MITOCW | 6. Hydrogen storage, and atoms to molecules

JEFFREY GROSSMAN: What we're going to do today is now, as I mentioned, shift gears. And we're going to go from atoms and molecules to solids. So the outline for today is, well, OK, so here we are. But remember, last time we didn't really talk about hydrogen storage. And some people-- well, like two people-- wanted to hear about hydrogen storage.

So I thought what I'll do is I will just briefly discuss this problem-- this energy problem, which is a very interesting problem and really, as I'll show at the very end, is another one of these huge phase space problems where quantum mechanical modeling is going to be important. OK. And then we'll move on to understanding what happens when you have a crystal. When you go from these atoms and molecules to an ordered array of atoms and molecules, which is a periodic crystal, what changes?

And there's something really important that changes in this wave function that we've been caring so much about. And that's due to something called Bloch's function, which we'll talk about. And it results in the orbitals becoming curvy. OK. So that's kind of the punch line. That's what we're going to build up to. And then next week we'll pick up from that and talk about what that means. OK.

Any questions at all? Thoughts? Hopes? Fears? Aspirations? OK. Right. That's my hydrogen storage introduction slide. And what are the two problems for hydrogen storage? Two challenges? Who can tell me? Yeah?

AUDIENCE: Making hydrogen.

JEFFREY GROSSMAN: Right.

AUDIENCE: And then storing it.

JEFFREY GROSSMAN: Why do we need to make hydrogen?

AUDIENCE: The Earth's gravitational field is [INAUDIBLE] so it all evaporates.

JEFFREY GROSSMAN: Yeah. Well, not all of it. There's still some of it. There's some of it with which we make from. But where is it? It's tied up. It's busy. You know? And you got to say, hey, I need you. Get off of that methane molecule or get off of this other molecule and come over here and be an energy carrier for me. That takes energy to make the hydrogen be available to use as an energy carrier. And then the other problem is what?

AUDIENCE: Storing it.

JEFFREY GROSSMAN: Storing it. Right. Because it's very hard. So I'm going to talk about the second problem because, again, there's sort of a molecular solution that's really exciting where computation can play a role. OK. So I'm just going to spend the first 15, 20 minutes here talking about this. I think this is-- there are high opinions about hydrogen-- gesundheit-- storage. And the hydrogen economy-- the hydrogen economy is this sort of vision that President Bush put forth. And he really kickstarted a large research program in this vision where you would be able to-- a simple chemical reaction between hydrogen and oxygen generates energy. What's that called?

There's a device that does that. That's a fuel cell. We're not going to talk about that part. We're not talking about what you do with the hydrogen because there's all kinds of challenges there too, by the way. OK. So there's really great research going on in fuel cells, which are what you put the hydrogen into to make electricity. There is a new national commitment. And there's going to be-- first car driven by a child born today could be powered by hydrogen and pollution free. Yes. For $10 million per car. OK.

I mean, I think a lot of people were excited about this. But this is a very large investment for government research, which is very little money. And in a technology that clearly has at least 50 years of research that's needed before you're going to see a trial. So maybe this should have said a child's future grandchild born today. And that would be cool. OK.

And yet, there are some really great programs going on to test the hydrogen economy. And those are the kinds of things we need to do now to lay the groundwork for all the challenges that have to be overcome. Again, I'm just going to talk about one of them, which is storage. But so I don't-- now, then Obama came in and he slashed the budget. Actually, he tried to kill it-- the hydrogen research in this country to 0, which I thought was interesting because in that administration the sense was well, it's a great technology. But it's a very long way off.

Let's try to work on-- reshuffle our investment a little into other things. Things that might give a shorter return in terms of technologies that are needed in clean energy more rapidly. OK. I've already shown this. I love this history of hydrogen. When you have a moment, just read some Jules Verne where he said-- I think I already read this quote. But he said, "I believe that one day hydrogen and oxygen, which together form water will be used either alone or together as an inexhaustible source of heat and light."

I think that's really cool that was in the 1800s. And then there are some things that happened along the way like that blimp thing that I showed you. But see, now that has caused a lot of misunderstanding about hydrogen in that it's, yes, it can combust. But how dangerous is it? So I'll show you a slide on that. Right.

So the problem in the storage is that the low volumetric density of anything that's a gas requires something that can densify it. So you got to compress it basically. Here's your metric gasoline. Remember, gasoline is this beautiful high energy density way of storing energy. 32 megajoules per liter compared with liquid hydrogen-- if you can liquefy it, it's 8. And gas under very high pressure-- 5,000 PSI is only 3.

So even if I squeeze this hydrogen gas a ton, it's still only a tenth of the energy density of gasoline. OK. So that's why storing enough hydrogen on board is hard. And it adds a lot of weight and volume. And this would be how much-- this is a little less. This is about 3,000 PSI-- 200 bar-- so that would be a gas tank of hydrogen, which is currently how some car manufacturers are making hydrogen powered cars-- again, $10, $20 million per vehicle-- that store hydrogen this way. OK.

If you could liquefy it, you can get down to smaller tanks. What I want to tell you about is something that I think is really exciting here, which is a chemical storage approach. OK. Now, right. OK. Of course, you can imagine that when you store things at this high pressure or at low temperatures and high pressures you have very challenging engineering and packaging issues. And that's one of the biggest concerns.

And because there's also a lot of misunderstanding of the safety of hydrogen-- I'm not saying it's completely safe. But people actually are looking at the safety of having something under that much pressure. OK. And so actually, when you have a hydrogen powered car, you tend to do a drop test, which isn't really true. They just are doing drop tests on the containers that they're developing. And

They drop it so that it's going to impact the ground at 52 miles an hour. And I guarantee you that one exploding drop test, and the market is going to have some serious issues whatever the cause of it is. But this is a real concern is the safety-- forget about whether it's hydrogen. But if you store anything under that high pressure, there are serious safety concerns and real packaging challenges. OK.

Remember, it's not just how the package operates when you buy it, it's how it operates after 10 years of corrosion and operation. OK. So I think chemical storage is a really interesting way to go. It does not involve high pressures. OK. Basically, in chemical storage, what you have is you have essentially a sponge. You have a material that soaks hydrogen up. So it literally just absorbs hydrogen and it changes into a hydride. And then you pull the hydrogen back out and it's just a sponge. OK.

Now the problem is that-- and there are lots of references. And there's lots of great places to read about some of this stuff. And I've put them here-- put some of them here. This is a really nice review. And the problem is if you look at the periodic table, you see a lot of times we're excited about materials design. And we look at the whole periodic table and say, what should we do today? Right?

Don't you all feel that way? That's how I feel. Every morning-- like what am I going to make today? Polonium! No. Ciborium. Where's ciborium? There it is. OK. That's a neat material. Ciborium carbide is higher than diamond. It's harder than diamond. Right? Now it's a problem that see ciborium only exists for 10 to the minus-- I don't know-- 5 seconds or something. But still, for that short of a time you can make really hard materials with it.

But see-- now-- OK-- it's a little tangent. For hydrogen storage, you got a big problem, which is density. Right? So if you're going to use a sponge to soak hydrogen up and then release it when you need it and then soak it back up, the sponge can't weigh 1,000 times more than the hydrogen. That's a problem. Right? Because then you're just going to add thousands of pounds of weight to your car.

So that really limits what you can use. And so only the light elements are really going to be useful here. And then you have a short list. And then you say, I don't want them to be really that poisonous. It might not be a good thing in the back of your car. Right? And so then the list-- you can essentially argue that the list is about eight elements that you might store. And that's just not a lot of room to play. That's why this is challenging.

As I'm going to show you, there actually is more room than you think. More and more room as research goes on. OK. And so there are a lot of materials that do fall into-- when you combine these eight elements together, you can make many different materials. And they do fall into a range of categories-- kinds of structures, kinds of elements, and so forth that can pick up hydrogen. Yeah?

AUDIENCE: I'm absolutely curious. What is metallic hydrogen or how is it made?

JEFFREY GROSSMAN: Well, that's-- Yeah. Let me get to the metal hydrides. OK. So these are some examples of the densities you can get to. OK. Look at the density of methane. That's a great hydrogen storage material. Why is it totally useless? Somebody tell me.

AUDIENCE: [INAUDIBLE] carbon.

JEFFREY GROSSMAN: Well, carbon isn't bad. What? Not so toxic. Not a problem. We can handle that.

AUDIENCE: Explosive.

JEFFREY GROSSMAN: OK. Explosive. That could be a little bit of an issue. We actually like that it's explosive-- the way we use it today.

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: It's hard to densify. You sort of have the same problem. All right. What if I could make liquid methane at really high densities? Why would that still be a really challenging hydrogen storage material? It's such a great weight percent density. Exactly. You see, a sponge that's going to-- a chemical sponge that's going to absorb hydrogen and give it back out when I want it, it's got to be just the right amount of binding. It's got to want the hydrogen just enough to hold onto it but not so much that it won't let it go. Right?

And it turns out that's really hard. That window of binding is really hard to tune. And here it's way too hard, way too high. So methane-- the carbon is holding on to those hydrogens. And you need to go to thousands of degrees to pull them off. You're not going to put a 1,000 degree Celsius furnace in your car-- heating system-- to pull off the hydrogen. First of all, you just explode your gas probably.

But also because it takes so much energy. Right? So it's the kinetics. It's getting this hydrogen in and out that has to be just right. And that's where these metal hydrides are quite interesting. They have lower densities. Higher though than the targets set by DOE, which was 6% at least some years ago. I forget what their target is today. So they're in a pretty good range to be interesting.

And there's been a lot of work. And I just put a few kind of papers and examples here. There's been a lot of work on these different materials. And in particular, functionalizing materials in different ways to see how they pick up-- how these kinetics change-- how they pick up hydrogen. In this case, you're still just looking at the weight percent. OK. Yeah. And same in this case. I'll get to the kinetics in a few minutes.

These are the sponges. Look at this. Sodium alanate doped with a little bit of titanium can give you up to 3.7% or 1.8%, depending on how you make it. And that's what it looks like. There it is before you fill it up with your fuel. And there it is when it's filled up. And then it's just going to go back and forth and back and forth. That's the concept, at least.

So that's basically just restating what I said. The metal soaks up and releases the hydrogen like a sponge. It becomes a part of the chemical structure of the material, so it doesn't require high pressures or cryogenic temperatures for operation. But it's the irreversibility that's the problem. How do you get to the right kinetics?

Now, here's a chart that I'm not going to go through. But it's, again, just more data for you to look at, if you want. And you can see that there's a lot of work going on here. There's a lot of really interesting research going on in this area for looking at materials that can form a hydride or not. So they can-- like sodium alanate can be sodium alanate, just sodium aluminum, the metal. Or it can soak up the hydrogen. And this table gives you what weight you can expect. And it gives you things like what temperature are you going to need to go to get the hydrogen out, because that's a really important parameter.

And so I'm going to finally come to-- oh. Now, I have a few sides here that I won't go through. But they're just here for you to look at, just looking at a few cases of different materials that have gotten a lot of attention in the last 10 years. And what I do is I tell you why they're interesting and what their challenges are. So we go through a few. There's aluminum hydride. You go from the pure aluminum to aluminum hydride, back and forth. You can get up to 10% weight. But it's almost completely irreversible.

Now, this is the interesting thing that I want to tell you about. And this is where you start to get really cool phase space opening up. Again, that's what I get really excited about. You look at a problem in energy. And you try to find new ways of opening up material's design, axes for designing materials. And this is one of them.

It turns out that-- you see in-- let's take magnesium. So I showed you aluminum, sodium. Here's magnesium, so another example of one of these sponges, these metal sponges. And when it's sponged, no, soaked, it looks like this. It's got hydrogen in it. And it's actually a pretty decent weight percent, 7.7 weight percent.

The problem is that this is the amount of energy it takes to get the hydrogen out. That's too much. What you need for an onboard hydrogen storage is you need that delta H to be somewhere in the range of 20 to 50 kilojoules per mole. And what is so cool is that-- what's been shown-- and this is just a bunch of data. But I want you to think size going this way and the tuning, that delta H parameter, on this axis. What's been shown is that, when it's a bulk material-- it's out here at 75-- and as you go down to smaller sizes, that gets tuned. And look at that. It tunes all the way down into the point where it's completely reversed the stability even.

And so what you see is that, just by changing the size, just by nanostructuring the material, what you're doing is you're changing the kinetics. You're changing the desorbtion energy by changing the size of the material. So that's an axis. That's a tunability axis.

Now, why is this interesting-- to what? To our class. Why is this interesting to quantum mechanics? Well, because these are all quantum mechanical calculations. And you can see that, even just the different levels theory, oh, you now know what some of these mean, because these are different DFT functionals. Just look at those, three different DFT functionals. Well, they give you similar trends.

But you can see that there's still some variation. If I go to classical potentials, it's very, very hard to know, when I engineer something into a new domain like this, if it's right. So this is really a problem that's best suited for accurate quantum mechanical methods, because you're going to make a classical potential that's fit here, basically. But all of the interesting stuff happens as you go down to smaller sizes. So it goes down into this window.

So notice that I might want it in this range. I might want the desorbtion energy to be in this range, which means I have a very narrow window of size that I can pick. I better get that right, that size right, if I'm going to try to make predictions of new materials. And that's where-- again, and then the phase space opens up even more as you talk about-- this is nanoscaling phase space that allows you to tune delta H. But you can also tune it by alloying different materials.

So now, you have this really cool playground. I have a bunch of different metals, sodium, aluminum, magnesium. I have size. And I have composition. What is going to give you the best fuel? What's going to give you the best kinetics? Perfect problem for computation and, really, a problem that quantum mechanics is needed for.

So that's my 20-minute hydrogen storage ramble. Any questions about it before we move on? And I'd be happy to talk more with people about hydrogen storage, if you'd like. It's cool problems. OK.

Now, I want to turn to this goal of going from atoms to crystals, to solids. Now, what we're going to do today is just lay some of the basic theory that we need to know. And then next week, we're going to start looking at the ramifications of that. We'll end with a band structure, which is really exciting.

How many of you have seen a band structure? Yeah. Is it fun to look at band structures? Have you gotten to that point? Yeah, it's really so-so. We'll get there. We're going to feel really excited about band structures, because it's just it's really cool stuff. And it happens because you go to that. So now, we're at this point where we want to know about crystals and not just atoms and molecules.

So what happens that we talked about so far is this. We talked about this on Tuesday. I have my atomic levels, say, S and P. And when I bring them together to form, say, a molecule, a dimer, like H2, well, then they can form combined-- they can form molecular orbitals. So that's the molecule there. And we talked about how you can get bonding status and antibonding states, because you have wiggles that are overlapping. And so they can be in phase and out of phase and so forth in the wave functions. And then you square it to find out the probability distributions.

But now, when I go to a crystal, you see you're taking this to the next level, to the next infinite level. So now, you don't just have another atom there, you've got an atom everywhere, all the way out to infinity. And what ends up happening is that, as we'll see, is that, instead of getting just these combined molecular orbitals that overlap a wave function with another wave function, you get these bands. You get these bands of energy states. And the structure of those bands is the band structure. And they're very-- these don't just look like this. They actually wiggle, which is what's really cool about that.

Oh, there's the wiggle. Yeah, they wiggle. I mean, that-- I just went from all doing all this, drawing this a whole bunch of times. And now, I'm saying they're wiggling. So they look like this. How is that possible? How can an energy level wiggle? What's it wiggling into? That's what we're getting to. That's called reciprocal space or k-space. So that's what we're going to get to.

And I think you all know this, but, of course, when you talk about a molecule, you don't usually talk about a metal. I mean, you talk about the spin states of the molecule. You can ask whether it's magnetic or not. But you don't usually say it's a metal.

When you have a solid, well, we know these terms. It can be an insulator, which would mean that you have bands filled. And we fill them, just like in the atoms and molecules. We get our bands. We get our wiggles states now. And we fill those with electrons, just like we did with the atoms and molecules. And if you fill them up, and you're in the middle of a band when you stop, you're a metal. If you're here, and you stop at the top of a band, and there's a big jump to the next band, it's an insulator. If it's a little jump, it's a semiconductor.

Anybody know what the gap of a semiconductor is, typically?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: One point what now? Say that again.

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Yeah, that sounds about right, 1 to 3. And what's an insulator?

AUDIENCE: Anything higher than the--

JEFFREY GROSSMAN: Anything higher, maybe? Yeah, 5, maybe. Yeah, I love it. And then there's the term wide bandgap semiconductor, which is really a term that's used when you really wish your material were a semiconductor. But it just has a really big gap. And most people would call it an insulator. We say, it's a wide bandgap semiconductor, so I hope it could be useful for electronics.

Now, I think most of you have seen crystal symmetries. I mean, you certainly saw it if you took 3012. How many of you have not seen crystals? So this is not about having a deep understanding of crystal symmetries. But there is something important that comes about from having periodic potential, which is the focus. So I just have-- I didn't want to go into details here. But I will just give you the very basic elements, again, in a couple of minutes.

When you have a repeating pattern, you can identify what repeats. And that's the unit cell in the crystal. It's a very powerful way of picturing an infinite material. Because how many atoms do I need to represent silicon? How many of you know? What's the structure of silicon? Anybody know?

AUDIENCE: Cubic.

JEFFREY GROSSMAN: Cubic, OK.

AUDIENCE: Tetrahedral?

JEFFREY GROSSMAN: Tetrahedral, yes. What's the symmetry? Come back to that.

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Any others? We'll come back to it. But-- oh, yeah, you have unit cells. And they get repeated-- the cell is repeated-- on the lattice. The lattice defines the repeatness, the repeatiness, repetition. No, none of those are good words. But the lattice defines how it repeats. Is it going to repeat like this, in a rectangular way? Is it going to repeat in a square way? And you fill all of space. If you fill all of space, then it's a particular kind of lattice.

Now, because a crystal is periodic, the whole point here is we don't have to model all the atoms. Because if we did, we'd need to model 10 to the 23rd, which would be a bummer. And so what's cool is that, since it's periodic, we can just model the ones that periodicalize, or repeat.

And these are the crystal symmetries that fill all of space. So this is all, for those of you who had 3012, I know this is just review. You have, basically, seven symmetry classes, crystal classes, sorry. Some of you talked about cubic. And then you have different types of unit cells, which, basically, is just whether you have, in the repeat cell, atoms in every corner, in every corner in the center, in the faces, all faces, some faces. Those are four options.

And when you bring it all together, you have 14 of these kinds of lattices, which are the ones that can fill all of space. Those are Bravais lattices. This is all mostly review, right? And it's not critical. But, yeah, is this feeling-- are you feeling good about this? Yeah. You like it.

So here's two different kinds of crystals. And then you have the crystal lattice, which is determined by these dots. And then you have the basis, which can be anything. You can put a basis on the dot.

Now, this is how we're going to talk to our code, by the way. When we model a solid, this is what we're going to tell it, because it needs to know. It's going to need to know. When you run your SIESTA code-- and we'll do that-- we'll run some SIESTA calculations next week-- it's going to want to know what your lattices, well, what symmetry lattice you have. Is it FCC? Is it simple cubic? And then it's going to want to know the lattice spacing. And then it's going to want to know everything in your basis. Is it one atom in your basis? Is it like FCC, with two atoms in your basis, which sounds a lot like silicon to me? Or is it something like, with Mickey Mouse, which cannot be entered into a computer? So that's how you're going to input structures.

Now, here's where it gets really interesting. And this is where-- this is really the key of today's lecture is the next five, six lines, next bit. There is something called an inverse lattice, which is also called reciprocal space. And I think because-- I think you did learn all this, if you had 3012, yes? So you all feel-- do you feel your oneness with reciprocal space? Yeah, I'm seeing some strong nods and some not-so-strong nods.

So this is a really important concept that, essentially, gives this. It gives us the wiggles. This reciprocal space is the language we need to describe the wiggles. So just to review for most of you, with each real space lattice, like the square that I showed you, you can make a reciprocal lattice. And it's the set of vectors that are commensurate with the real space lattice. And you can define them very, very ingeniously. If the real space lattice is vectors a, b, and c-- oh, like here, it's a 2D lattice. So this would be like a. That would be vector a. And maybe, this would be vector b. This would be vector b. Which one? Any thoughts? We're just brushing up here.

But you call them a star, b star, and c star. And the way they're defined is in a very important way. First of all, a star-- that's the reciprocal vector-- times a is 1. So there's a normalization. And secondly, there's something a little more mathematically rigorous, which is that it's the cross product of the other two. So a star is the cross product of b and c. b star is the cross product of c and a. So you can write down-- basically, when you have your real space lattice and-- hello there.

[DOOR CLOSES]

Why do I have those little n's there in front of those vectors to define my real space lattice? This is what we use to talk about lattice? Why are those n's there?

AUDIENCE: Signify the twilight zone.

JEFFREY GROSSMAN: The twilight zone? Very good guess. What does n usually mean when I put it in an equation?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: A what number?

AUDIENCE: Integer.

JEFFREY GROSSMAN: Some integer, yeah. Why? I don't know. We just like n for integer. It just happened. So why would those be integers? a1, a2, a3 are the vectors of the lattice. And now, I have integers there. Why?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Yeah, because this is my lattice. This is my lattice. It goes off to infinity. so it's n is 1 to get here, 2 get there, 3 to get there. That's why it's n. It's an integer times the lattice factor. And it gets me to any other lattice point, depending on what my n's are. Now, the same-- in reciprocal space, you construct another lattice, which is given by these mathematical expressions, as I said, just cross products of the first lattice. And you get a reciprocal lattice, which we like to call G. We say that those have their own lattice vectors and their own integers in front that take you anywhere you want in the reciprocal lattice.

Now, a couple of important things, one is, if I take e to the iG.R, where R is a lattice vector in real space, and G is a lattice vector in reciprocal space, I get 1. That's important. You'll see in a minute why. But also, if I happen to write a function that looks like something like this, where I have it as an exponent, e to the i some reciprocal lattice vector times R, where R can now be anywhere in real space-- R is just a vector-- it's not a lattice vector-- then that function will automatically be periodic in the real space. Isn't that cool? That function will automatically be periodic. That sounds like something we might want.

Now, here's a simple picture. This is a real space BCC lattice. And when I construct the inverse lattice using the mathematical rules I just showed you, I get this, which is cool. BCC turns into FCC. When you do the inverse lattice, you get a new lattice, which happens to be FCC. So it's just a new space, but it's reciprocal space. Now, why is this so important? We're getting there.

Within this reciprocal space, you can define a zone. And you can define it very simply. You just draw-- you just go out to your-- you just go out to the next point here. And you draw your bisection lines. So you go out to these points. And you draw lines. In this case, it's a 2D lattice. So the area that's carved out is a zone. And that, when you do it with just to the first neighbors, when you do it like that, and you draw the lines, you get the Brillouin zone.

Did you guys talk about Brillouin zone in the fall? It's just this very first zone, first-- I don't want to get too technical here. But it's the zone we care about in the calculations. This part of the reciprocal space is all we need, this Brillouin zone. He was a cool guy. And you can go out-- you can keep doing this and go to the next nearest neighbors and drop bisecting lines and create the next volume. And here are just a few examples.

The first Brillouin zone is what we're going to be interested in. This is what it looks like for BCC and FCC lattices. And then you can go out to further and further points. And you get some really interesting volumes here. Again, I'm not going to go too much into this. But we do care about this Brillouin zone. And I'll tell you why when we get to the band structure.

No, I'll tell you why right now. You see-- and then I'll come back to it, because it might not make total sense right now-- you see, the Brillouin zone is an area of-- it's a volume, in 3D, of space, of reciprocal space, not real space, reciprocal space. And what ends up happening-- so again, I'm jumping to the punchline here-- but I want to tell to you while you're thinking about this Brillouin zone-- is that, you see, when you move around in reciprocal space within this first Brillouin zone, what ends up happening is that the wave function can change, depending on where it is in that zone.

Now, that's a result of having a periodic potential and this thing called Bloch's Theorem, which we're going to talk about next. But that is what leads the variation in the energies is what leads to the curviness. This curviness, if you want to think about it, is a tour through the Brillouin zone. I take a tour through this special zone in reciprocal space. And I find that the wave function varies.

So I may take a tour by going from the middle of the zone out to one of these edges. Maybe I'll go up to the middle of the plane here of the phase and back to the edge. And you cruise around this Brillouin zone. And that's what gives you wiggles. That's how you get the wiggles. I mean, the crystal is what gives you the wiggles. The way you calculate them is by cruising around in reciprocal space in the code.

By the way, in this part of the class, I'm very purposefully not going into technical details of the codes. However, if anyone is interested, I would be very happy to work with you or share with you more details about how the codes are doing these calculations, what's the math under the hood, what kind of loops are happening. And you're certainly welcome to download codes. There are free ones that-- for solids, you can download, for free, SIESTA, which is what's running on the hub. You can download PWSCF. You can download ABINIT. These are just a few that come to mind. They're free. You can download them. Most of them, I think you can run on your laptop.

And if you're interested in going more under the hood in the codes, I'd be very happy to talk to you. But that's not the focus of this part of the class, as I've said. For molecules-- as I've said, there are many codes here-- this is just a very short list-- but there's GAMES and NWCHEM, which are a few that come to mind, both free. And then there are bunch that you pay for.

If you want to spend some money, if you got 5, 10 grand to spare, first, come see me and--

[LAUGHTER]

--I'm kidding. But you can buy VASP. Or you could buy a code called Gaussian, which are both-- we heavily use VASP in my group. These are very good codes, actually. But they cost money. They have some-- these different codes are all doing the same thing. They're all doing Schrodinger. And they're all using their approximations we talked about. And they have different advantages and disadvantages, which, again, I'd be happy to talk with people about, if they'd like to dig a little deeper.

Now, all of this stuff about the Brillouin zone, which comes from the symmetries of the crystal, comes into play because we have periodic potentials. That's it. That's the point. So I now went from a potential that looks like this. Well, let me try to-- if there's an atom here, there's a potential well that an electron might feel as it gets attracted to the atom. And I went from putting, maybe, two atoms together to now having an array of them that go out to infinity.

Now, that has repercussions. And so the potential, now, can be written. So you could try to write the whole thing out as a function of all of space. Or you can just say, hey, for every plus R, I get back to V, because that's basically what it is. It's a periodic potential in the lattice. So the potential now, every R, which is a lattice vector, is the same.

Now, it turns out this is actually really hard to solve. And in textbooks, in quantum textbooks, like if you take a solid state physics class, what you'll see is that they'll show this picture, especially from a long time ago-- there's some really good solid state physics texts from the '70s. And you look at some of those older ones, they'll show those pictures, say, it's too hard to solve. And I love that, because it's not anymore, because we can use computers to do it, which is what we're going to do in this class.

But back then, and even longer before, it was too hard to solve. And so people would basically model a crystal going back exactly to the problem of an atom and the potentials being so hard to solve analytically unless they're simple. They simplified this. And if you make it a periodically repeating square well like that, you could solve it analytically.

And for those of you who are interested, this is called the Kronig-Penney model. And you can look up-- I think that's how you spell Penney. You could look up the solution to that online, if you want. It won't happen-- we're not going to do it in the class. But beyond simple things like this, which is not a very realistic crystal, although you do get some key physical meaning out of this, beyond that, you need a computer, which I think is pretty cool.

So now, we get to Bloch's Theorem, which is what gets us to this dependence, this wiggle, this wiggle. So we're setting it up. We have reciprocal space. We defined this first zone in reciprocal space. We said that, if you go through the zone, things change. Bloch's Theorem is the reason. It's the reason why things change as you tour through this zone.

There are different ways to talk about Bloch's Theorem. Here's a fairly simple way to look at it. So if you write the reciprocal lattice vector like this, 2 pi-- and the 2's are just there to make math a little easier, so you can write it however you want. This is that integer. There's the reciprocal lattice vector. If you write it like that, then, if you take this exponential--

[SNEEZE]

--gesundheit-- which I've already alluded to before, and you do that, actually, explicitly out. So R is a vector in real space. R is a vector in real space. Now, if I dot R with G, which is a reciprocal lattice vector, then I get the reciprocal lattice vector dot that. And that's just alpha, beta, gamma, or just the coefficients of the real space lattice vector, because R will be somewhere in real space. And so I can represent it, in terms of the real space lattice vectors time some coefficients.

And what you can see when you do this, it's very simple math. What you can see is that, as you vary where you are in real space, then, well, these things are going to change. Alpha, beta, and gamma would change between, say, 0 and 1. And the function e to the iG.r changes as well.

But you can see from this little derivation that, since these are integers, this function is always going to vary with the periodicity. So this is what I said. Here's the math behind it. I said this before. So you now have a function, e to the iG.R And that's the reason why. If you just spend a few minutes staring at it, you'll see why this is true. You have a way of making a function automatically periodic.

Now, why do I care? Well, because if I have this periodicity, if I have this ordering-- here, it's drawn is an approximation. Here, it's drawn as maybe more realistic, what my potentials look like. Then the values of some function, like the density, should be what at each lattice site? Well, I have it there in blue.

AUDIENCE: They'd be identical [INAUDIBLE]

JEFFREY GROSSMAN: Thank you. Thank you very much. Now, that seems obvious. I mean, I've got, basically, an array that goes on forever that's the same every lattice vector. It's just the same thing. This is a pure, perfect crystal. There are no defects. It's completely unrealistic, because, as you all know, there are defects in reality. But we can put those into the simulation as well. But for this derivation, there's no defects. So you have infinite crystal. And what that means is that, everywhere, the properties should be the same. If I sit on this atom or this atom or in between these two and then in between those two, the properties should be the same, if I go by a lattice vector.

Here's the kicker, though. The wave function is not the same. And that's really the key. The wave function is not the same. It's almost the same, but it's not. It's periodic. The wave function is periodic but only when it's multiplied by a phase factor.

And that is Bloch's Theorem. And there are three or four different ways that it can be derived. I will post them onto the Stellar website. They're not something you need to know for quiz or homework. But that is Bloch's Theorem. It's that the wave function in a infinitely repeating periodic crystal is going to equal some function that is periodic, some function that's periodic that has the periodicity of the lattice, some function, u, times the phase. And that, this is that function u. You see, it's periodic. It equals it, if you go plus big R, plus one lattice vector. So if you move over by a whole-- when I see lattice vector, by the way, let's bring it to reality. I just mean if silicon were cubic, I'd just be going from one silicon atom to another. That's a lattice vector. And simple cubic, I'm thinking.

And so you have a function that also is the same in that lattice distance, as you go from, say, one atom to another in the simplest case. But the wave function is that times the phase. And that's really important, because that brings in a new variable. In fact, this is a new quantum number. That brings in a new quantum number. This is a quantum number, k, that lives in inverse space.

So Bloch's Theorem says that, if I go from one point in space to another point that's translated by just a lattice factor, then I equal my original wave function time this phase. And you can show-- I mean, this is actually trivial, because this is a complex number. So when you square it, you can show that the squares are the same, which is really important. The charge density in the lattice is periodic. Does everybody see that? The charge density in a crystal should be periodic. Between any two silicon atoms, the bond is the same for as long as you can see, 10 to 23rd bonds. It's a whole lot of sameness. And you can see that the equations show that it is. But the wave function can vary by this phase.

You can also show that if psi k, this thing that I'm going to talk about more, is a solution to the Schrodinger equation, then psi k plus any reciprocal-- this is a reciprocal number. Remember, this is a number. k is a vector in reciprocal space. That's the Bloch's Theorem. That's a reciprocal vector that lives in reciprocal space dotted with the lattice vector.

And if I add the reciprocal lattice vector to it, then that also must be a solution. So that's also another consequence of Bloch's Theorem. So here's the-- I know some of you might not quite be feeling your oneness with this. That's fine. We'll talk about this a little bit more next week. I don't need you to go into great fundamental depth in Bloch's Theorem and how it's derived. And I'll show you, you can basically-- because proper derivations require some more knowledge of quantum mechanics. And I'm trying to avoid that. But basically, one of the easiest ways to look at it mathematically is that the translation vector associated with the lattice commutes with the Hamiltonian. Anybody know what that means? Yeah?

AUDIENCE: Is that like how we take ab equals ba?

JEFFREY GROSSMAN: Yeah, kind of. Yeah, so you can switch the order of the operations. But that's, again, not-- we don't need to know that. What we need to know is this. This is what we need to know. This is the punchline of it all. So we've gone through some derivation. We won't do more much more derivation. But this is the punch line. This is what you got to take out of this, so please do take this away.

When we had hydrogen atoms, when we solved the Schrodinger equation for a hydrogen atom, we saw that the way we did it was we imposed spherical symmetry. So we had a symmetry. We did have a symmetry. It wasn't a crystal symmetry, which I showed you, 14 Bravais lattices. But it was a symmetry, spherical. And when I imposed that, we saw that there are-- these quantum numbers came out, remember? We did that. And that was so cool, because it just solved so many of the issues of the time, just the fact that electrons were quantized was so important. All right.

Now, we have a new kind of symmetry. We have something called translational symmetry. We're still solving the Schrodinger equation, but now it's a periodic solid. And when this kind of symmetry is in the game, we have a different kind of quantum number. That's what matters most here. We have a different kind of quantum number. We have a quantum number that is a reciprocal lattice vector. It's a vector in reciprocal space. That's the key.

And because we have-- you see, just like-- so these l's and m's had their rules. This could be plus or minus that and so forth and so on. And so you could-- they lived within I don't know. They lived within in the counting of the principal quantum number.

Now, we have a different situation. We have a quantum number that can vary. It doesn't have to just be 0, 1. Or it's not necessarily tied to the principle quantum number. But it can vary. And its domain of varying is that Brillouin zone. That's it. So that's where it can play. These guys have variations dictated by the principal quantum number. This has variations dictated by the Brillouin zone. That's really the key here, the Brillouin zone, which comes about from reciprocal space. Is everybody with me?

Well, here's just a drawing. I don't even know where-- I should really have a reference here. This is one of my Google image searches. And there are many. And you can look at drawings online. But if you have a very simple wave function-- that's the real and imaginary parts-- and you have some periodically repeating function-- so that's my psi, and that's my periodic function-- then you can get a sense of this variation that I'm talking about. This is a very simple one-dimensional example.

So I have a one-dimensional wave function. And I have a periodically repeating function. And remember, what Bloch's Theorem says is that that is now how I'm going to write a solution to the Schrodinger equation. It's going to be a combination of a plane wave like that, where k is in the reciprocal space, and some periodically repeating function.

And just to illustrate that you can get variation now, check out what happens when I change k from, say, something not equal to 0 to something like pi over a, you can see that these functions change dramatically. The wave function of the crystal changes. Everybody see that? So that's really important. And the reason that's important and the reason this is all going to come home for us as we move on to seeing why this all matters is that that means you have energies that also depend on k. The energies also depend on this variation in reciprocal space. All right.

So now, if I'm in reciprocal space, and I move from the origin out to the edge of the Brillouin zone, not only am I changing my function, I'm changing this. I'm changing-- the position of this level can vary now. It now can vary. It can move up or down. And that's the key result, the one that's going to matter most to us. Is everybody-- any questions? This is-- yeah?

AUDIENCE: I was just wondering, is the k right here that we're dealing with, is that the same as the crystal momentum?

JEFFREY GROSSMAN: Very good, yes, the crystal momentum would be that times h bar, yes, which is like momentum, kind of, but not really. But it is, sort of.

AUDIENCE: So it--

JEFFREY GROSSMAN: Quasi is a good word, momentum.

AUDIENCE: So it it an inverse lattice vector or--

JEFFREY GROSSMAN: Yeah.

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Ah, well, that is exactly it, yeah, yeah, yeah. And you can get a feel for-- as you vary k, so then things happen, like the momentum can change. And that means the velocity can change. And if the velocity can change-- well, actually, the mass can change as well. And if those things can change-- of course, it's not really changing. The mass of the electron isn't really changing. But the effective mass, the mass that it feels in the crystal, is changing.

And, boy, is that important. And we'll talk about that, because, from the way that-- here's my levels in an atom or molecule. And now, remember, I said that they do this. From the way they do this, how heavy an electron feels itself to be in the crystal varies. It has an effective mass that's dependent on the wiggles here. And because of that, that's directly related to how fast an electron can cruise through the crystal. It's directly related to the mobility. So the transport properties are deeply dependent on this wiggling.

So Bloch's Theorem is a formal theorem that tells you that you have to write wave functions in such a way that you have a dependence on the inverse lattice. And then how that dependence enters into a system or a material is very complex. And it depends on solving the Schrodinger equation for the material.

But you see, you can think about it like this, if you want. Here's my inverse space. And I'm going to change where I am in reciprocal space. Remember, again, I only have reciprocal space because I have a crystal. I have a lattice. So I have an inverse space. And if I change where I am in inverse space, these would be my new energy levels. You get a new set of energy levels, those e's that I just showed you, for every point in space, in k-space, every point in k-space. So now, this is just blown up.

It used to be the good old days, last Thursday. We just had these levels. We just got through talking about how you get these from-- you can build up two atoms, three atoms. And you get these levels. And they didn't go anywhere. And now, they've blown up, because anywhere you go in this reciprocal space, they can change. They can change.

So now, you need to compute those same levels in the computer for different points in k-space. And that's what a computer does when it solves for a solid. That's what it does. That's basically the difference, is you now have an extra degree of freedom that you didn't have in your atoms and molecules or an extra quantum number that you need to explore, k.

So what are my levels at 0? Well, there are these. I don't know. Well, they're not here. What are my levels here? They look like this. Here, they look at this. And that's how the computer does it. It computes the same thing. It computes the energy levels, fills them up. But at each point in k-space, they can be different. And this is exactly that difference. You change where you are in k-space. And look at that. This level starts going down. This level goes up. I don't know what's going on here. Maybe that's this one. That one's going up. All kinds of things can happen as you cruise around phase space, in k-space. Those energy levels will change.

And that is what leads to a band structure. That's what a band structure is. It's just a continuous change of energy levels as a function of k-space. And each of these bands is still just an energy level. So how many electrons go into it? Still just an energy level, it's just a weird one that wiggles depending on where you are in the reciprocal lattice. But how many electrons do I put into this band as I fill them up?

Two, I still just put two electrons in here. And then I put two electrons in here. And then I put two electrons here. Oh, but look at that. It was actually two bands. That's tricky. So you get these really interesting behaviors, where bands can merge and become degenerate. Ah, but that's not really that different, is it, then the idea that you could have states like this, where I had-- this is just the atom, 1S 2S, 2P. I had three energy bands that had the same energy. That's called degeneracy. Here it is in the hydrogen atom. There it is in a very complex crystal. Well, it's actually a simple crystal. So you have degeneracies, where-- these would be like two levels that are the same energy.

But now, I'm cruising around in k-space. And I get to a part of k-space where they no longer are the same. They actually split. This one goes down. And these two go up, let's say. And so their degeneracy splits. And you see that all the time in band structures. But there are a certain number of total levels here. And you fill them up, just like we did for an atom or a molecule.

Now, somebody tell me what-- so that's a band structure. We'll talk about the band structure in all of its glory next week. But we're not done. Somebody tell me-- by the way, this is a beautiful thing. Are we feeling that? I mean, is it a little emotional moment for you guys, a little bit? Yeah? I felt that. There's so much in the band structure. There is so much material science, so much physics and chemistry, in this band structure, so much to learn about a material, just from this.

So we still have occupied and unoccupied. That wasn't supposed to do that. Oh, why is it doing that? OK, there we go. So you still-- that's what I was saying-- you still will fill them up. And then you'll have-- what is that?

AUDIENCE: Bandgap.

JEFFREY GROSSMAN: That's the bandgap. But what's interesting about this bandgap? Yes?

AUDIENCE: It's indirect.

JEFFREY GROSSMAN: It's indirect. And now, that's what indirect means, you see. Can I get an indirect-- remember, we had the molecules. We had the molecules. This is a molecule. Those are my energy levels of a molecule. And this was the gap. Can I have an indirect bandgap in a molecule? What do you think?

AUDIENCE: If it's a molecule of silicon.

JEFFREY GROSSMAN: Well, even if it's a molecule silicon, can I have an indirect bandgap? Why not?

AUDIENCE: It's not periodic.

JEFFREY GROSSMAN: It's not periodic. Therefore?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Yeah, there is nothing to vary. K-space does nothing for me here. Yeah?

AUDIENCE: Can you explain what an indirect bandgap is?

JEFFREY GROSSMAN: Yeah, yeah, absolutely. And I'm going to talk about a lot. Yeah, sorry, I jumped a little ahead. I get a little excited. Indirect bandgap is such a cool thing. And it's such a pain point in silicon. You see, if I want-- what you're going to do in homework 2, and what we talked about last Thursday, is that, if I shine light onto this material-- remember, these are all occupied-- what I can do is kick an electron up in energy. That's a photoexcitation. And that's what allows me to store energy from the sun in the molecules you're going to work on in your next problem set.

But you see, that's just a direct bandgap. Why is it direct? Well, because it's just the bandgap. In a molecule, there's no direct or indirect. But this is direct, because you just have the energy from the sun. And that's the energy that it needs to go up.

Now, when you have k-space, things are different. Because now, these things, these energies, they wiggle. And here's the kicker. You see, what's the gap now of this material? Well, here, they wiggle. Don't look at that for a second. Just look at this. I now don't have a molecule. I have a periodically repeating solid. And therefore, I get these wiggles of each energy band. And now, I shine light on it. Where does this electron go? Is this the gap of the material? That's the key. Is that the gap? Well, it's the gap at this point in k-space.

But here's the real important part. There is a lower energy gap in this material. If I'm able to go from this point k-space to this point in k-space, then the gap is only this big. This would be called a direct gap. And this would be called an indirect gap. And that is why silicon solar cells are expensive. We will talk about that next week. But that's why silicon solar cells are expensive.

You see, when you have to go to a different part of k-space to create your excitation, well, you need help. You can't do it with just light. You need some assistance. You've got to call it in. And that means it's a lot harder to do and, therefore, a very inefficient process. And as we talked about last week, and as you'll do in your homework, you want to absorb as much of that sunlight from the sun as you can. So if your gap-- our next application-- not Tuesday but probably next Thursday, we might start to talk about it-- will be solar cells. And we'll talk about solar cells then. But you don't want your bandgap to be too high, because if it's really high, remember, you're not going to absorb much of the sun.

Now, it also can't be 0 or close to 0 for a similar reason of the solar fuels but different. But it's related. And we'll get to that later.

But the point is that this gap is very high for a solar cell. This is a big gap. You want it to have a small gap. It does have a small gap. Silicon does have a small gap from here to here, 1.1, beautiful EV. But it needs to call it in. It needs help. It can't just get that from the light alone. And therefore, that's a very low efficiency process and a very low probability process. So yes, it can absorb light, if it has help at those lower energies. But it's very infrequent. It's very improbable.

And that indirect bandgap is the reason why silicon is not a good optical absorber, does not absorb light efficiently in the parts of the spectrum that you'd like it to. It can absorb light, if you make it thick enough in that part of the spectrum. But that's not what you want to do. But you got to do it. So that's the indirect bandgap. Now, does everybody see-- but, see, it has a direct gap at gamma. Does everybody see this? It's a really cool important--

[PHONE RINGING]

--result. Tell them you'll call them back unless it's about the band structure of silicon, whoever's phone that was.

Now, somebody tell me what would happen if I spaced my molecules-- this is a silicon solid. Now, what would happen-- oh, let me, in the last few minutes of class-- uh-oh, what's it doing? Yeah, that doesn't look good, does it? Somebody tell me what would happen if I spaced my atoms in the crystal further and further apart. What's going to happen to that band structure if I make them go further and further apart?

AUDIENCE: You'll smooth it out.

JEFFREY GROSSMAN: What is that?

AUDIENCE: You'll smooth it out [INAUDIBLE]

JEFFREY GROSSMAN: You'll smooth it out. What will happen eventually?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Yeah, exactly. So I can plot the band structure of an atom. And what would I get? My variation in case based will be? What would the band structure-- what would the variation in k-space for an atom be, just an isolated atom?

AUDIENCE: Zero.

JEFFREY GROSSMAN: Zero variation, exactly, everything's flat. You're the same everywhere in k-space. You're just back to the picture that we've been working in. So let's just see. Now, you'll use this to do molecule calculations for your next homework. But we'll do some calculations. I just want to show one last point. And we'll do some calculations also next week. Oh, it's loading. The nanoHUB toolkit is loading. How do I-- do you think-- tell me, while this is loading-- if it ever finishes-- tell me what you think is going to be an additional convergence parameter for solids. Think about this picture. It looks like that may never load. Think about this picture here and tell me what you think is going to be an important convergence parameter for solids. Yeah?

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Yeah, it's exactly right. I mean, because now, how am I going to know if the variation is correct? This variation I'm telling you is extremely important for crystals. This is what goes to a band structure. This is what gives you your band structure. Is it right? Well, did you do enough of these energy level calculations at enough points in k-space? The code will now have that as an input, you see.

Ah-ha, there it is, beautiful. I think this is a bust here. Ah, oh, this is exciting. This reminds me of the days of dial-up modem. I just read about them. I don't know about them, of course. So here you go. This is SIESTA. It's not letting me scroll down again, beautiful-- run JML viewer, solid. It's not responding. That's also interesting. Oh, there's the scrollbar. Can I run it? It's really not-- yeah, I can't even click this. Ah-ha, oh, yeah--

AUDIENCE: [INAUDIBLE]

JEFFREY GROSSMAN: Right. That's the first time that's ever happened.

AUDIENCE: I got that last night.

JEFFREY GROSSMAN: Yeah. Well, so anyway, that would have been a band structure of silicon. But what you can see here, look at this. Oh, but look under here. You see, don't pay attention to that. Look at this, k-point density. That is a new convergence parameter for solids. Can I get a wiggly band structure for silicon with just one k-point in my simulation? You can, actually. And I'll tell you why. Will it be right? No. And I'm going to pick up on that point to make sure we understand this convergence parameter when we start next week.