of the differential of that quantity needs to be equal to 0. Or if you want, I mean, this is a generic term. You have a set of what are called Euler-Lagrange equation, basically. That is nothing else than differential analysis.

That is you are asking yourself, what are going to be the conditions that need to be satisfied by the charge density in order to satisfy the variational principle? There is always this sort of 1 to 1 correspondence. You have a variational principle.

It gives you differential equation. Or you have differential equation. You can rewrite them in a variational principle. We have seen that for the Schrodinger equation. And we see this, in particular, now explicitly for the Kohn and Sham orbital.

So I'll actually go directly to the explicit expression of the Kohn and Sham orbitals. Again, remember that what we have done is we have defined a variational principle that acts on a universal density functional F plus the charge density and the external potential. And we have decomposed, we have extracted, from this universal functional sort of terms that are large and physical.

And we have sort of pushed all the many-body complexity of the problem in something that we call the exchange correlation functional. That is, again, a functional of the charge density. We don't know yet what that function of the charge density is. But luckily, it's going to be small. So in a moment, we'll approximate it.

And then we ask ourselves, what are the differential equations that derive from this variational principle? Well, in principle, I had written them here. OK. We just need to take the variation with respect to the charge density and imposing the Lagrange multiplication constraint.

And so this would be basically that the charge density needs to satisfy this set of equation, the sort of functional derivative of this non-interacting quantum kinetic energy plus a number of terms that really contain the external potential, the Hartree interaction. And the exchange correlation need to be equal to the Lagrange multiplier that fixes the number of electrons. We are not able to calculate this functional derivative because, remember, the quantum kinetic energy of the non-interacting system is again written as a later determinant.

And so there is sort of, you know, this type of back in which, even if we had written everything in terms of a charge density, we are not able to explicitly calculate not only the derivative of the true interacting electron's kinetic energy with respect to ρ , but we are not even able to calculate the functional derivative of the non-interacting kinetic energy with respect to ρ .

But what we are able is actually to calculate the derivative of that non-interacting kinetic energy with respect to the orbitals that describe the Kohn and Sham electrons. Remember that these non-independent Kohn and Sham electrons have an exact solution that is a later determinant.

And so we know there are trivial many-body wave function is a later determinant composed by a single particle orbitals. And the functional derivative of that independent non-interacting electron's kinetic energy with respect to the single-particle orbital is now trivial and is just minus $1/2 \Delta^2$. So at the end of all these sort of complex formulation, what we are left with is something very simple and probably something you should focus your attention from now on.

We have now a set of Kohn and Sham equation that are the differential equation that the electrons need to satisfy in order to satisfy the variational principle with the caveat that, in this Kohn and Sham equation, there is at term, an exchange correlation term, that we still don't know what it is. It's sort the formally defined as the functional derivative of the exchange correlation energy with respect to the charge density. But we'll need to approximate somewhere.

And what this equation describes is not anymore the true electrons in your system, but they describe this cousins of the true electrons. They describe this Kohn and Sham non-interacting electrons that have their own orbital ψ_i . And that will give us a ground state charge density that, if the exchange correlation functional was exact, would be not only this, as obviously the same ground state energy of our interacting electron system, but it would be the exact solution of the problem.

OK. So this equation look a lot like a Schrodinger equation. They look a lot, if you want, like the Hartree-Fock equation that we've written before. Because what we are seeing is that the a Kohn and Sham electron i fills a quantum kinetic energy operator, fills a Hartree operator, fills the external potential, and then fills this sort of remaining term that is the exchange correlation potential.

Again, if we knew what were this exact exchange correlation potential, we would have an exact solution to the problem. But we know a very good approximation. And then if you want finding the ground state, it's not very different from finding the ground state of the Hartree-Fock equation with the caveat that actually this term here is going to be much simpler than the exchange term of the Hartree-Fock equation.

If you go back to the first slide to the Hartree-Fock equation, the last term is that numerically very complex expression in which we sort of take the orbital, and we put it inside an integral differential operator. Now, it's become simpler. And that's all if you want. So the Kohn and Sham equation look very similar.

In practice, they are simpler to solve. They tend to be more accurate in most cases. And that's, at the end, what leads to the success.

But what is critical for all of this is having a reasonable approximation to the exchange correlation potential. If we had the exact exchange correlation potential, everything would be exact in this formulation. We would find the Kohn and Sham independent electrons that were sort of the ground state electrons for that charge density that is ultimately equal to the charge density of the interacting electrons in this external potential.

OK. And we have the Euler-Lagrange or Kohn and Sham differential equation in the previous page. I written here sort of, you know, just for reference also what would be the total energy of the system. And usually, if you had an independent electron, the total energy of the system is trivially the sum of each of the single particle energies.

OK. If you have 10 electrons and they don't interact with each other, you can calculate what is the energy of each of these 10 electrons. Sum all of them, and that's the total energy of the system. In this case, it's more complex.

And the total energy of the system can't be really written as that, but it's got other terms that depend on the charge density. That's sort of this is, in summary, what your total energy is. And again, there's nothing else than kinetic energy term sort of a Hartree term functional charge density, this exchange correlation functional, and the interaction between the external potential and the charge density.

But this is actually different from the sum of the eigenvalues. That would be the sum of the expectation values of ψ_i calculated on the single-particle orbital where T is, again, just the simple quantum kinetic energy. And the VKS is this Kohn and Sham potential.

So if you want to calculate the total energy of your system, even if it's made of independent electron, you can't sum just a single particle orbitals. But you have to sort of deal with this expression. Nothing complex in this, it's just sort of a caveat that is relevant when you want to sort of-- you know, this is the reason why we can't really find out the equivalent of the [INAUDIBLE] theorems for Hartree-Fock.

This is why at the end these single-particle energies are ultimately not physically meaningful. They sort of don't give us the total energy of the system just by taking the sum over all of them. OK. So in order to make this into a practical algorithm, the only part that remains is finding an approximation to that exchange correlation term, to that last term.

Remember, we had sort of defined this density functional. We have been able to extract two meaningful terms, the Hartree electrostatic energy and the non-interacting Kohn and Sham kinetic energy. And we have said what is left is a function of the charge density that we call the exchange correlation functional.

How we are going to approximate that? Well, we go back to the Thomas-Fermi idea. We are going to do a local density approximation to that exchange correlation functional.

So again, what we want to calculate is the exchange correlation energy for any arbitrary charge density. Sometimes I call the charge density n . Sometimes I call the charge density ρ , but they are always the same.

So how do we do this? Well, we don't have the full solution. But what we can say, again, is that, for an inhomogeneous charge density that changes values and then drops to 0, I can calculate the exchange correlation energy for this charge density distribution by sort of decomposing it in infinitesimal volumes. Inside each infinitesimal volume, I can say the charge density is constant.

And you see, I make a local density approximation. That is I say the contribution to the overall exchange correlation energy of this inhomogeneous system can be broken down. And each infinitesimal volume will give its own contribution to the total exchange correlation density.

You know, in principle, it's not correct. I mean, our problem doesn't have to be local in any way. Actually, as people say, this exchange correlation functional, the true one, although we don't know what it is, we know that is ultra non-local. So it can't be decomposed into terms that independently sum up.

So in principle, we can't do this. But in practice, it tends to be a good approximation for a lot of cases. And so what is going to be the contribution to the exchange correlation energy from this infinitesimal volume?

Let's say the charge density there is 0.5. Well, what we need to do is we need to find out what is the exchange correlation energy for the homogeneous electron gas that is at this density. That's something that, with some advanced computational techniques, we can actually find out almost exactly.

So we would know, if we had a homogeneous charge density 0.5 everywhere, what would be the charge density per unit volume. And we can find out what is the exchange correlation charge density per unit volume not only for 0.5, 0.6, 0.7, anything. And what we are saying is that, in this non-homogeneous problem, we construct the overall exchange correlation energy by summing up these different pieces.

And so this is what Ceperley and Alder did in 1980. They basically found out what was the almost exact sort of closely to numerical exact solution for the homogeneous electron gas. That is for a system in which you have only electrons homogeneously, so the charge density is identical everywhere. And those electrons interact.

So you can calculate the energy of this interacting electron problem exactly as a function of the density. OK. So you change the density in your sort of volume, and you find out what is this energy. And then you can calculate, for any of this density, what is the Kohn and Sham quantum kinetic energy. You can find out what is the Hartree electrostatic energy.

And so you can also find out, for this specific case of the homogeneous gas, numerically what would be the exchange correlation density. And so that's basically a function. So for the homogeneous gas, that is for the case in which n doesn't depend on r , people found out what was basically this exchange correlation energy.

It was calculated as a function. This is a function of what people call r_s . r_s is the radius of a sphere that contains one electron. So it's a sort of inverse quantity with respect to the density.

So numerical calculation, what are called quantum Monte Carlo calculation, really solved the interacting Schrodinger equation problem. But for the specific case of an electron gas that has a homogeneous density, they were able to do that for various density. And so, now, we have a function for the homogeneous problem.

For the non-homogeneous problem, we take a local density approximation, and we say that the overall exchange correlation energy is given by the integral over all the infinitesimal volume. And each infinitesimal volume will have a certain density and will contribute with its own density. If the density is going to be equal to here, this will be the value of the contribution of that infinitesimal volume.

If the density somewhere else corresponds to this, this will be the corresponding. So we really match up this overall exchange correlation term from all the little infinitesimal volume exactly as Thomas-Fermi had done, but now we do it for a term that is a much smaller term in our problem. Thomas and Fermi had done it for the quantum kinetic energy.

Instead, what Kohn and Sham do, they do it for what is left from the universal functional once you have taken out the electrostatic and once you have taken out the quantum kinetic energy of the non-interacting electrons. At this point, if you want 1980 and even before without the computation, with some sort of analytical approximations to this curve, density functional theory becomes not only a theory, but also a practical algorithm.

We have a set of expression for the exchange correlation term. And so, now, it's just a matter of trying to find out what the solution to these problems are. And because somehow conceptually we start from the homogeneous electron gas, it turns out that this approach worked especially well for solids.

I mean, the valence electrons in a solid are much less structured than the electrons in a molecule that they need to drop to 0. So the charge density in a solid overall varies less dramatically as a function of space than the electron density in atoms and molecules. And these are actually sort of what were summarized the numerical result of Ceperley and Alder.

So they had calculated this exchange correlation energy as a function of the density. And that was actually a computational curve, a set of dots. And this is often cited, again, per Perdew and Zunger in a sort of paper of theirs, among other things sort of suggested the analytical interpolation of all the numerical data. And so you see it's something somehow exotic.

But while it's defined, this is just not even a functional. It's just a function of the charge density. So it's something that is very simple to calculate in practice.

And so at this point, density functional theory, is a well-defined theory. So you see 1980, Ceperley and Alder do this quantum Monte Carlo calculation, find out sort of what is this exchange correlation energy. Perdew and Zunger write out a simple interpolation.

1982, sort of the first time that I think we see sort of where all of this is going, Marvin Cohen in Berkeley sort of has been working for two or three years. Alex Zunger was there. [INAUDIBLE] him, a number of his students, they have been able to actually write out all the electronic structure codes that are able to solve the density functional equation for the case of a periodic solid.

And so they address the case of silicon, sort of the most important material in electronics. And so what they do is they are able now to calculate the energy of that system as a function of the atomic position and, in particular, as a function of the lattice parameter. So you know, first thing that they do is they take silicon in its diamond structure, so the FCC lattice with two atoms as a basis. And they calculate that energy as a function of the lattice parameter.

And it looks something like this. And then obviously, as you have learned by now, you look at what is the minimum of that energy. And that is the theoretical prediction of the lattice parameter. And there is [INAUDIBLE], you know, 1% error. They look at the second derivative.

This curvature here is really the bulk models of your problem, again, 5% 10% error. And then they say, well, let's suppose that we have silicon not in the diamond phase, but let's suppose that we have silicon in the beta tin phase. And so this is also experimentally known.

And we know in the beta tin what is the lattice parameter of silicon. And we know from the Maxwell construction what is the pressure at which we would have a transition from, say, diamond to beta tin. And again, you know, I can't remember what was the error, but it's substantially correct.

And they were able to actually sort of calculate the sort of complex zoology of all the high pressure phases of silicon. And it was in remarkable agreement with the experiment. So 1982, this is [INAUDIBLE] and Cohen. But in particular, Marvin Cohen in Berkeley showed that for a-- Marvin Cohen.

For a realistic case, density functional theory is able really to give us quantity of prediction. Marvin Cohen has actually become, this year, the president of the American Physical Society. OK. So this is really the beginning of density functional theory as a practical approach.

And in many ways, what has happened between 1982 and today is that we have become better and better at solving the algorithm for this, overall, still complex computational problem. And you see a lot of this in the next lecture that follows. And we have become somewhat better, not really dramatically better, in calculating that exchange correlation energy.

In a way, sort of the ideas of Kohn and Sham from 1965 of having a local density approximation is still very good. I mean, it's not used nowadays any more that much, but it's as close as-- what we can do now is not really that much better. And as you can imagine, sort of what people have done that was a bit better was introducing gradients in your problem.

So you're trying to guess what the energy of an inhomogeneous system comes starting from what you know about the homogeneous electron gas. Well, maybe you should somehow throw in into your problem also the first derivative of the gradient of the density. And so people did that fairly soon in the early '80s. And sort of using the gradients was actually much worse.

There was a miracle in the local density approximation in which the actual expression of the local density approximation satisfies a lot of symmetry properties and scaling properties of what would be the exact exchange correlation functional. At the time, people put in gradients. All these sort of symmetries and scaling properties were sort of thrown to the dogs. And actually the GGAs-- sorry, the gradient approximation, were working much, much worse.

And so people need to realize, sort of in the late '80s, the work of Axel Becke, of John Perdew especially, a lot of it, you sort of need to introduce gradients in ways that still satisfy a lot of these analytical forms. And in many ways, by now, there is a sort of generalized exchange correlation functional that's been sort of developed in the mid-'90s by Perdew, Kieron Burke now at Rutgers, and Matthias Ernzerhof. That is called the PBE functional.

That has become sort of the workhorse. So a lot of the time, you'll see sort of density functional calculation done in the PBE, GGA approximation. But again, these are important improvements, but if you want just sort of very little on top of the local density approximation of the [INAUDIBLE].

The chemistry community has also sort of done a number of very intriguing developments. In particular, there are things that the Hartree-Fock does very well. In particular, because you have the sort of exchange term in Hartree-Fock, you cancel, remember, the self-interaction say, in the single-electron problem coming from the Hartree, the electrostatic problem.

Density functional theory, in theory, in its exact formulation, would be self-interaction corrected. But in practice, it is not. If you solve the hydrogen atom with density functional theory, you have that the electron interacts with the charge density created by the same, by the electron itself.

And so what sort of the quantum chemistry community has done is, well, they said let's take LDAs, let's actually take GGAs that seem to work very well. But let's actually construct an exchange correlation functional that has a little bit of this, but it's got also a little bit of what we know worthwhile in the Hartree-Fock equation. So they construct hybrid functional which there are sort of pure density functional terms and the sort of Hartree-Fock exchange term mixed in.

It makes the equation much more complex. And if you want, it's a sort of less pure formulation of density functional theory, but it can work reasonably well or very well especially, again, for atoms and molecules. And this is where we are, basically, with exchange correlation functional.

I think I'll stop here for today because that's actually a lot of work. What we'll start seeing in the next class is how we actually solve this equation in practice. On March 8th, you're going to your second lab in which you will actually study the energy of a solid using density functional theory.

What I said today is probably the last of the conceptual lectures. And I understand that some of it is very complex. There is reading material posted on the Stella website. There is the Kohanoff-Gidopoulos paper on density functional theory.

And some of the readings that I've given are very useful. The two best books that are also cited at the end of this lecture are probably the one by [INAUDIBLE] or the one by [INAUDIBLE]. And they are both called *Density Functional Theory* or *Density Functional Theory In Practice*. And they are cited on the last page. Otherwise, this is it for today and see you next week.