NICOLA MARZARI: Wonderful. OK. So welcome to class 5. We are actually counting the lab as class 4 in the numbering. What we'll see today is really a wrap-up on some of these ideas on the behavior of electrons as quantum particles. And we'll introduce really the first electronic structure method in the modern sense-- that is Hartree-Fock theory-- that you'll see as a very simple, conceptual framework. And it really derives directly from the Schrodinger equation and from the reformulation of the Schrodinger equation as a variational principle.

Next class, we'll start with density functional theory. That is a completely different approach to the problem than Hartree-Fock. Although, in practice, it results in equations for the wave function of the electron that are formerly fairly simple. Historically, Hartree-Fock has been the method that has developed first, especially from the quantum chemistry community. And because it derives from the variational principle, it can actually be augmented with perturbation theory. So whenever you need very accurate calculations, things like molar [INAUDIBLE] approaches and other perturbation theory approaches on top of Hartree-Fock can actually help you out. But they tend to be very expensive.

OK. Let me, in one slide, remind you of the most fundamental concept from last class that we have seen. That is the de Broglie relation. This is something that tells us that if a particle has a momentum mass times velocity p, well, then there is a fundamental constant in nature that is called the Planck constant-- that's written here-- such that this relation is satisfied where lambda is the wavelength of that particle.

So basically, particles have wavelength properties. But the real issue is that only electrons are light enough to have wavelength comparable to the inter-atomic distance, so to give rise to diffraction phenomena. And so this is why we actually need to treat the electrons with the Schrodinger equation due to their wavelike properties. And in general, we don't really need to nuclei as a wave-like particle.

So this was one thing. The other important thing that I'll repeat over and over again is that when we move from a particle-like description, where the only important quantity are the position and the momentum, to a wave-like quantity, well, we have a completely different computational content. That is, a wave function is actually defined by assigning the amplitude of the wave at every point in space and at every time. So in practice, it's a continuum field that in every, say, computational calculation needs actually to be discretized and approximated in different ways.

And then I introduced what is the equivalent of the Newton's second law of dynamics for actually quantum objects. So classical particles evolve according to the law force equals mass times acceleration, where the acceleration is really the secondary derivative of the trajectory. Quantum particles obey a different fundamental law that's basically been discovered by Erwin Schrodinger in 1925. And the other major player where Werner Heisenberg, Paul Dirac, and many others. And I've written it here in the most general form for the case of a single electron, so a particle that is described by a wave function psi, a function of space and time.

Very good. The machine [INAUDIBLE] beep.

OK. Professor Ceder will take care of this. And let me continue. So we have the descriptor that is the wave function. And we have a potential. A potential is the general concept. It could be, say, the electromagnetic potential that is coming from the nucleus of an atom.

So suppose that you are studying a hydrogen atom. Well, the nucleus has an attractive potential for the electron that is just 1 over the distance between the electron and the nucleus. So V here is really the same potential that you have learned in classical dynamics and electromagnetism. But now, instead of acting on a particle, it acts on the wave function. And the way it does, it just multiplies the wave function.

So what the Schrodinger equation is telling me is that whenever I have a potential V, the solution for the dynamics of the electron will be given by the solution of this second-order differential equation, where here this is a Laplacian. We have a second derivative with respect to space. And so the wave function needs to satisfy this equation.

In most cases, to actually deal with problems in which the potential does not depend on time-- suppose that you are studying a molecule. What is your potential? Think of, say, the benzene molecule. Well, you have six carbon atoms in a ring and six hydrogen atoms also in a ring. And in each nucleus, there is a Z/r that is an attractive potential for the electron. And that we can either think of at a potential that doesn't change in time-- or even if it changes, because the molecule is a certain temperature and so atoms move around, what it turns out will happen in practice is that electrons are so much lighter than nuclei that for all practical purposes they move so much faster that they see the nuclei basically as fixed in time.

So if you think of a particle like a nucleus that has a huge mass and a particle like an electron that has a very light mass, well, even if the nuclei move, the electrons always are so much faster to rearrange themselves to be in the minimum energy configuration. We'll actually see more of what is called adiabatic approximation.

So the important thing here is that, for all practical purposes, we consider in most problems the potential as not really dependent on time either because the atoms are not moving or because even if they move, they move so much more slowly than the electrons. Then the electrons can always [INAUDIBLE].

The form that the wave function can have. And I'll briefly sketch out this derivation here. So whenever the potential doesn't depend on time, this is how we proceed. We actually make an hypothesis-- often, this is called an ansatz-- in which our wave function can actually be separated into the product of two terms-- a term that depends only on space, we'll call it phi; and a term that depends only on time.

So we are making this hypothesis. We have decided that the potential does not depend on time. And we see what [AUDIO OUT]. What we have now is that whenever we apply, say, the Laplacian secondary derivative with respect to space, well, [INAUDIBLE] the f component of the function, the time-dependent component. So the Laplacian of psi can be written actually as f times the Laplacian of phi.

And then I'm not writing the explicit dependence on the variables. But we have the potential times the wave function, phi f. And then we have i h bar. And now, the derivative with respect to time of phi-- well, a phase-dependent part is not affected. So we write it as pih times df/dt.

OK. So this is our first step. And now, we take this expression. And we just divide it by the product of phi times f. And so when I do that, what I obtain is minus h bar squared divided by 2m Laplacian of phi divided by phi plus V equal to i h bar 1/f df/dt.

And this really is the end of the derivation because something very important happens at this point. Look for a moment at the right-hand side of this equation. You see it's just a constant-- the Planck constant, i, is the imaginary unit-- times 1/f df/dt. So everything that's written on the right-hand side here depends only on time.

The left-hand side, on the other hand, we have a term that depends only on position. Phi is a function of position. And V-- remember, our initial hypothesis-- does not depend on time. The potential does not depend on time. So the left-hand side [AUDIO OUT].

Now, the only way such a relation can be satisfied-- that is a term dependent solely on position can be equal to a term that depends only on time-- is if each term separately. That's the only way the overall function of r can be [AUDIO OUT] overall function of t, if they are constant. Basically, because r and t are independent variables, there is no relation.

If you want, in this ansatz [AUDIO OUT] down the Schrodinger equation in two parts-- the left part being equal to a constant, and the right part being equal to a constant. So there is a simplification. We can deal with separate equations for the time-dependent part and for the space-dependent part. What is the left-hand term equal to a constant becomes what is called the stationary Schrodinger equation. That is the equation that we'll try to solve over and over again in our calculation. And it's the term that I've written here.

So the stationery Schrodinger equation is written here. And this is the differential equation that, in principle, is complex to solve because the potential can have an arbitrary complex shape. But again, think of the potential as being the attractive potential for the electrons generated by all the nuclei in a molecule or in a solid.

And the time [AUDIO OUT] has become trivial to integrate. And we see this is the time part of the Schrodinger equation. We see, actually, in the next slide why this is simple because this is just a first-order differential equation. And we are looking, in general, for a function whose first derivative with respect to time is equal to the function itself times a constant. [AUDIO OUT] equation to integrate because the exponential function satisfies this condition. When you take the exponential, you just get the exponential itself times a constant. And so really, there is no analysis [AUDIO OUT]

The other part, the space-dependent part is the one that is complex to solve. And we'll see here just a few examples [AUDIO OUT] If we want the simplest example possible, that is the case of a free particle. What happens to an electron that doesn't feel any potential? And again, its wave function is going to be the product of a space-dependent part phi times a time-dependent part f. The f term [AUDIO OUT]. The space-dependent term here is the solution of the stationary Schrodinger equation in the hypothesis that the potential V is equal to 0. So I've removed from the stationary [AUDIO OUT].

Again, this is a fairly simple differential equation to integrate because what we are looking for is basically a function whose secondary derivative is equal to the function itself times a constant. And then again, the solution is just given by an exponential, OK?

Now, I'm looking in particular at the problem in which I'm trying to find a solution phi for a value of this constant E that is positive. And so when you actually work out the algebra, you see that what you need as a term in front of the x in the exponential is the square root of a negative number, is the square root of twice the mass times E divided by h bar squared. And so that's why we get this imaginary unit here. It's basically because we have rewritten this equation as the square Laplacian of phi equal to minus 2mE divided by h bar squared f.

And you see straightforwardly that if you take the secondary whatever of the functions that are written here, well, we'll get, by taking the first derivative, a term i square root of 20 divided by h bar. And when we take the second derivative, we get that term again. And the square of that term is a square of i that gives you my minus sign.

OK. So this is the solution. We have actually found the wave function for our free particle. And the wave function is the product of [AUDIO OUT] times the time-dependent part. And in the next slide, I am actually plotting this wave function in space. Sorry, let me jump to this slide. This is it.

So I am plotting it. For simplicity, I've called it a different coefficient. E over h bar, I've called it omega. And square root of 2mE divided by h bar, I've called it t. So this is the wave function for a free electron. And this is what we call a plane wave. And the reason why is that is simple because if you think of what this term is, the exponential of a complex number is really a combination of sines and cosines.

And now, suppose that you look at the amplitude of this wave function at a certain point in space-- that is at a certain x equal to x0. What you see is that that amplitude will have a kx factor that doesn't change because we are sitting at a certain x0. But what is changing with respect to time is the second term, omega t. And so you see an oscillating amplitude with a period omega at any point in time.

Or in a different way, if for a moment you think that what is this field of the wave function at a frozen instant in time-- that is for a certain time t equal to t0-- well, it's nothing else than a complex exponential. So it's a complex-valued function that has a cosine or sine projection, depending if we look at the real or complex axes.

So what you need to think of when you think that at a free electron is nothing else than this infinite oscillatory field propagating in space. But it has really no beginning and no end. And one of the important things is that the wave function really contains all the information that we might want to know about an electron. And we will see in the next slides how we actually obtain the physical properties about an electron from the function.

But the simplest property in [AUDIO OUT] of finding an electron in a certain position and a certain time. And so [INAUDIBLE] that wave function amplitude at a certain x and a certain t gives me actually the physical probability of finding an electron. That means that if I have the wave function of an electron, I can take at every point in space the square models of its amplitude. And so what I have now is a probability distribution. And what quantum mechanics tells me is that if I'm going to make a measurement and try to see where the electron is, well, I will find it in different points in space with a probability [AUDIO OUT] into these square models.

And you see one of the first conclusions from our analysis of the Schrodinger equation in the case of a potential that does not depend on time is a Schrodinger equation in which the wave function can actually be written as the product of a space part times a time part is that the probability of finding the electron somewhere does not depend on time basically because [INAUDIBLE] square models of psi that can also be written as psi times its complex conjugate.

What you have is that the term exponential of minus i/h gets multiplied by its complex conjugate. That is the exponential of plus i/h. And those terms cancel out. So in the probability distribution for the electron, we have only the square models of the space part. That is to say that the probability of finding an electron does not depend on time. It's just a function of space if the potential does not depend on time.

You see, [INAUDIBLE] our plane wave. The potential does not depend on time. If we take the square models of this function, well, what we have is really a constant because we are just taking an imaginary exponential times its complex conjugate. And so that product is a constant. So what we discover really is that the electron is free as a probability distribution that is constant. That is, you can find a free electron anywhere in space. Yes?

AUDIENCE: [INAUDIBLE].

NICOLA MARZARI: So this is actually the solution in three dimensions. So what the difference is, if you work out the algebra-- and we can look at it after class-- is that what you have is-- in the space term, you have really a scholar product in three dimensions. That is, what you have is that now a point in your three-dimensional space is described by a three-dimensional vector r.

And now, you can have solutions that are classified-- if you want, this k is actually called the quantum number. It's what classifies all this possible continuum of solutions. And if you think, k is telling you what the wavelength of this plane wave is and what is its orientation. So really, what I am plotting here is specific plane waves that, if you want, is a k vector that is ordered in this direction.

So if we were in one dimension, you have, if you want, the equivalent of a sine or a cosine. And your only degree of freedom is the wavelength. But if you are in three dimensions, your degrees of freedom are not only the wavelength-- that is the distance between these crests-- but also this direction. And any arbitrary k vector is actually valid. So you can have plane waves with all possible wavelengths and all possible orientations.

And actually, this gives me a good chance to mention another sort of physical observable that comes from the wave function. The first one that we have seen is the probability distribution. And that's obtained by taking the square models. Another one is what is called the quantum kinetic energy of that particle. And the quantum kinetic energy is really just given by minus h bar squared divided by 2m.

So the quantum kinetic energy is given-- well, I'll describe it in more detail in a moment. But it is obtained by really taking, in a slightly more complex way than what I am saying now, the second derivative of the wave function. So the second derivative here with respect to the space of this wave function would give me a k square term. That basically means that a plane wave with all wavelengths corresponds to electrons with all possible energies.

But there is something other that is very subtle that is reminiscent of what in quantum mechanics people call the indetermination principle. So this free electron, as you see, is an electron that is distributed equally in space. So we can find it with equal probability here, here, or everywhere else. And it is actually a perfectly well-defined second derivative with respect to space. It has a perfectly well-defined kinetic energy, has a perfectly well-defined momentum.

And that's really one example of the indetermination principle. That is, there is a fundamental rule that quantum particles satisfy. That is, you can't actually measure their momentum and their position simultaneously with arbitrary accuracy. And so a free electron, if you want, is an electron that has perfectly well-defined momentum, perfectly well-defined kinetic energy. And for this reason, it has perfectly undefined position. That is, the electron can be found anywhere. And so this is, if you want, an exotic result coming from the Heisenberg indetermination principle.

I wanted to give you another physical example, getting closer to reality. Suppose that, for a moment, we are studying a metal surface. This wouldn't be very different from what you have studied in your first laboratory. What you are studying is basically a slab. And you have been finding quantities like what is the energy, what is the lattice parameter, what is the surface energy.

Suppose that now you are using quantum mechanics. Well, what do the electrons in the metal look like? And we'll see in next classes that an electron inside a metal really feels and behaves very much like a free particle, especially in very simple metals, in metals like sodium, potassium, even aluminum to a certain point. There is a very delicate cancellation of attractive and repulsive terms for the electron in the metal.

So the net result, to a very good approximation, is that the high energy electrons, the valence electrons, really feel almost free. I'm saying almost free because they are really confined inside the box that is your metal crystal inside the box that is given by your metal slab. And so to have a simple but very good approximation, we can think of the potential felt by an electron in a metal as a type of potential.

I'm thinking of a case in which, on this side, on the left, I have really my semi-infinite slab. And so the potential that is drawn by this thick line is actually 0 for x smaller than 0. And then there is a confinement. So there is a step. This is a little bit like a well. There is a potential difference v0 that contains the electron inside the slab.

So you really need to pay an energy v0 to get out of the slab. But this is in physical terms what people would think of as the work function. The work function is really the energy that you need to pay to pick up the highest energy electron in the metal and bring it out, bring it very far away from your slab.

And so to a good approximation, the potential that these electrons close, as we say, to the Fermi energy feel is this. And what we are trying to find now is a solution for the Schrodinger equation for a case of an electron having an energy. Actually, the E, that constant in the Schrodinger equation, is actually the total energy of the particle. So we are looking for a solution for an electron having an energy that is basically between 0 and v0. That means that that electron classically is really confined to the left side of the potential.

And so what do we have here? Well, what we have is that, on the left, we have again, a very simple Schrodinger equation that is minus h bar squared over 2m d squared over phi equal to E times phi. So this is, on the left side, the Schrodinger equation for the free particle. And we know the solution. And it's just being given by one of these plane waves.

But now, the difference is that, on the right, we have all of a sudden a potential. So the equation on the right is going to be minus h bar squared over 2m times delta squared phi. Remember now, in the stationary Schrodinger equation, we have a term that is given by the potential that, in this case, is just a constant times the wave function. And this is going to be equal to d phi.

What's the difference between these two equations? Well, let me actually rewrite the one on the right side as minus h bar squared over 2m delta squared phi equal to E minus v0 phi. Well, in both cases, we are trying to find a wave function whose second derivative is basically equal to the wave function itself times a constant. But the big difference is that we are actually looking for physical solutions for an electron that has an energy lying somewhere in between 0-- that is our conventional minimum-- and v0. That is the energy cost to get that electron out.

So what we have is that, for the left side equation, what we are trying to find is a second derivative in which, you see, the constant is going to be minus 2mE over h bar squared. So it's a negative number. So we need to take a second derivative and get a function times a negative number.

In the other case, remember, what we are looking is for a solution in which the energy is between 0 and V0. So this the sign of the coefficient here has changed. Here, before, it was positive. Now, it's negative. And with the negative sign on the other side, it means that what we are looking is for a function whose secondary what is equal to a positive constant times the function itself.

And all this long story is just to say that the solution on the left will be given by an exponential that has an i term in there. So it's a complex exponential. Well, the solution on the right-hand side will be given by an exponential that has a real term coefficient. And so what we have is on the left side a periodic oscillatory solution typical of the free electron. And what we have on the right side is actually a decaying exponential.

And so what we have is that our free electron is going to have a wave function that really looks like this-- free particle like inside the oscillatory and exponentially decaying outside the surface. And this is how truly electrons in a metal-- and in most metals, it looks like the wave function decays exponentially. That's actually why people, say in 1981, could invent something as fancy as the scanning tunneling microscope.

You see, the STM is one of the fanciest instruments that we have that can actually be used to see atoms. And what does an STM do? Well, an STM comes with really a nanometer-sized tip. And what the STM measures is the current between, say, the metal and the tip. And it's very sensitive because, you see, since the wave function decays exponentially, moving the tip by a small amount will change exponentially the current going through the scanning tunneling microscope.

So we can actually move this paper and have an enormous response in the current to a very small displacement. So we can actually measure the topography on the top of a metal surface with great accuracy because basically what the scanning tunneling microscopy is doing is really filling up these exponentially decaying tails coming out from the metal, coming out from the metal surface.

OK. So I'll show you just a few examples so that we get more and more the feeling of how wave functions look, getting closer and closer to physical problems. Keep in mind this general idea-- if we have got zero potential, we have this wave-like solution. So a typical problem that is very simple to actually solve analytically would be the one in which we have an infinite square well. That is, we have a particle that feels zero potential between, say, minus a and a and infinite potential outside.

And this qualitatively starts to be very similar to what an electron in an atom feels. And electron in an atom doesn't really feel a potential that is 0 in a region and infinite outside. It really feels an attractive potential that is 1/r. So the potential is actually shaped very differently. It's going to be a Coulombic cusp ending up in 0.

But you see, the solutions are very similar. And we can understand them better if we actually look at the solution for this case. And again, what we have is a problem in which, between minus a and a, we have 0 potential. So the solutions are going to be free electron-like, wave-like. But now, we have a new condition. That is, what we have is that being the potential is infinite, say from this point onwards on the right and from this point downwards on the left, what we need to have is that the wave function needs to have 0 amplitude outside this region.

If the potential is infinite, you can think physically that there is 0 probability of finding the electron. It's truly infinite. So it's fully constraining the electron. So the wave function needs to be 0 from here onwards and from here onwards. And so another great discovery of quantum mechanics is that the only sine or cosine-like solutions of the Schrodinger equation that are such that they have 0 amplitude at this point and at this point there are sines or cosines with a wavelength that is compatible with this distance.

So all of a sudden, our solutions that, in the case of the free electron, could have any wavelength in the world have now become quantized. There is only a discrete set of solutions with wavelengths that are compatible with the distance between the two infinite, confining sides.

And this is the same concept of an organ pipe and the music that it plays. When you play music in an organ pipe, you are really exciting either a sound wave with a wavelength corresponding to the fundamental harmonica. Or the only other notes that your organ pipe can produce are actually higher harmonics. And so they are, again, sound waves that will have 0 amplitudes at the borders. Or same thing, say, with the chord of a guitar.

And so the wave functions for a confined potential are actually quantized. And they have corresponding energies-- that is, in this specific case, go actually as the square. Although, this is less relevant for our case. So you will see that, in most cases, like when we look at the solution for an atom in a confining Coulombic potential, we'll actually find only a discrete set of wave functions with discrete energy levels.

And again, we can get some hints on how this solution would look like. If you think for a moment at what would happen if our square well, instead of having infinite confining walls, would have only finite confining walls with a finite height, it's really the same case as the metal surface because now you have a finite wall. You have a finite wave function decaying exponentially outside in that region.

And so what was, you remember, our fundamental harmonic-- the second harmonic, third harmonic, fourth harmonic, what were those oscillatory solutions inside the box now start getting these exponential tails decaying in the vacuum. And this is really how solutions for the Schrodinger equation of an atom look like. And I don't want really to bore you with the algebra. Some of you might actually have seen this over and over again, if you have taken a quantum class. I'll just give you one slide with the conceptual framework of what we should do if we were to solve the Schrodinger equation for a single electron in what we call a central potential.

This is a general concept. Central potential is a potential that depends only on the distance from a center, but not on the angle of distribution. And so central potential would be written as V of r, where r is the modulus of our vector, is just the distance. And the algebra is fairly complex. But the general idea is that this is now our Schrodinger equation. We need to find a wave function such that the application of the second derivative plus this potential is equal to the wave function itself times a constant.

And because somehow we are dealing with the geometry of a central potential, it's convenient to write the Laplacian, the second derivative, not in Cartesian coordinate, but in spherical coordinates-- that is, in coordinates which, instead of giving the x, y, and z components of a vector, we give the distance from the origin and the two angles, theta and phi, that that vector makes with respect to different axes.

Again, the solution is fairly complicated. So I won't really go into this. But this is how our Hamiltonian-- this is how the left part of the stationary equation would look for this central potential, having just rewritten basically this second derivative in Cartesian coordinates. And when one goes through all the algebra, one finds out that the function-- the space part of the wave function can be written as a term that depends only on the distance from the center, from the place where the nucleus is, times an angular part. And if you are familiar with this, we call this angular part spherical harmonics. And this would be the radial part of the wave function. That is a solution of a slightly different, one-dimensional Schrodinger equation.

Again, this is just the start, if you are interested to take this. But somehow, this is all the algebra that gives rise to the periodic table. That is, when we study actually what are the solutions of the Schrodinger equation for a central potential, well, we find that we can classify the solution as we were classifying the solution in the particle in a box depending on, if you want, the fundamental harmonic and the higher harmonics. Well, we can still classify the solution depending on the angular distribution-- so what are actually the L and M indices of the spherical harmonics. And we can also classify the radial distribution.

And so all these possible solutions give us all the possible states of an electron in a hydrogen atom. And you probably have seen this over and over again. But it's really the fundamental alphabet that gives rise to the periodic table. So for the hydrogen atom, the fundamental solution is one in which the electron is distributed with spherical symmetry around the nucleus.

And if we look at the probability density as a function of the distance from the center, it's something that really looks a little bit like this. So the probability of finding the electron in the hydrogen atom at a certain distance really has a maximum at a distance that is, I believe, at 1.5 bohrs. I need to check actually this number. The classical radius of the hydrogen atom is 1 bohr. It's 0.529 Angstrom. And the maximum, I think, is at 1.5. But basically, there is a maximum of probability. And then it decays again.

But then there is a whole zoology of excited states that can have, say, a more complex radial part. And we classify these-- you probably remember this from your chemistry. We call this state a 1s state where 1 really refers to the radial part and s refers to the angular part.

And the next state would be a 2s-like state, in which, being s, the angular part is still the same. It's spherically symmetric. But now, the radial part has changed. And it actually changed sign. So it goes inside. Then it goes back to 0. Then it goes again. And it goes back to 0.

And then there are states like the 2p states in which the angular part starts to play a role. And so this would be a specific p state that, if you want, has two lobes with opposite signs across a plane of symmetry. And then there are more complex states like the d states and so on and so forth.

And a very important thing is that really this angular symmetry comes from just having considered a central potential. That is a potential that doesn't depend from the angular variable, but just from the distance. And so these solutions have the same qualitative difference not only for a single electron in a hydrogen atom, but, say, in general for an electron in an atom where really that electron will feel not only the attractive potential of the nucleus, but also the repulsive potential from all the other electrons.

But to a great extent, that repulsive potential of all the other electrons is going to be a fairly spherical symmetry kind of potential because all the other electrons, when you take their charge density, are going to be roughly spherically symmetrically distributed. And so the solution really, for one electron in a central potential, does not only apply to the hydrogen atom, but applies to really any atom in the periodic table to some approximation. That is to the approximation that we consider. The repulsive potential that all the other electrons have for this, say, top valance electron in a generic atom, say iron, is that the only approximation is that these repulsive potential is also spherically symmetric. That is not true but is true to a very large extent.

OK. Now, this concludes, if you want, our general panorama on what is quantum mechanics. And now, really, we want to go into electronic structure methods. That is, we want to arrive at what is called the Hartree-Fock solution. That is, again, one of the fundamental techniques, especially in quantum chemistry.

And to do this, I need to give you a little bit of nomenclature. Again, if you have never seen a set of quantum mechanics or if you have never taken a quantum mechanics class, it would be very useful to have a look at some of the books that I've given you in the bibliography, either some fundamental books like *Quantum Mechanics* or *Physics of Atoms and Molecules,* both by Bransden and Joachain, that are very good quantum mechanics books, or some of the electronic structure books, like the Phoenix books on inter-atomic forces or the Richard Martin book, or the Kaxiras book.

But the nomenclature that we'll use over and over again is what is called the bracket nomenclature of the Dirac. And so in general, a wave function is actually represented by this sign here. This is called [INAUDIBLE]. Again, that means nothing else than our function. That is an amplitude defined everywhere in space or everywhere in space and time. And in general, it's a complex amplitude.

And now, one of the fundamentals of the rules of quantum mechanics is that, say, a wave function corresponding to different states of an electron-- say you are considering the function for the ground state of the hydrogen atom, the 1s. And then you are considering the function for an excited state, like the 2s. So the wave function for different states are going to be orthonormal. What does it mean?

It means that when we take the scalar product, that scalar product is going to be either 0 or 1, depending if we are taking the scalar product with the wave function itself or with the wave function of a different state. So this delta ij is what is called usually a chronicle delta. It's a symbol that means this is going to be equal to 1 if i is equal to j or is going to be equal to 0 if i is different from j.

And the scalar product between two wave functions is written in shorthand notation as this. It's written as a bra times a ket, a bracket. But again, that's nothing else than a shorthand form for the proper definition of the scalar product. Again, you are probably not heard of Hilbert spaces. But this is a vector space of wave function that has a metric defined. And so we can define something like a scalar product by taking the integral of the wave function on the left that has been complex conjugated times the wave function on the right.

So all wave functions that are solutions of a Schrodinger equation satisfy this orthonormality normality property. If you take this integral, that is going to be equal to 1 if you are just taking the square of the wave function. And it's going to be equal to 0 if i is different to j.

And you see why it's equal to 1 actually if i is equal to j because remember what is psi i star times psi i? Well, it's just a square modulus of psi i. So psi i star times psi i in a certain point r in space gives me the probability of finding the electron in point in space. And when I integrate that probability all over space, it becomes obvious that that number must be 1 because what is the probability of finding an electron anywhere in space? Well, you'll find it somewhere. So the probability of finding it anywhere-- that is the integral of psi squared as a function of r-- must be equal to 1. So that's the physical connection.

And the last definition that I need is that of expectation values. That is, once we have found a wave function for this electron-- as I said, we know everything that we need to know about that electron. And so we can extract all the physical properties that we want.

It's like, in classical mechanics, if you have the trajectory of your electrons, you can calculate at any instant in time what is, say, 1/2 times the mass times the square velocity. That would be the kinetic energy of that particle. Similarly, if you know the wave function of that electron, you can calculate any kind of physical quantity. And one of the most important physical quantities, apart from the probability of finding it somewhere, is what is the energy of that electron.

And this is the shorthand term in the bracket nomenclature of what would be the energy of an electron. We call this an expectation value. So in quantum mechanics, for every physical observable, like the energy, there is going to be an operator that acts on the wave function and is such that its expectation value gives me the physical quantity I'm interested in.

So if I want to know the energy of an electron that has a wave function psi i, I need to calculate this expectation value, psi h psi i-- that will give me the energy. And the quantum mechanical operator that gives me the energy is what is called the Hamiltonian operator, h, that I've written here. So the Hamiltonian operator is nothing else. And I forgot it here. And sorry, there is a Laplacina.

The Hamiltonian operator is nothing else what we have seen in the Schrodinger equation. It's minus h bar squared divided by 2m times the Laplacian plus the potential. So if you want to calculate what is the energy of this electron, what you need to do is to apply the energy operator, that is the Hamiltonian, to the wave function. So you need to take the second derivative with respect to the wave function. With the appropriate coefficient, you need to sum the potential times the wave function.

And now, to this new quantity that is again a field that is a function of r, well, you need to take that multiplied by the complex conjugate of the wave function and integrate it all over space. So if you want, it's a much more complex operation. But that's exactly what are the rules for quantum objects.

You have a Schrodinger equation. You find its solutions. And then the solutions are the ground state or the excited state wave function. And if you want to calculate what are the physical values of what we say are observable quantities, like the energy, you need to take an expectation value of the appropriate operator. And if you want the most fundamental operator, it's the Hamiltonian h that is just written here. And the expectation value that is written in shorthand form here is nothing else but the integral overall space of the complex conjugate of the wave function times what we obtain by applying to the wave function the Hamiltonian operator. And we integrate that in space.

Now, it's actually simpler than it looks because remember for a moment that this psi is actually a solution of the Schrodinger equation. This psi is a solution of the stationary Schrodinger equation. So we know already, because the Hamiltonian is really-- remember, it's the left and term that is in this stationary equation.

So we know already that, by the fact of this being the solution, applying this operator to this wave function is going to give me a constant times this wave function. And so the concept, we call it nothing else than E with a subscript i. So this times the wave function gives me a constant times the wave function itself. And I can take the constant out of the integral sine. And I'm left with constant E of phi times the integral of psi i star times Ci. And that's nothing else than 1. And so this is, if you want, the explicit solution of why this is epsilon i.

Of course, if you have never seen this, it might look very arcane. And this is why I urge you to read some introductory quantum mechanics textbooks. If you have seen it already, of course, it might seem trivial. It might seem trivial to you.

OK. And now, in the next three or four slides, we go really into the two fundamental concepts of computational electronic structure. That involves two things. One, it involves finding the solution of the Schrodinger equation on a computer-- that is, on a system that is really not able to do analysis, if you want, is not able to do analytic derivatives and analytic integrals. And so we'll how we actually deal in practice with this issue.

And then in the second set of slides, we'll give you the fundamental concept that is a reformulation of the differential equation, of the Schrodinger equation, in a different form that is actually computer-friendly and algorithmic-friendly. So we have a Schrodinger equation that we know we need to solve. But we can actually rewrite it in a form that is much more convenient. And respectively, you can think of them as the general concept of expanding wave function in a basis that transforms all our analysis and integrals and differentials in matrix algebra. And I'll show you in a moment why that is the case. And in the second part, we'll see how the Schrodinger equation is transformed into a variational principle. So really, what you are seeing now is, I would say, the central content of today's class.

OK. Let me first go back to the Schrodinger equation as you have seen it before. And now, I'm using actually the shorthand term H, this Hamiltonian operator, that is again nothing less than minus H bar squared over 2m times the Laplacian plus the potential. And so the Schrodinger equation tells us that, for a given potential, we need to find a wave function psi such that when we apply on it those derivatives and those multiplication contained in the Hamiltonian operator, that is H, what we obtain is nothing else but the wave function itself times a constant.

So this is the Schrodinger equation in shorthand form. And we can even be more compact and write it in the bracket formulation on the right side as H psi equal to epsilon psi. So this is our Schrodinger equation. And now, this is the fundamental step. And this is what really makes all of this solvable on a computer.

What we say now is that any generic wave function-- OK. So we are still considering one electron in three dimensional space. So what we have is really an amplitude field all over space. Well, that amplitude field can actually be written as a linear combination of an infinite number of simple functions times a coefficient. So we are saying, well, we can expand every possible field into a linear combination of orthogonal functions that would be our basis function.

Say, if you have seen Fourier analysis, you have seen that, in most cases, a well-behaved function can actually be expanded as a linear combination of sines and cosines. Or in general, if you have seen more of analysis, you have seen that, in a lot of these Hilbert spaces, you can define what are called complete sets of orthogonal functions. Sines and cosines are a complete set of orthogonal functions. If you take sines or cosines with different wavelengths and you integrate them over a space, you get 0 unless the wavelength is the same. And by using an infinite number of sines and cosines with different wavelengths, you can describe any function that is, in some ways, smooth enough, that doesn't, say, infinite discontinuities.

And so what we do really, in most of our computational application, is that we define a basis set. Let's say, for the case of solids, it's actually going exactly to be the basis set of plane waves, those E to the i kr with all possible wavelength and with all possible directions. That is an orthogonal set. And it's complete.

And so once we decide what is our basis set, say sines and cosines, and plane waves-- and there are a lot more that I'll describe in the following. Well, at that point, our function needs to be specified by a set of coefficients. And in all practical implementation, we won't use infinite sets. If you have got a well-behaved function, you don't need to describe-- it probably won't have oscillation with extremely thin wavelength. So you can expand a wave function into a combination of sines and cosines that have progressively shorter and shorter wavelengths.

But at a certain point, you can say, well, I'll stop here. I don't need a resolution that is thinner than what is physically reasonable. I mean, if you are looking at electrons, well, they are going to have oscillations that are of the order of the inter-atomic distance. But they are not going to have oscillations that are of the order, say, of the diameter of a nucleus. It just doesn't make any physical sense.

So you can understand, for every physical problem at hand, when you can actually stop this infinite expansion in your orthogonal basis. And at that point, your wave function becomes defined just by a finite number of coefficients. And so suppose that for a moment you have only 10 basis functions. It could be sine of x, sine of 2x, sine of 3x, sine of 4x, up to sine of 10x in one dimension. Well, once you have decided that those 10 are your good basis function, your wave function is described by 10 numbers. It's just a vector.

And so what you need to do is find those 10 numbers. So if you want, what was an analysis problem now becomes a bit of a linear algebra problem in the ways you'll see in a moment, in which we really need to find those 10 coefficients. We don't need to find any more integrals and derivatives of functions.

And so let's actually see how this develops. Remember, what we need to solve is the Schrodinger equation that I've written over here. And now, I have decided that I've got an orthogonal basis. And I am going to do some algebra. In particular, I take this Schrodinger equation above. Remember, it's operator applied on the wave function equal to a constant times the wave function. And what I do is I say I multiply this relation on the left and on the right by the complex conjugate of phi m.

So in going from here to here, what I do is I multiply this times the complex conjugate of phi m. So it's phi m star. And then I integrate everything over space. And so you see, when I take H psi, I multiply it by phi m star. And I integrate. What I obtain is something that, in shorthand bracket formulation, can be written as phi m H psi This is nothing less than a shorthand for the integral of overall space of phi star m times what results from applying H to psi.

Same to the right-hand side-- I multiply E times by phi m star. And I integrate over space. Now, E is just a constant. So it can come out of the integral sine. And what I am left with is the integral of phi m star times psi. And again, it's very important that you go back just after this class and you rewrite explicitly all these algebraic terms to make sure that you become comfortable with them.

So I've done this operation. This is what I have obtained. And now, what I do I exploit my hypothesis. I've said that my wave function can be written as a linear combination of my basis function with certain coefficients. So in this integral, now I substitute for psi at sum of wave function with appropriate coefficients. And as usual, I can take the sum and the coefficient out of the integral sine.

So what I'm left with is a sum of the Cn that multiplies the integral of phi star m H phi star n. This is what I have on the left-hand side. And now, on the right-hand side, this is likely trickier to see. Again, I'm substituting for psi that sum. So what I obtain here is really-- let me write it as an integral for a moment-- is the integral over all space of phi m star times the sum over n of Cn phi m.

I can take a-- sorry, it's a sum over-- it's a bit difficult to see. Let me write it more clearly. It's a sum over n Cn phi star n. OK. These are just coefficients. I can take them out of the integral sine. So what I'm left with is sum over n Cn times the integral over the r of phi n star times phi m. For some reason, I wrote this down here. So it's just a phi n.

And now, the integral of dr phi m star times phi n is going to be equal either to 1 or to 0, depending if m is equal to Min or m is different from n because, in our hypothesis, we have said that these basis functions are orthogonal. And that orthogonal means we take the integral of them. If they are identical, it gives 1. If they are different, it gives 0.

So in all the sum over the n, there is only one index that will be identical to this. So for that case, the integral gives 1. Otherwise, it gives 0. So what is saved in all of this is only the coefficient that corresponds to this m coefficient here. So what we obtain from this is the Cm times a constant.

OK. So again, I've rewritten the Schrodinger equation by multiplying it by phi m star, integrating it. And what I obtain is a new formulation of the Schrodinger equation that I have also in the next slide. And that we are actually going to analyze.

So this is nothing else than your last slide. And again, what we need to find are these coefficiencies. Those have become now our solution. And we can actually write this explicitly using a bit of nomenclature. That is, we can call that scalar, that expectation value-- phi m H phi n, we can call it that shorthand H m n. We call it actually the matrix element of the Hamiltonian over the two basis phi m and phi n.

And so again, our Schrodinger equation has been rewritten in compact form as this. That is, the physical problem tells us what is the potential that the electron feels. The potential specifies what the Hamiltonian operator H is because it's, again, just the Laplacian plus the potential. And so once we have decided our basis set onto which we develop our wave function, what we need to calculate are all these matrix elements.

Now, these H m n are explicit numbers. Once my potential is well-defined, once my bases sector is defined, those H are just numbers. And they actually can be written out in a matrix. And my Schrodinger equation has been rewritten in this form. That is, I have that this matrix times the vector of coefficient of my expansion needs to be equal to a number times the same vector.

And if you want, I have two things to find out. I need to find out what are the values of E for which this linear algebra system is a solution at all. And we know from linear algebra that there aren't an infinite number of values of E for which this system has a solution. And I'll comment in that on a moment. And once we have found those values of E for which there is a solution, we need to find the solution. That is, we need to find this vector.

And so again, our problem is matrix times vector needs to be equal to a constant times vector. And we actually-- again, I don't have the time to go into linear algebra. But we know this can actually be rewritten as a Hamiltonian matrix, an H matrix minus an E on all the diagonal terms times this vector equal to 0. And we know that this linear algebra solution-- this linear algebra problem has a solution only for values of E such that the determinant of the matrix H minus E times the identity is 0.

So our goal is first finding those values of E for which this determinant is 0. And we call those eigenvalues, are the only values of the energy that are allowed in our quantized Schrodinger equation. And then for each of these eigenvalues, E, there is going to be a vector. There is going to be a set of coefficient from C1 and Ck that satisfies this linear algebra problem. And we call that specific vector of coefficients an eigenvector.

So this is an eigenvalue equation that only certain values of phi which this equation is a solution. And those values of phi for which it has a solution will give rise to the eigenvector that satisfies this equation. And in a computer, you see the only thing that we need to do is calculate this matrix element of the Hamiltonian, find its eigenvalue, and find its eigenvectors that are all well-defined linear algebra problems.

And so this is the first fundamental conclusion. We can always rewrite our quantum mechanical problem into a linear algebra problem once we specify a basis set for our function. And depending on the problem at hand, we can choose basis sets that are more appropriate or less appropriate.

If we are studying, say, electrons in a metal that would look like free electron-like, a basis set of plane waves with different wavelengths is a very good choice. If we are studying solutions, say, in a molecule, maybe a basis set in which each state looks more like atomic orbitals would be a more appropriate choice. And again, we'll see this in the next classes.

But now, the problem has become a linear algebra problem. And there is another conceptual and last step for today's class that I want to highlight. That is very powerful because, especially when we move from trying to find the solution for a single electron to finding the solution for many interacting electrons, it will give us a systematic handle to move in a problem that becomes conceptually more and more complex. We have discussed how there is this exponentially exploding complexity.

And there is what is called a variational principle. That is nothing else but reformulation of the Schrodinger equation. And what is this? Well, what I am saying is that there is what we call a functional of any arbitrary function. What is a functional? Well, it's something that, given a function, operates on that function and produces a number.

So we call our functional E of phi. It's an algorithm that eats as input a function and gives as output a number. And the explicitly definition of this algorithm is given here on the right-hand side. And what is it? Well, for any arbitrary function, what we need is to calculate the expectation value of the Hamiltonian. So we need to calculate again the integral over space of phi star times the Hamiltonian operator applied onto phi. And we divide that this by the integral of phi star times phi.

OK. This is an operative definition. I gave you a function. What you obtain back by calculating this integral and taking the ratio is a number. But now, the important thing is, what can we prove?

Well, we can prove this fundamental theorem that tells us, for a given Hamiltonian-- that is, for a given potential-- you can throw into this functional any arbitrary function. You can try to calculate this ratio for any phi. And what you'll find is that the number that you obtain for any phi that you throw in is going to be always greater or equal than the ground state energy of your electron.

Not only that, but in particular this number is equal to the ground state energy of your electron, the function that you have used is really the ground state wave function, is the wave function corresponding to the lowest energy of the Schrodinger equation.

And so you see this gives us a sort of trial and error practical recipe to try and find out what is the ground state energy of an electron in very complex potential because the only thing that we have to do is try a lot of wave functions. And what we will obtain as our best guess is the wave function that has the minimum expectation value.

It will never be an exact solution, unless we examine all the possible wave functions in the world. But it's a solution that becomes better and better the more systematic we become. The more wave functions we try, the better our solution will be, the closer it will be to the ground state energy.

And I think I'll leave it as an exercise-- and this is my last slide-- to be proven by you for next time. And that is, I'm asking you to go back and try to prove this variational principle. And the only operation that you really need to do is, again, expand your wave function phi into a linear combination now of states that I can call chi of n that are actually the eigenstates of the Hamiltonian.

That is, we have a well-defined Hamiltonian operator. So in principle, at least formally, we know that it will have a set of solutions that we write as H applied to this eigenfunction is going to be a number times the eigenfunction itself. And the set of solutions of a Hamiltonian are actually in themselves a complete orthonormal set. So we use that complete orthonormal set to expand our wave function as a linear combination of these eigenvectors.

And with this ansatz, wave function expanded in a combination of eigenfunctions of the Hamiltonian, you can go back and prove by yourself the variational principle in the previous slide. And that, again, is probably the most powerful principle that we have to develop all the many-body solutions to the electronic structure problem.

And we'll see that in next class on Thursday. And again, all of this, if you have never seen quantum mechanics, might seem very Arcane. So either read some of the readings that I have given you or just come and see me. Fix up an appointment.