MITOCW | 9. Some review and introduction to solar photovoltaics

JEFFREY C. GROSSMAN: So today, what I want to do is, as requested and promised last week, today we'll spend some time just reviewing some of the things we've talked about up until now and some of the concepts that you might find questions around on the quiz. So maybe I'll ask you guys, just to make sure you understand each of the key concepts.

I'll also, as part of this review, we'll look at a couple of questions, a couple more questions, from last year, from the quiz last year. You have a practice quiz and in solutions, and that would be a good idea to look at. Those are posted on Stellar, as well. That's not to say that that's exactly what you're going to get. But you might get-- in terms of topics, those are good ones.

But what's not on the practice quiz is sort of any pictures of a density of states or a band structure. I can almost guarantee you you'll have sort of one of each of those on the real quiz. So you'll have a band structure that I'll ask you some questions about, as well as a DOS plot.

So we're sort of supposed to be here. And I still hope to get to solar cells. And we have time, so we're going to talk about solar cells. But I know that, since the quiz is Thursday, we want to take a good chunk of today and just make sure that we have a good sense of what to expect and do a review. But I hope to get to our beginning of talking about modeling solar cells today, as well. And we'll pick up on that after the quiz.

Are there any questions just about the quiz, which is Thursday? It's open book, open notes, no phones, PDAs. Yeah?

AUDIENCE: How many questions can we expect?

JEFFREY C. GROSSMAN: Somewhere-- definitely no more than 100, and-- [LAUGHS] I'm kidding. 10-- I don't know. Does that sound about right, something like that? 12. OK, so there we are.

Now, I do want to, since Lynn already made a little announcement about part 2, I wanted to start today-- so that's what we're going to do. I wanted to just, even though I just postponed the piece that-- oh, I'm going to have an office hour tomorrow at 4:00. Is that what I said, 4:00 to 5:00? Or did I say 5:00 to 6:00? 4:00 to 5:00, I think. But if anybody has questions, as always, send me an email. And I'm happy to answer electronically or set up a time to meet that works on your side.

So that's very good. And how many of you have looked at problem 3? A couple of you, OK. So are there any questions that anybody has about problem 3 right now who have looked at it? Go ahead.

AUDIENCE: Well, in terms of-- how do you find maximum efficiency?

JEFFREY C. GROSSMAN: All right, [LAUGHS] that's a good question. That's a really good question. Anything more specific?

AUDIENCE: You know the maximum efficiency is going to be related to the energy going in versus going out. But how do you determine, I guess, the energy going out?

JEFFREY C. GROSSMAN: Yeah. Yeah. OK, so let me talk a little bit about this problem to make sure that we kind of know where to go with it. And the key setup here is actually really part A, in a way. It seems pretty simple. But it's kind of the core piece of information that you need to understand.

And I'm going to use this yellow chalk that's actually white to draw. Let's not forget what it is that we're talking about, which is basically an energy landscape. Remember, in capturing the sun's energy, what we're trying to-- what we're doing-- and in many energy technologies, what we're doing is we're pumping something up an energy hill.

And in this case, we pump an electron. We shine light on it. And the molecule is in the trans state. And then it gets excited because the light, the electrons from the photons from the light, excite electrons in the molecule. So that's that pumping action that's happening. You're pumping electrons within this molecule up to a higher level.

When you do that, the molecule is allowed to go to here just from that energy from the light. So the light's energy is being converted into creating electrons that are higher in energy. And that allows the molecule to go from this structure to this structure. And that's allowing you to store this much energy. So don't forget this picture as you think about this homework, because this homework is all about this picture.

Now, who can tell me-- we talked about this in class already when we talked about this whole solar thermal fuel concept. Who can tell me why-- who can tell me the answer to part A? Let's just see if we can do that together. Yeah?

AUDIENCE: Is it because there's a energy [INAUDIBLE] between the trans and the cis states that's higher than natural cis energy?

JEFFREY C. GROSSMAN: OK, so here I'm going. I'm shining light, and I shined light of this energy-- or if you want to think about it as HC over lambda of that amount of energy, just going between wavelength and frequency. And I shined light on this trans state, and I only shined light with this amount of energy. Can it possibly be converted to here?

It can't, because we can't-- now, some of you took 3.012, and you know we don't violate the laws of thermodynamics. Those are untouchable. You can't get something for nothing, right? So you're not going to get to store this much energy if you only put in this much. That kind of makes sense.

You can't put it up on some shelf of energy, some chemical shelf, which is a way of thinking about this, if you haven't given it enough to get up there-- unless you use a lot of thermal vibrations, but that's not what we're doing here. You could use heat. But you can't get it with this input less than output. OK, so that's sort of what part A is asking. Does everybody see that?

Now, here comes the fun part. But, you see, it's not just-- this is the molecule sort of going about its business. This is the happy-go-lucky molecule. But then we have the sun. We have this part. Where does this come from?

Well, this is the sun, you see. And that has its thing that it does. And its thing that it does is it has intensity that comes in as a function of-- this has probably nothing to do with the real curve, but I draw the sun's intensity different every time I draw it.

But this would be, say-- well, this could be energy or wavelength or frequency. Let's call it energy. And so you have a dependence of intensity of the sunlight that strikes the Earth or the atmosphere-- those are different-- on the energy that you get. So there's some energies of light that have a lot of intensity and some that have very little.

Now, what's the key connection here between these two? Who remembers? Which is really what part 2 is about, question 2 is about-- what's the key connection here between this curve and this picture? Yeah?

AUDIENCE: So only photons with a sufficient energy will be able to excite your molecule from the trans to cis states. So only some part of that curve with energy greater than or equal to delta H will be able to do that. So it can only capture that much of the sun's total energy?

JEFFREY C. GROSSMAN: Yeah, exactly. And there's something else, too. But that's exactly what we need for a problem 3. That's exactly it. So what I've told you-- what we did already is we said, well, you can't get more energy out than you put in.

So you've got to have at least delta H. Minimum of sun's energy is delta H. That's the absolute minimum you have to put into this to get delta H stored, right? Sorry, that's kind of hard to read. I'm not liking this yellow-colored white chalk, because it's too thick. So the minimum sun's energy is-- that's better-- is delta H.

But you see, there's also now-- what happens is-- so let's say I can-- let's say that delta is somewhere here. I don't know. Call it one electron volt. well, what I've just said in part A is that anything below that, anything below one electron volt, cannot be used to store energy. So any sunlight energy that's below that is wasted. It's not going to do anything to charge that fuel, because it's below this amount. On the other hand, everything above that will charge the fuel.

But now here's where the question of efficiency comes in, because is it really-- what would I really like to do here in terms of charging this fuel? Somebody tell me the difference between a photon of sunlight energy that's here, that charges the fuel, versus one that's out here that also charges the fuel. Somebody tell me what's different or similar between those two parts of the spectrum, both of which convert my fuel. Yeah?

AUDIENCE: The one that's higher energy has less energy wasted, because delta H is constant. So once you get above it, the more above it you get, the less efficient it becomes.

JEFFREY C. GROSSMAN: Exactly. Exactly. So I can charge the fuel now because, I said, I can't have less than how much I'm storing. That's a rule but I can charge you with anything above that except for one thing that I'm going to tell you about in a second. Or you're going to tell me, because I know somebody knows this.

But if I use this amount of energy from the sun, well, I still only stored that. That's my delta H. So that means I wasted a whole lot. And that's what I want you to tell me. What's the efficiency?

So if I'm all the way down here, you can say, well-- and this is what we talked about in the lecture. If I'm all the way down here, then I can absorb all this light and use it to convert. But light up here is really wasted. It's super wasted the further you get up in energy. So where is the sweet spot? There's going to be a sweet spot. That's what I want you to tell me in part B, OK?

Now, there's something I'm not telling you which is really important here that's not part of that question. But there's something else that matters a lot that's part of part B-- number 2, question number 2. What have we not considered yet? And in particular, what about it?

AUDIENCE: Gap.

JEFFREY C. GROSSMAN: The band gap. The gap, or the gap of the molecule-- and you see, because that's the other component here. So these are-- problem 3 is talking about theoretical limits based on how much the molecule stores and how much sunlight shines on it. But there's this other thing that problem 2 talks about, which is the fact that the molecule will not absorb any light lower than its gap. And that's why those two problems are very I think complementary to one another.

So all of that comes into play. So even if I say, well, it stores in EV, so theoretically, it could absorb all of this. Actually, if its gap is 2 EV, it's only absorbing this. But we're not talking about the gap in problem number 2, OK? All right. It's fun. This is fun, right? Any questions? We're integrating the sun. Any questions about that problem? Yeah?

AUDIENCE: So to find the energy that's lost, do we just have to subtract the delta H energy from all of the high-energy states and integrate that new area?

JEFFREY C. GROSSMAN: Yeah, it seems to me like-- so you figured out in the earlier problem how to figure out that, if you integrated this, you would get, like, how much of the sun's energy that molecule is absorbing. And you used the band gap as the cutoff. But now it seems like maybe you want to use delta H in a similar way, because you're looking at sort of a theoretical efficiency and ignoring the gap.

Now, then, what is the efficiency? Well, it's how much energy that molecule can take in from the sun-- divided by that, the amount that is stored. Did I answer your question, or did I dance around it? Was that helpful?

AUDIENCE: How do you, like, physically calculate that amount?

JEFFREY C. GROSSMAN: Ah, but that's what you-- you chose it. You just picked it. You said, I'm going to say it stores 1 EV, because that was delta H.

AUDIENCE: But if there's one of these per--

JEFFREY C. GROSSMAN: Per molecule.

AUDIENCE: [INAUDIBLE]

JEFFREY C. GROSSMAN: Per molecule is the way to think about it, right? And then there's-- so that's how much energy you're storing in each molecule, and then each molecule is getting how much energy from the sun? Right? And between those, you have an efficiency. It's basically 1 divided by the other.

And you know which one to divide by the other, because if you divide it, and it's more than one, you should do it the other way. That's a hint. No, but seriously, are there-- did that make sense enough? OK. Now, question C is a little bit-- taking that a little bit further. But it's that same exact concept that-- yeah, OK. Any questions? Yeah?

AUDIENCE: I'm just a little confused. So when we calculate the band gap, that's the amount of energy needed for it to absorb energy from the sun.

JEFFREY C. GROSSMAN: Right.

AUDIENCE: Then how does that relate to the delta H? Are those separate?

JEFFREY C. GROSSMAN: Yeah, that's a great, great question. And that really is-- I want you to think about them separately for this problem. So they really are, of course, intertwined in fairly complicated ways. But here, what I want you to do is suppose you could just make the gap. At any delta H, you could just make it equal to delta H. That's really what you're doing here, because you're taking a kind of theoretical limit exercise in this.

That's not the case. It's not as tunable as that. Although, you can tune the gap in these materials to quite an extent. But here I'm saying, suppose that the amount it absorbs is, in fact, set not by the gap but by this other constraint that is part A of this question, which is that you just can't convert it unless you have as much as delta H.

That's just-- that there's no way around. You can't tune around that. That's just it. You can't get to here unless enough energy from the sun is this or more. So that's really ignoring the gap.

But in reality, it's going to only absorb photons at the gap or higher. But if you found it-- now, if you were to happen to do 3B and get a maximum in a curve, let's suppose, and that maximum occurred at a certain delta H, then you might say, well, that's where I should try to get my gap to that point. That might be some guidance.

Of course, that's not actually what you want to do. But as we ignore the gap, you can think about it that way. It provides some guidance into where you might look at-- these kinds of exercises in theoretical efficiencies can always be useful for those reasons. Does that answer your question?

AUDIENCE: I think so.

JEFFREY C. GROSSMAN: Definitely, I'm very happy to talk about this more. Office hours, tomorrow at 4:00 and also by request-- so just send me an email. Or if you-- I think a lot of you know, if you send me an email, I'll try to write back pretty quickly. So if you have questions, I'm happy to answer. Are we feeling good? Yeah. OK.

Nope, we're not going to look at a recommendation letter together. [LAUGHTER] That wouldn't be appropriate. [LAUGHS] Wait a second. But there was-- yeah, let's get that out of there. And there was a-- aha, here we go. What did you do?

Now, this is not this year's quiz. But this is last year's quiz. And I'll do this first, because then we can review. So here's a couple of questions from last year's quiz. Let's just focus on this one. Oh, what are basis functions, and how do if you have enough of them. Somebody answer that for me first. What are basis functions, and how do if you have Enough yeah

AUDIENCE: So basis functions are a set of functions which you can take combinations of to create an approximation of what the exact function should be. And you know you have enough of them if whatever you're trying to calculate you use basis set and then a, I guess, more refined basis and do this a little bit. And it sort of converges to some value.

JEFFREY C. GROSSMAN: Right. Exactly. There's a really important part of that. So that is-- basis functions are mathematical functions-- Gaussians, exponents, plane waves, wavelets. Don't use wavelets. But they're kind of funny. They're neat functions. But it can be anything. It's just a function.

And you just use them. You use a series of them usually, a sequence of them that you add together, to make up the complexity that is psi, which is the wave function, the wave function that we're after in this part of the course. So it's just a representation, but it's one that you don't find in classical simulations that you did in the first part. But you do find it here. And it's really important to know when you're converged. And say that part again. When are you converged?

AUDIENCE: When you use -- when you take whatever you're trying to calculate--

JEFFREY C. GROSSMAN: Ah, stop right there. That's it-- whatever you're trying to calculate. What are you trying to calculate? Give me an example.

AUDIENCE: Total energy of a system.

JEFFREY C. GROSSMAN: Total energy of the system. Now give me another example.

AUDIENCE: HOMO-LUMO gap.

JEFFREY C. GROSSMAN: HOMO-LUMO gap. I love it. We could go on like this, but I won't. But now, are the number of basis functions you need to converge the representation of your wave function the same for the total energy or the HOMO-LUMO gap?

AUDIENCE: No.

AUDIENCE: Depends.

AUDIENCE: [INAUDIBLE]

JEFFREY C. GROSSMAN: It depends is always a good answer. You can always write that. Don't put it for your name, but you can put it for-- well, I don't know. Maybe you do need the same number of functions for those properties. But you need to look at them on a property-by-property basis, no pun intended. OK? So very good.

Now, without solving any equations, which electron do you think would require more basis functions to describe well the 2p electron in carbon or the 3p electron in silicon? Who can tell me what they think? Yeah?

AUDIENCE: 3p electron in silicon.

JEFFREY C. GROSSMAN: Well, you need-- now, hang on. You need more basis functions for 3p? Tell me why.

AUDIENCE: [INAUDIBLE] more electron attraction.

JEFFREY C. GROSSMAN: Well, what is it that makes you need more basis functions? What is it that makes you need more basis functions? Yeah?

AUDIENCE: It's like a more complex wave function.

JEFFREY C. GROSSMAN: OK, so if the function-- if the wave function looks like this versus, say, a wave function that looks like that, which one do you think I'm going to need more functions for? I'm going to need more basis functions for this one. Does everybody see that?

Now, and then the question is, OK, so if you put that down, you're already doing really well, because on these questions, what I'm looking for isn't even-- if you didn't know the answer to what 2p carbon or 3p silicon, which one is more wiggly, but you knew that you needed to know that to answer the question, that's already-- that's, in my opinion, 4 out of 5 points, because that's the key. The key is what-- I'm trying to just get at the key things you need to know in computational quantum mechanics, some of the key ingredients. And that's the key is that you need more basis functions if the electrons function wiggles more or wiggles more quickly.

AUDIENCE: But it's [INAUDIBLE].

JEFFREY C. GROSSMAN: What was more for carbon?

AUDIENCE: [INAUDIBLE]

JEFFREY C. GROSSMAN: Because the-- you see, it's what you said, actually. You have more screening in silicon. And so the outer electrons, they're further out, and they actually wiggle less. They're more smooth. That's not always true. But between silicon and carbon, that's true. I think I talked about that in lecture 2.

And it's part of why carbon can make such strong bonds. So carbon has no p electrons in the core. Silicon does. So the screening is very different. A p electron in carbon sees no p electrons in the core. But a p electron in silicon does. It sees two p electrons in the core.

So that screening, that shielding, makes a huge difference in the kind of bonding that these two atoms can do. That's why we're made of carbon and not silicon. But that's not the question.

Now let's do another one. Materials are composed of nuclei and electrons. When the Kohn-Sham equation is solved, solutions only for electrons are obtained. Why do we not care about nuclei? Come on, that's a good one, right? Sam?

AUDIENCE: So basically, nuclei are 1,000 times heavier than electrons.

JEFFREY C. GROSSMAN: Right.

AUDIENCE: But realistically, electrons are basically still [INAUDIBLE] motions in saying that electrons are [INAUDIBLE].

JEFFREY C. GROSSMAN: And do you remember what that's called? It's that guy's back, the tattoo.

AUDIENCE: Born-Oppenheimer.

JEFFREY C. GROSSMAN: Born-Oppenheimer. See, that's going to be it. You're always going to remember that guy's tattoo on his back, and you're going to think Born-Oppenheimer. It's effective.

OK, and then we'll do one more. What does k-point sampling refer to? Below are the band structures computed for two different materials. Which requires more k-points to converge? And what I'm looking for here is not a long essay. It's really just a sentence to explain the reasoning. So somebody tell me which of these might need more k-points. Which band structure would need more k-points? I see this. Yes, why?

AUDIENCE: There's more variation. There's more wiggles with it, so you need more points to get after [INAUDIBLE].

JEFFREY C. GROSSMAN: It's the same-- you see, these are-- this is also just a convergence question, OK? Did everybody see that? This is another convergence question. I mean, you're not going to just get convergence questions, but those two were.

And then we did this one. Did everybody see this last time? OK. This is that band structure that you got, but your advisor spilled coffee on it, and this is the only copy you have. And so I'm not-- you won't have a coffee-spilled-- well, you might have a coffee-spilled band structure, because it's kind of a fun way to ask questions. But you'll definitely have a question about band structures. So make sure you kind of are comfortable with the concepts that I'm going to-- we'll review right now with band structures. So those are a couple of nice examples of the kinds of problems you might get.

AUDIENCE: Yeah, you can see a coffee stain in the example. Don't [INAUDIBLE] because [INAUDIBLE] put in there.

JEFFREY C. GROSSMAN: Yeah, we're going to actually use real coffee this time. [LAUGHTER] OK, good. So what we're going to do now-- so any questions? The questions are great. It's really helpful-- questions on the p set, questions on those questions? Questions on the questions? Questions about--

AUDIENCE: The Celtics.

JEFFREY C. GROSSMAN: What was that? The Celtics? They're going to wrap it up. Yeah, tonight. Anyway, OK-- I just like sharing a little something like this each time. Has everybody seen this one? With great power comes great responsibility. Vision without action is a dream. Action without vision is a nightmare. This is my reminder. When you do calculations, this is what counts most. don't just start computing. Think about what you're doing.

I'm going to take you through a little bit of a tour of some of the key concepts that I think would be important to know about that you might get questions on. You might get a question on-- and I think there's a practice quiz question or two on some of these-- concepts of what led to quantum mechanics, which we talked about in the first lecture. So why did we need a new physics? Why did we need something new?

And the fact that you have-- as a result of a lot of research in that time, what came out of it was that matter has both wave and particle character. So we've talked about this experiment. We've talked about that experiment. So you would know if I asked a question about those experiments, maybe, one of them.

And we found that that, actually, light can behave like a particle, and matter can behave like a wave. And it would have a wave vector k that's related to its momentum and a frequency. And that's kind of really cool. So if I asked you what the wavelength of a baseball was-- I think that might have been on the practice quiz-- then that's something you could compute, for example. I won't ask you that, but you kind of could compute the wavelength of something.

And then that took us to-- well, OK, so you have to represent matter now with waves. So we're going to have this function to do that. So that took us to this function. We said there's going to be this function. It's a wave function. Well, that's a creative name. It's a function that represents waves. OK, that's good.

And we also said-- we didn't really explain this much, but we said, but you can't-- we don't actually know much about the physical meaning of this function. But we do know that, when you square it, or since it's complex, you multiply it by its complex conjugate, that you get the density of this quantum mechanical particle.

And we said, this is it. This is what we need. We need this function, because in quantum mechanics, that function tells you where electrons are, the probability density of electrons. And so that's the thing we need. Because if you know that, then you get all these other properties, see? Once you have this, that's what the DOS comes from. That's what the band structure comes from. It came from solving for that.

And then the question is, well, what are you solving? And so what we needed there was the F equals MA of quantum mechanics. We needed the equation that governs the behavior of this wave function. And that's the Schrodinger equation. That's it.

This is it, right? So do we have the function that we need, which when we solve it, we get all these properties that we really care about, that we can use to make solar cells and solar fuels and lots of other things? There is an equation we need to solve to get that wave function, and that equation is the Schrodinger equation. And we took time out, because we don't like time. It just complicates things. And so we did it for the stationary solution.

And the Schrodinger equation is H psi equals E psi, where H is the total energy. So it's the kinetic energy plus the potential energy. And when you write these out, you write out the kinetic energy as this second derivative. And the potential-- well, that depends on what we're talking about. But if we're talking about, say, an electron in a hydrogen atom, then it's E squared over r. That's your potential, the potential that that charged particle feels. So that's a hydrogen atom. That's the electron in a hydrogen atom.

I'm going through this quickly, because I think we are all feeling OK about this. But if anyone has questions, please raise your hand, please, because if you have a question, it's very likely someone else has the same question. Any questions?

Now, you can solve this equation, actually, very easily. We did this, I think, in the second lecture, maybe. And you get solutions for that wave function. And we talked about how one of the key results here is that you get quantization of the energies of the wave function. And what that means is that the energies can only have certain values-- nothing in between.

And we talked about the magic of that and how that explains these spectral lines that were observed long before. It finally explained those. So I don't know like calculating the energy differences here or how much energy it takes to allow electrons to move from one level to another-- that sounds like a good problem to me. and units, so forth.

Now, the other piece of ingredient that was really important is that, actually, electrons-- they have this angular moment-- they have this spin. And it was observed by putting them-- shooting them through a big magnet and basically finding that-- what was observed? What was observed wasn't just that they had spin but that they only had one of two kinds of spin. So instead of getting a spread, you would think you would be applying a force on these electrons, which are magnetic, since they're spinning.

But they're not. But that's how we like to think of them in our classical minds. You would think that you would get a nice continuous spread of force acting on them, causing them to separate. But instead, you only get two spots. That was really important, because they told us that these there's another kind of quantum mechanical number, which is the spin number, which can be up or down-- only up or down.

And then you put that together, and you put together your solution for the Schrodinger equation, and voila. You get, essentially-- oh, you add on a little bit of Pauli. You put in some Pauli exclusions-- just a little bit. You don't want to over-Pauli-- anyway, never mind. Which it says that, OK, we got these quantum numbers-- you know, N, L, M, and now the spin. And no two electrons can have the same set, which results in the fact that you cannot put more than two electrons in one of these energy levels.

And remember, these energy levels are kind of like the key ingredient we're after in this class. It's really one of the key ingredients we're after, where do those electrons want to sit, because it tells us so much about properties of materials that are interesting.

Now, that really allows you to go to a description of the whole periodic table. The problem is that that was a description based on one electron and one proton. We solve for that. We could solve for that. And so we did, and we got the levels, and that was really neat. And then we had rules about how to fill them, and that was really neat. And then you can actually explain a lot of chemistry that way. You get your S and your P and your D orbitals, and you fill them.

The problem is that, actually, when you have anything but hydrogen, you have more than one electron. and so that really requires going back to the Schrodinger equation and adding in the interactions between electrons that was not in the original hydrogen atom. And that's hard. That's the hard part, hard stuff. And so we turn to computation. That's really hard to do analytically, and it gets much, much worse the more electrons you have. any questions up to this point? All right.

So how do we do that? Well, you've got to-- so we're using computation, but you can't just throw this onto a grid or throw this into MATLAB. It still isn't doable. And so there's sort of two branches in computational quantum mechanics, one that loosely is labeled quantum chemistry and the other kind of more solid-state physics, density functional theory. And both of them make approximations. And we talked about those approximations.

And what they're approximating is the Schrodinger equation. They're simplifying it, because even as simple as that may look-- just throw that into MATLAB-- it doesn't happen. You can't solve it when you have more than a couple of electrons-- five electrons, I don't know, six. That won't be on the quiz. [LAUGHS]

But you just can't solve it exactly on a computer unless you have the age of the universe. And even then, it's too hard. So we've got to simplify this equation. And mostly in the quantum chemistry world, what you do is you simplify this.

We talked about using basis sets, basis functions to represent this. Well, you can restrict the degrees of freedom in that function, as well. And that makes that equation much easier. And the other thing you can do is you can actually change-- so that's changing this part, and the other thing is you could change this part.

And that's what physicists mostly did, and now everyone holds hands and sings "Kumbaya," and everyone's happy. Back then, there was a lot of two fields, physicists versus chemists, and all that. But we're all happy together now. So chemists do density functional theory. Physicists don't mind wave function-based methods, as they're called.

The result-- and this was one of my red flag key results here is that what you've done when you do this is you have taken a problem that involved all of these interactions-- remember, 1 over r 1, 2 meant taking into account the interaction between electron 1 and electron 2. And that just gets really painful and hard.

And so what you've done in both categories is you've completely changed the picture into what's called a mean field picture. So each electron is only now really solved in the context of an average field of the other electrons. That's the simplification key. That's the key simplification. So the mean field methods are really what enable us to do computational quantum mechanics for large systems.

I don't really think I need to review this too much, because I did just review this, I think, a week ago. But the density is a nice thing to work with, because unlike the function with sort of-- if you wanted a grid to represent each-- a grid of points, even as the number of atoms in the system grows, the density grid is just the same. So the number of points you need to represent the density is constant, while the number of points you would need to represent psi grows exponentially.

So it's a really hard problem in the context of scaling with size for the wave function, but the density offers this really nice scaling. And so that's what density functional theory is is it's a method that relates-- it shows that the density can be related to the wave function. And then you just work with the density, and you throw out the wave function. You bring it back in later, but that's basically what the theory does.

The problem is that it pushes out-- it has this sort of term that you talked about in lecture 3 or 4 that you have to kind of approximate, this exchange correlation potential. We talked about that. And the exchange correlation potential-- let's get to that-- is not known. If you knew it, it would be, actually, an exact method. But it's not, and so you make approximations. And these are actually two of the approximations that you have as options in the NanoLab tools.

Now, what these approximations are is not part of this class. That gets into kind of more complicated equations that we would have to cover that I don't want to do. But what I want you to pull out from this is that we are not solving the Schrodinger equation exactly. We are making approximations. And those approximations need to be checked.

So you see, there's two kinds of convergence here. That's the key, right? And this is where I come with responsibility. One kind of convergence is k-points, basis sets. But another kind of convergence is, where are you in accuracy space? Where are you? Do you know?

Because you are making approximations. When you pull down that option on the toolkit to say GGA or LDA, what you're doing is you're changing the form of this. Which one is right? You're still not solving the equations exactly. So how do if you're right? Throw that out there as a question.

AUDIENCE: Find an experimentalist.

JEFFREY C. GROSSMAN: Find an experimentalist. Bother them. Say, can you measure this? And they say, no, are you crazy? My advisor just told me to work 90 hours a week on something else. So then what do you do, because it's not in the literature? Yeah?

AUDIENCE: Try a bunch of different approximations and see if any of them agree.

JEFFREY C. GROSSMAN: See if any of them agree. Let's suppose half of them agree, and half of them disagree. Say I had 10 functionals to choose from. What else could you do? Or are you done? Is that good enough?

AUDIENCE: Maybe run one more.

JEFFREY C. GROSSMAN: Run one more.

AUDIENCE: The tiebreaker.

JEFFREY C. GROSSMAN: The tiebreaker-- I love it.

[LAUGHTER]

Sadly, there are papers in the literature that kind of take that approach. It's a little too loosey-goosey. But it was a good idea. OK, what else? Well, is it good enough? I mean, if I had 10 functionals-- by the way, there are hundreds of functionals now to choose from in density functional theory. If I had 10, and half of them agreed, but the other half didn't, what do I do?

AUDIENCE: Apply quantum chemistry.

JEFFREY C. GROSSMAN: OK, why?

AUDIENCE: It's a whole different theory.

JEFFREY C. GROSSMAN: Whole different theory-- good, OK. Go to a different theory for quantum mechanics. See what that agrees with. But see, that may have its own whole-- it does have its own whole world of approximations. But that's the right-- that's sort of the right way to think about it, because there are theories that are more accurate and less accurate in how they solve for-- how they simplify the Schrodinger equation. So you can try to go to more accurate, or what are known to be better accurate, theories.

Now, there's one other thing to do. I told you that, in this particular case, it's a solar fuel that you just calculated. You think it's going to be revolutionary but only by one functional. The other functional says it's really bad. You went to an experimentalist. They said no. And you can't do higher-level theory. Anything else you can do?

AUDIENCE: Take a poll?

JEFFREY C. GROSSMAN: Take a poll [LAUGHS] of your group members? [LAUGHS] That's good. I like that-- computational people, people computing. What else?

AUDIENCE: Request more funding.

JEFFREY C. GROSSMAN: What is that?

AUDIENCE: I said, request more funding.

JEFFREY C. GROSSMAN: Request more funding-- you're talking like a professor.

[LAUGHTER]

What else? Anything else? There is something else you can do. So the key is-- I said that the experiment for that fuel hasn't been done. But--

AUDIENCE: Try a different fuel.

JEFFREY C. GROSSMAN: OK. Use the same level theory on a system that has been done that's related, that's closely related. While I modified azobenzenes and make a good fuel, that hasn't been made yet. But azobenzene has. Did my theory work well for all of the data I can get my hands on that's relevant to what I'm simulating for that material?

This is validation. This is validation. It's not the same as convergence. I said there's sort of two kinds of convergence. This kind is called validation, and it is critical in computation. It is a critical part of computation.

Please don't go away from this class without remembering that part. Know where you are. Test your calculations. Be confident in them because you validated them. Too much computation goes on that doesn't have that, and it's a lot of wasted time-- [LAUGHS] computer time, but also people time.

Now, so we can get a lot of properties. We can get properties of-- I've talked about lots of different properties you can get. I won't ask you anything on the test about properties we haven't actually really talked about in class, OK? But you can calculate a lot of things.

We just talked about this. The one thing-- OK, did you exit the scf at the right loop? Don't worry about that, because the code just sort of does that for you. Was my basis big enough? We talked about that, right? Convergence for molecules-- was my box big enough? Now, why do I have a box for molecules? What does that even mean? Yeah?

AUDIENCE: So you're going to use plane waves as your basic set, and they're periodic. And a real molecule's not going to be periodic. So you don't want to have it see itself. So you need a really big box.

JEFFREY C. GROSSMAN: Yeah, exactly. Exactly. So if I have-- so a lot of these codes, especially plane-wave codes, were originally developed for solids. But they work fine for molecules. Actually SIESTA's not even a plane-wave code. It uses a different kind of basis. It uses a more Gaussian-like, localized functions basis. But it's still a periodic box. It's based on a periodic box.

So that means that when you input something like an atom, if I want to simulate that one atom, then I need to make sure that I leave enough space so that it's not going to feel its periodic image in all directions. So for a new molecule, is my box big enough means leaving vacuum between the molecules.

And then we talked about solids. And that's certainly fair game for the quiz, even though we haven't had a homework problem on the solar cells, certainly I wouldn't talk about that. I won't talk about solar cells on the quiz. Or I should rephrase that. [LAUGHS] I won't ask you questions that we haven't talked about in lecture. But the band structure of a solar cell-- well, band structures we've talked about a lot, right?

Now, the way we built up our solids part is we said, well, OK, now we're talking not about some molecule that can have some shape and then gets repeated like this. But we're actually talking now about a crystal that goes on forever and ever. And so it needs to have a kind of lattice. And we talked about how you can define that, just like we defined it in class, and you've seen it in other classes. You define it in a computer.

And then we talked about the inverse lattice, and I'm not going to go through this again. But we built this up. Why did we build up the inverse lattice, the understanding of that? Where does that come in? Why do you need to know about inverse lattice? Yeah?

AUDIENCE: Because that's how we define the Brillouin zone, which is where we define the k-space vectors.

JEFFREY C. GROSSMAN: Good. OK, and why does k-space matter?

AUDIENCE: [INAUDIBLE] associated with [INAUDIBLE]

JEFFREY C. GROSSMAN: Yeah, so that's exactly-- the inverse lattice is the reciprocal lattice of our real lattice. It's really important in crystallography, so I think a lot of you have seen this. And you can define by just drawing these perpendiculars to the nearest neighbors you defined the first Brillouin zone, which is where the energy levels, those precious energy levels of this molecule that I want-- that first Brillouin zone is where in the inverse lattice-- see, this now becomes inverse space, also known as k-space. That becomes a degree of freedom.

And so that makes these guys move. They can even move and cross one another. And that is the difference between a solid computational quantum mechanics on a solid-- what you can get out in a molecule. And the Brillouin zone is the playground of this space that matters. Because as we showed from Bloch's theorem, if you go outside of the Brillouin zone, you can just wrap it and get back exactly to where you work. So your function and your energies won't change.

So all that matters is to know and understand and compute, which is what the code does, the variation inside this Brillouin zone. That's why we defined it, because we just don't need any other zone. And we got here by looking at periodic potential, and the result of solving the Schrodinger equation in the presence of a periodic potential is that you get this new constraint on the wave function.

And the key here is that-- OK, so this is just saying you can go one lattice vector away and get back to same thing. That's why I just said about only the Brillouin zone mattering. But the key result of Bloch's theorem is not here. Ha. But the key results of Bloch's theorem is that you have this k in the first place. The key result is that you have a new index. Just like the quantum numbers came out of the hydrogen atom, you have a new index that can vary. And as it varies, it changes your levels.

And we spent some time talking about this. So please let me know if you have any questions about this. I just talked right into the mic. [LAUGHS] (LOUDER) Let me know if you have any-- oh, sorry. [LAUGHS] Does everybody understand that? By putting-- by mapping quantum mechanics and all of our machinery, Schrodinger equation, approximations to it-- but remember, H psi equals E psi. H has v.

And by having v be the same everywhere in space, we got this new degree of freedom, this new thing that's critical. And this new thing is what makes a band structure. So if I showed you a band structure like this, what am I simulating?

AUDIENCE: [INAUDIBLE]

JEFFREY C. GROSSMAN: What is that? Forget these other ones. Just look at those.

AUDIENCE: It's a molecule.

JEFFREY C. GROSSMAN: Yeah, it's a non-periodic system, right? If the bands are flat, you don't have this variation in k-space. And if you don't have the variation in k-space, well, at least to within what the system can feel, it's not a crystal. It's not a periodically repeating potential.

It may be, or it may be really close. What if you had a molecular crystal, which exist? There are many molecular crystals. But they're really far spaced apart. These molecules are weakly interacting.

Well, you might get, then, something-- you might just start to see this-- and we've played with this in the computer. You might just start to see some little wiggles, feeling that effective the variation in k-space. But you won't see very much.

And then as the interactions, or as the potential that's periodic, gets stronger, well, then this variation can get very high. Any questions about any of that? So that's kind of the key point there. And we talked about the kinds o things you can get. And we also talked about how-- so this is density functional theory. We talked about how, when you solve for the band structure, you first converge the density. That's a separate calculation.

And then what am I doing here? How do I get this? The third point is sort of silly. You plot. But point 2, what am I doing? Somebody explain point 2. Yeah?

AUDIENCE: You go in the Brillouin zone, and you look at the different points in k-space. And then, using those points, you define potential for band gaps.

JEFFREY C. GROSSMAN: Yeah. Well, you find-- yeah, you find the band gaps. You find the energy levels at each point. But as we said, as you just said, you're doing this for lines in the Brillouin zone. How do you choose which lines?

AUDIENCE: Your choice.

JEFFREY C. GROSSMAN: My choice-- but I need to choose. Sam?

AUDIENCE: You pick the high-symmetry region.

JEFFREY C. GROSSMAN: Yeah, it's the high-symmetry parts, right? We talked about that. Because why?

AUDIENCE: Nature likes symmetries.

JEFFREY C. GROSSMAN: Well, that's a good answer. [LAUGHS] That's always a good answer. Nature does like symmetry. It's a beautiful thing. But is that really why that's what I do for my band structure? What does that mean?

AUDIENCE: After reaction occurs, [INAUDIBLE].

JEFFREY C. GROSSMAN: Pretty much. That's where the variation that could happen in the energy levels is going to happen. And that's what you want to capture, right? So a band structure is a simple two-dimensional way of cruising through this kind of complex three-dimensional Brillouin zone where things are varying any point I go. But if I go just along the high-symmetry points, then I get the variation that's usually most important.

And then we talked about how you fill these up to the Fermi energy. Is the for energy always at 0?

AUDIENCE: [INAUDIBLE]

AUDIENCE: No.

JEFFREY C. GROSSMAN: Yeah. So if I didn't tell you where the Fermi energy is, and I asked you to tell me if it's a metal or an insulator, could you? Would it even be possible? Why or why not? Yeah?

AUDIENCE: Because then we'd see whether or not the bands are constant, right? And if they're constant, then we know it's going to [INAUDIBLE].

JEFFREY C. GROSSMAN: Yeah, and so if I leave that piece of information out, which I did last year, and I give you a band structure that looks like this, and then let's say you have bands up here, well, everybody is really excited to call this an insulator. I'm excited to do it. I can hardly hold back. This is an insulator.

But hang on. If I didn't tell you where the Fermi energy is, what if the Fermi energy is here? You got to have all the information to answer the questions, right? So know what information you need if you're asked a question about a metal insulator. And you know-- yeah?

AUDIENCE: Why do we typically begin with the energy at 0? What would be a case where we vary it?

JEFFREY C. GROSSMAN: It's only because it's sort of a-- there's no good reason except that it's convenient.

AUDIENCE: OK, so usually it's just static?

JEFFREY C. GROSSMAN: It's just nice to shift them so they're always at the same place. And then we can compare things more easily. Why is this definitely going to be a metal if I have an odd number of electrons? OK, there's a little discussion there. I want to know what you guys are saying.

AUDIENCE: Confirming.

JEFFREY C. GROSSMAN: Confirming, OK. You're validating-- I love it-- using the group consensus. Crowdsourcing is very powerful. Anyway, don't use it for computing.

AUDIENCE: [INAUDIBLE] if there's not enough electrons, then a band's only half filled. The Fermi energy has to be in that band.

JEFFREY C. GROSSMAN: Why? That's exactly right. Why?

AUDIENCE: The Fermi energy is where you fill up until it's--

JEFFREY C. GROSSMAN: That's it. Did everybody get that? Fermi energy is the energy that you fill the electrons to. So if you have an odd number of electrons, well, how many electrons go in each one of these bands?

AUDIENCE: Two.

JEFFREY C. GROSSMAN: Two. So if I have an odd number of electrons, one of them is only going to be half filled. That means my Fermi energy has to cut it. It's got to cut it somewhere, which means I have a band crossing the Fermi energy, which means it's a metal-- has to be.

You can think about the same for an atom, except that atoms are metals. But most atoms have that case. They have half or partially filled levels. You don't fill all the p electrons in carbon but we don't think of the carbon atom as a metal, because atoms and molecules don't really have this kind of behavior. But it's the same idea. You're partially filling levels.

We talked about-- how are we feeling about direct versus indirect gaps? Good? OK, we talked about that. Yeah, liking that-- that could be a good question. And we talked about other things that you can calculate-- vibrational properties. We did talk about magnetization, right? Now, this is not-- sorry, this is actually from a different code we used to use. So just ignore this. We used to use a different code than SIESTA. And that was the input for it.

And this is showing that you can do calculations of, say, different phases of a magnetic material like iron. And how would I calculate the magnetization of those materials? This was in lecture something, some number of days ago. Yeah?

AUDIENCE: I guess you could put on and apply the magnetic field and then see where [INAUDIBLE] is.

JEFFREY C. GROSSMAN: You absolutely could, and that would be really hard. But you could do that, actually. And we do do that. But that's a hard calculation.

What is the magnetization of material what's it due to, anyway? What part of the materials is due to? Yeah?

AUDIENCE: A difference in density and space between the spin up and spin down.

JEFFREY C. GROSSMAN: Yeah. Yeah, it's due to electrons. It's due to the spin of the electrons. That's what gave us the Stern-Gerlach experiments. It was the magnetization possible of the spins of the electrons. It was the fact that a magnetic field could exert a force on those.

Now, we said that, in your material, you have spin up electrons and spin down electrons, the precious things that were computing this whole second half. And you fill those up. And you fill them up. According to the Pauli exclusion principle, you fill the levels up with these electrons, right?

But when you get to a solid or, even in atoms, you don't always necessarily have the same up and down electrons. You can have differences. And when you have differences between them, you can have a net magnetic moment. And we talked about that before.

And then we said, well, OK, if I had an atom, then you can have a net magnetic moment. Just count the number of up electrons minus the number of down electrons. But in a solid, in a crystal, you now have these electrons in these bands. You need to use something else. And that's where you need to use the density of states.

And so if you have sort of the density of states-- now, remember-- versus, say, energy, and this is something you're all now familiar with from the homework, but we talked about this, also, how it relates to magnetism, and that, in the SIESTA tool, you could plot, for example, the spin up electrons. So let's say these are the spin up electrons. And then you can plot the spin down electrons.

And that's a little hard to see because there's three curves with one color. But the main point is that the up electrons and down electrons could be very different in where they are in energy, which translates into what where the peaks are in the DOS.

Now, you see, what matters, though, is not the difference across the whole DOS curve. What's going to matter? It's not the whole DOS that matters. It's only part of it. Which part? Yeah, it's the part up until the Fermi level. What are the differences in where I filled electrons? Between the ones that would be up and the ones that would be down, right?

Now, and that got us to talking about this spin-polarized thing that we talked about last time. And that's a little button on your simulation tool that you can check or uncheck. So if something is spin-polarized, it allows the up and down electrons to be different, to have different energies. So I just I just told you that difference is what gives you magnetization. So if you don't allow it to be spin-polarized, then you won't get magnetization, right? Yeah?

AUDIENCE: Isn't there a spin up and spin down electron in every energy state [INAUDIBLE] that are all going to have the same energy?

JEFFREY C. GROSSMAN: Ah, very good question-- and that is exactly what spin-polarized does. You see, so this is what you're talking about. You're saying, well, isn't this just in one level? But it actually, it turns out, that that's what's called a restricted-- you can say restricted closed shell or restricted open shell-- formalism that is valid for many, many materials and molecules, where in fact, there's no difference.

But in reality-- in reality-- even when it's restricted, you still should write these as a sort of one spin channel and another. You could call it alpha is spin up, and beta is is spin down. And each one of those has its own set of orbitals and wave functions. So in reality, that's what you solve for.

Now, in many materials, it turns out alpha and beta electrons do have the exact same energy level, but not always. And actually, in exactly what you were talking about, when I apply a magnetic field even to a material that's not very magnetic, you can cause big shifts in these. You can-- depends. That depends on the material.

But when you apply external perturbations to the system, you can split these so that actually you do have this picture where the energy of the spin up channel for that energy level is different than the spin down channel. And that's exactly what spin-polarized does. It allows those energies to be different. Without that, you can't really study magnetism correctly. That's a good question.

OK, and so we talked about some other things. We did talk about how you could calculate electrical conductivity-- so that's fair game-- from the band structure. There's an equation in the lecture from last week on that. We didn't talk about thermal conductivity. We've talked about optical properties and magnetization. That looks like it's just repeating the first and fourth bullet, which is interesting to me.

But these are the kinds of things we can calculate using the band structure in the DOS, which is what we've focused on a lot in the last three, four lectures. So that's certainly I would think you should know about, how to get some of the key properties from the band structure in DOS in these first four, excluding thermal, which we didn't talk about.

And with the convergence questions, we got to have a convergence question, right? You just-- you got to. You would feel cheated if you didn't have one, right? And I don't want you to have that feeling. When you have a solid, k-points now becomes a convergence parameter.

So that's kind of our review. Any questions? Any questions about that at all? Any thoughts or comments? Any other questions? We're good? Any questions about the quiz?

OK, let me just take five minutes to do a little stuff, get it out of the way, so that after the quiz we can dive into-- or do you guys just kind of want to-- maybe we stop here, huh? Should we stop here? Except five minutes on solar right before quiz. Yeah. I'll tell you what-- I'll do my little energy slides, and then we'll start solar. Because this isn't really solar, but it's related.

And I don't think I showed these before. Did I show these before when I was motivating research and energy? I really like this. We talk a lot about global warming. And I think that's a really important topic. And there's some really great work and, unfortunately, not enough understanding, I think, on-- [LAUGHS] I don't even know where to begin.

You know the polls show that half of this country still doesn't think that there's any evidence that it's anthropogenically linked. But anyway-- OK, so let's say we don't talk about that. And we ignore these sort of really hard scientific facts. There are other reasons other reasons to think about renewable energy.

And I like this one. I don't know how many of you have seen something like this, but this is-- the United Nations puts this out. This is the Human Development Index. What's that Mean I feel pretty developed. I mean, does that just mean I can go to Starbucks and get a latte when I want?

No, this means health care, education. It means I can read. It means I could maybe have a light on at night to read. But it's primarily some sort of key indices that talk about sort of the well-being of a person.

And that, you can see, is incredibly strongly correlated with how much energy a country gets. So this is the amount of per-capita electricity use. And that's this Human Development-- it's basically a well-being index. As you can see, some people get surprised that Canada beats us. So how do they beat us?

AUDIENCE: It's cold.

JEFFREY C. GROSSMAN: It's cold. It's really cold up there, right? But you can just see the strong correlation. The question is, when they-- see, there's enough fossil fuels for everybody here, probably, certainly if you go with coal. There's a whole lot of energy in fossil fuels, and we could lift a lot of these people up the curve. The question is, is that really how we want to do it?

Now, the other point I want to make-- and this will be the other intro point. Just so you have in your minds when you're talking to people about energy, it's not just about global warming. And this was a great experiment that was run accidentally when 256 power plants went offline in the Eastern corridor.

This is one of these stories where one plant goes off because a mouse chewed through a wire or something, and then the whole country feels it. But it was a great test bed, because they were offline for quite a lot. All these things shut down. Everything had to shut down.

And so people took planes up and did testing and published these results of the air quality. And it's incredible to look at the data. You look at all kinds of stuff that affect what we breathe, what we see, how we live, who has asthma. A lot of that stuff goes down instantly. So there are different reasons than just global warming.

And I like this map. I don't know if I showed this to you. But this is how much we consume scaled by consumption. This is the country, the world map.

[LAUGHTER]

We're pretty big-- pretty big. There are some places that are pretty small. OK, so you scale it by country. I mean, one question that comes up and gets modified is, how much energy do we really need, or power? In 2002, we burned energy at a rate of 3 and 1/2 terawatts. What's it going to be in 2050?

Well, if you make some assumptions about how many people there are, and if everybody used energy like us, which is really inefficiently, then we need 100 terawatts in 2050. We only have 13 now, 14 now. We need a whole lot. And we like to think that people are going to be more efficient, and so that becomes the target-- 30 terawatts, 30 to 50 terawatts is what we're going to need.

How do we generate that? Well, this is-- and this is all just, again, building up to solar, which we'll start next week. This is how we've generated it so far. We burned a lot of wood, and that was kind of dirty. So we burned coal, and that was really dirty. But there's so much coal, and it's so cheap.

[LAUGHTER]

And then we found oil, which is this magnificent energy carrier. It's a solar resource. All these are solar resources, by the way, including hydro.

Now, natural gas, with fracking-- this is going to go-- from this it's going to go like this and just sort of take over this chart. Fracking in the last few years has done more for energy than anything has in many decades. But that's not that's not what I'm talking about. I'm talking about this green sliver, which is where I like to sit. And we separate out hydro, because at least on-shore hydro is fairly tapped out.

And then you've got that green sliver. And the thing is that, if you look at global warming curves, CO2 emissions, people talk about wanting half of all the energy to come from that green sliver by 2050. So you back the numbers out. We need 30 terawatts in 2050. That's how much the world needs if we're really good at how we use it, 100 if we're like us.

And you want half of that to come from a green sliver, which isn't really expanding much. And notice, it's sitting on a slope like this. This slope is still-- could go even much higher much faster.

This is a really tall challenge. This is the challenge that I like to think about, is how can we actually do that. And solar PV, I think, is-- and I'll end on this side, and so we'll start we'll pick up from here on the technology part and the science part next week.

We use about 15 terawatts today. Does anybody know how much we get from the sun? I think I did talk about that. What's the number we get from the sun? We use 15 terawatts a year. How much do we get from the sun per year?

AUDIENCE: [INAUDIBLE]

JEFFREY C. GROSSMAN: 40,000-- roughly 40,000. There's just is a whole lot of energy that comes with the sun. The energy released by an earthquake we get from the sun in a second. You probably heard this. Every year, we get that amount of energy in an hour from the sun.

Here's what I like-- you may not have heard. The total resource of oil, including the 2 trillion barrels we've used, roughly, and the trillion more that we're going to use, for sure-- that amount of energy resource you get from the sun in two days. It's an incredible resource, right? But apart from just painting a barrel black and heating water with it, we really don't use it much. And even there, we don't use it much at all.

Solar photovoltaics is an extremely appealing way of trying to capture this resource and really change that green sliver. And so that's what I want to talk about next, after the quiz. OK, so see you all Thursday, office hours tomorrow. Any questions at all, please send me an email.