MITOCW | 4. Application of QM modeling: Solar thermal fuels (I)

JEFFREY C GROSSMAN: So we're here. So we're in lecture four, and this is really exciting because we're going to be talking about an application. We sort of spent three lectures introducing and building up some of the framework that the computer solves to do quantum mechanics, and now we're going to actually look at a real problem. It's a really cool problem. And then that'll sort of-- we'll follow up with this. We might do a little bit more of this to start on Tuesday, and then we'll talk about hydrogen storage is another problem.

We'll go back after that to a little more formalism to get to solids because these are molecules so far, and then we'll do some more problems. OK, so that's our plan.

What I want to do today is I want to review a little. Since I didn't-- so Michelle came in and gave the lecture, lecture number three, because I was in San Francisco. And so I'd like to review some of the key points from that lecture. So we're going to review a little bit to start.

And then I want to do some interactive calculations together because, first of all, there's no better way to spend time, really, with a person or a class or any-- to compute together is to know one another. And through these interactive calculations on the hydrogen dimer, we will pose some questions and answer them together, make sure that we're kind of collectively understanding some of the key points of the first three lectures.

Then I'll tell you about why this is such a cool problem, what solar thermal fuels are, and why this is such a cool energy problem. And then we'll end with a discussion and some more interactive calculations of the solar thermal fuels and kind of talking about why we need quantum mechanics to tackle this problem. So that's our plan.

Is anybody else-- yeah, we're good with that? We got a thumbs up. I'm ready to go. I love it. You can give me a little private thumbs up like that any time, and I love that kind of feedback. That's helpful. And I was actually thinking that you were thinking of the Celtics securing the division title anyway.

I think you talked about this. This is sort of where you started because we had this kind of quantum mechanics that we couldn't solve. And then we said, well, but you can solve it analytically for hydrogen, and we did. And we said that that explained the periodic table, amazingly, if you only had one electron and one proton. Unfortunately everything has a lot more than that, and what happens is that when you put more than one quantum-mechanical particle-- by which I mean what?

AUDIENCE: More than one electron.

JEFFREY C GROSSMAN: Electrons. For us, that's the quantum-mechanical particle that we care about. Of course there are more quantum-mechanical particles than that in the world. Everything is quantum mechanical, but those are the things we really care about in this class. And if you put more than one into the whole thing, then you've got to think about how they talk to each other, and that's the killer.

So you can talk about how they talk to the ion. That's this 1 over r term-- how they talk to the proton I mean, right? But talking to each other, that's this many-body problem. It's called the many-body problem. That's really hard, and analytically it's a nightmare, and that's where computation comes in.

Unfortunately, so this is sort of showing-- this is just all review for the first little bit of this class. I want to talk about review. Those good-old days of one electron are over. They were good. They were fun. We had a blast for one lecture, and now we're moving on, and we're going to multibody, many-body problems.

And that's the many-body Schrodinger equation. And you can see that the thing goes from this where you get those hydrogenic orbitals and everything's beautiful to this where it's just a complete mathematical nightmare. And this cannot be solved analytically. And so these are sums over all of the ions, sums over all the electron-ion interactions and sums over all the electron-electron interactions. This is the killer right here.

We make some approximations. That's how we get there because as I talked about in the beginning, even if our computers were seriously like 10 orders of magnitude faster than they are today, we still wouldn't be able to solve this problem in a straightforward way. We cannot solve it directly and exactly, so we have to make approximations.

One of the first ones we make is-- oh, and that's just those are the labels. One of the first ones we make are-- right, there's the equation. That's the Schrodinger equation-- is this Born-Oppenheimer approximation. I think Michelle probably showed you my tattoo. Did you see the tattoo? That was my-- I tried to find a good image for Born-Oppenheimer, and that came up first.

And then did she talk about-- no? So when I found the image, I found it on a blog. And that's a dangerous thing because there's a long trail of discussion. And it was interesting that the whole discussion was not about computational modeling and it was not about physics, Schrodinger, or Born-Oppenheimer. It was entirely about whether this guy was going to be able to find dates or not in his life.

And it was actually a very engaging discussion, and it came out-- it was like 50% said definitely because of the tattoo, and 50% said no way. And so I don't know where that-- but anyway.

Now this is another cartoon that just shows that the electrons are the flies, and the protons, the nucleus, are these cows. And they move really slow, bulls. I didn't mean to dis. These guys are going really fast. This guy's kind of slow, and that's really the point. Electrons are fast and light, and so it's a good approximation.

How much lighter are they than the proton or the nucleus?

AUDIENCE: 1 over 2,000.

JEFFREY C GROSSMAN: Yeah, it's a couple-- it's like 1,000, right? So that's enough lighter that you can say, you know what? At any given time, it's a good approximation to say that this thing is pretty stationary with respect to these things buzzing around. That's the Born-Oppenheimer approximation in cow language-- OK, cow-fly language. Actually, this is more Google image art.

So this is the approximation we make. What you can see is that we just get rid of those nuclear terms. We treat them as if they're not moving and they don't really matter because at any given time what we care about is the electronic structure with the atoms fixed. That's what we're talking about here. And you can solve for it. It's a really good approximation in many cases.

There are some fields where it matters, where this approximation actually can break down like in superconductivity. We're not going to go there. For us and the things we care about, that's sort of-- the positions of the atoms are frozen, and then we solve for the electrons. That's fine, and that's a good approximation.

OK, so any questions about Born-Oppenheimer, the Born-Oppenheimer surface? You'll hear people say that, the Born-Oppenheimer surface, and now you know what they mean. They mean the energy surface where the electrons are always in sort of their ground state with respect to the nuclei positions because they always have enough time to get there because they move so much faster than the nuclei. That's the Born-Oppenheimer [INAUDIBLE]. You can pull that out as well in conversation.

Now that's one approximation. That kind of helps. It really doesn't help the key problem, which is that many-body-interaction thing. So that's like the real-- that's the real issue here. How do we get over this electron-electron interaction? And don't even let me say it, electron-electron-electron interaction because you can have like three-body effects. It's a many-body world, but we can't do that. We can't do that on a computer in a good-enough time scale to be applicable to materials, so we simplify.

And you covered this, right? This is not-- but we're getting back into our feeling with this, right? But you did cover this. Am I correct? OK, good. One person got it. But thank you for that in the back.

Now, OK, there were basically two paths because they saw this and they knew, they being the people thinking about computational materials, physics, and chemistry back in the 1940s. They knew they needed to do something.

And so there were essentially two paths. There was a path that most chemists took, and there was a path that most physicists took starting in sort of the '60s really, actually. The path that the chemists took is to say, you know what? We're not going to mess with the Hamiltonian. We are not going to mess with this. This is right. The physics of this is correct, so we don't want to play around with that. Most of what the chemists did was to play around with the wave function.

So what they did is-- let me go back. Sorry. I think I had the Schrodinger equation here. H-- remember Schrodinger equation, H psi equals E psi. Well, they played with psi. So instead of saying that psi can be complex as it needs to be with all the freedom that it needs to have, they said no, we're going to start to restrict that freedom. That's really how quantum chemistry sort of began.

I mean, there was some perturbation theory, but a lot of the real advances in quantum chemistry in the beginning happened in making approximations for this, for the wave function. They said keep H, mess with psi. Make it simple. And if you make it simple, it becomes a tractable problem, right?

How many of you have heard of a determinant, a Slater determinant? Slater was here at MIT, and it was a really important contribution to quantum chemistry was to be able to write psi, keep the important properties that you need but to write it in a much simpler-- in a very simplified way.

So you lose information. It's not the same psi that you need. It's not the correct psi, but it's sort of an approximate version of it. That's kind of where quantum chemistry-- that's what Hartree-Fock theory is based on.

Then you have sort of the physics world in the 1960s. And I've shown you the picture of Walter Kohn, who is the only person to win a Nobel Prize in computation, so far at least. And he won it for a density function-- for his development of density functional theory. Now that is taking sort of the opposite approach. What that is doing that is saying, OK, ignore psi. Psi is just too hard. Even if you simplify it, it's a really hard thing to write in a computer and to represent accurately, and so let's just forget about that and work only with the density. I take it you did talk about this last week, right?

So in density functional theory, that's where it gets its name. You just get rid of psi by not thinking about it and by solving the problem of the density instead of the wave function. So it's the density of the electrons instead of the wave function of the electrons.

Now when you do that, effectively-- and again, my goal here in this class is not to go deep mathematics here because I know many of you haven't had quantum yet, but I want you to come away with an intuitive picture for what's happening. What happened in the 1960s when these communities were really developing computational quantum mechanics for the first time?

And what this does-- no, but stay. It's still going to be good. OK, go ahead. We'll fill you in when you come back.

What this does to say that I want to think about the density instead of the wave function is effectively it modifies H. So now instead of modifying psi, you actually are changing H considerably-- considerably. But you hope that you don't change it so much that it's wrong or that it's unphysical, right?

And density functional theory effectively is a theory that simplifies H, the Hamiltonian, the expression for the energy. You basically get rid of those complex, many-particle interactions from H and you put effective potentials into it. That's density functional theory.

Now, both of them get rid of this many-body problem. Actually, see, what you do in quantum chemistry is you change the wave function so it's a single-particle wave function, which basically means when you solve the equations, there are no more many-body terms left. And in density functional theory, you change the Hamiltonian so that you explicitly get rid of the many-body interactions. Either way, you're left with a single-particle picture. That's really the trick. In both communities, what you end up with is a single-particle picture.

Now that's something that you can solve in less than the age of the universe on a computer, and that's the key. You're left with these single-particle pictures.

What is this single-particle picture? Who can tell me? Did you talk about that? You go from a many-body picture to a single-particle picture. Take a guess. Yeah, I see that you want to guess. Yeah, yeah, go ahead.

AUDIENCE: It's one where all the variables in your theory only sort of depend on-- all the things in your theory only depend on the variables for one particle.

JEFFREY C GROSSMAN: Basically yes. I mean, that's exactly it, right? So now my electrons-- my electrons are like this. In my real system, here are my electrons, all those E's, and there they are. But what I'm saying is that this isn't-- I can't describe this because, look, that's when I have to take into account these guys. Look, that's this term here, the R minus r is the relative positions of two electrons. And I even need to take these guys and these guys and those guys, and that's the many-body part. That's not solvable, basically, not for computational material science.

So what we need to do is-- I mean, it's solvable in certain ways, but it's very hard. I should put it that way.

So the single-particle picture is to say, sorry, but you're going to lose all this individualness here, and each electron-- I'm going to now map this guy over here-- is only going to feel some potential field, some mean field, some mean potential average of all of those other electrons. It swims in an average potential now.

And so I basically have just eliminated the problem. The problem was this. It's too hard to solve on the computer, certainly analytically but also on computer. And so I've changed it to this. That's basically what both of these things do. Quantum chemistry and density functional theory both result in this picture, this very simplified picture. It's called a mean-field picture because each electron is in a mean field of the rest of them.

They do it in different ways. Quantum chemists do it by simplifying the wave function, and the physicists did it originally by simplifying the Hamiltonian. And there was a lot of really interesting sort of discussion, to put it lightly, about which path was better. And then I think now both communities, I think, work in both ways. There's a lot of back and forth.

But density functional theory is definitely the one we're going to work on with this class because it strikes a balance. It strikes a very nice balance as a method that can capture enough accuracy. It sacrifices something. It definitely sacrifices something. You approximate the Hamiltonian. But it doesn't sacrifice-- it still is pretty accurate, and it's been shown to be pretty accurate for many, many, many problems.

And you can see that it's also right in this region here, which is a really nice region to be in. Now why is this a nice region to be in on the vertical axis?

AUDIENCE: You can solve for larger molecules.

JEFFREY C GROSSMAN: You can solve for large molecules, yeah. What else? Yeah?

AUDIENCE: It's growing pretty quickly, so in the future you'll be able to do even more atoms.

JEFFREY C GROSSMAN: Totally. Nice n-cubed scaling-- well, sorry, n-cubed scaling with the method with size but also increase in the speed here.

What else? What else might this be a nice sweet spot for computational materials design? 1,000 to 10,000 atoms, sort of where the limits of DFT are. Well, what are we solving for? Electrons, right? We're solving for those properties of electrons.

Now, why is this a nice sweet spot? Well, when might I need less or more atoms than that?

OK, so let's say I'm in coupled cluster, which is one of these ways of making the wave function simpler. It's a very accurate method, but you can only do today, I don't know, 15 atoms accurately, maybe 20. What would be limiting about that? Is 20 atoms enough? Yeah?

AUDIENCE: If you're trying to figure out, say, the electrical properties of some material, you don't really have enough space to take into account some three-dimensional block of stuff.

JEFFREY C GROSSMAN: And when would you run out of space? What matters?

AUDIENCE: Boundary conditions and things like that.

JEFFREY C GROSSMAN: Yeah.

AUDIENCE: So if you're talking quantum dots or things like that, you have different sizes contributing to the properties of the material.

JEFFREY C GROSSMAN: Yeah, and you can't really explore those with just 20 atoms. Definitely a good point. Anything else? Why else might this-- so it's not just-- it's the size. When I hear it's the size of the material you want to study and 1 to 10,000 is a pretty good region, you can play a lot-- welcome back. You can play a lot with that size range. You can model a lot of materials in that size range.

But importantly, the thing you're modeling are the electrons. And so what counts, it's not just about how many atoms you can put into your simulation. That's not what counts. You see these titles of papers like million-atom simulation, billion-atom simulation, trillion-atom simulation. OK, that's cool. You get a lot of atoms. Good for you.

But what matters? What matters is did you need those atoms for the property you care about? Did you need them? Now in some cases, maybe you do. But for electrons, very often they're spread. What they want to do is kind of more dominated by a few nearest-neighbor distances, maybe 10-nearest-neighbor distances in a crystal.

In some cases they're very spread out, like in a metal, and then we can use periodic boundary conditions, and we can still capture all the physics. But when you have interfaces or roughness or molecules, the electrons aren't going to-- even if you put a million atoms in, you won't see anything different than if you put a thousand atoms in.

And that has-- for many problems. For many problems, not all, but for many cool materials-design problems, that's the case. And that's why this is such a nice sweet spot of a method because it hits in this range where the stuff we care about, electrons, happen to kind of play in this phase space of distance. That's where DFT is. That's why it's so powerful.

Any questions? And right, I'm not going to review. I just kind of went through this. The approximation is to work with the density, and you sort of throw everything into a density formalism, and you punt on the exchange-- on this interaction term that's all about this V. So density functional theory is about what functional you use to capture these many-body effects in a single-particle way. That's really what it comes down to.

And this is all sort of review, right? I kind of went through this. You will not be tested on this math, but I think you went through it already last week. Correct? Some nods. OK.

And so you get basically an equation where the potential that I just showed you can be written as this potential plus this exchange correlation functional, which is basically a function only of this one electron. That's why it works so well. It's not a function anymore of all these other electrons. I kind of want to make sure we get the key points.

Now the way you solve this in a computer, which is what the nanoHUB does for you when it works-- I had some interesting crashes last night on the nanoHUB-- is basically you have this equation. So what density functional theory does, you see, this is the beauty of it.

What does that look like to you? I mean, that looks like something that we did. , That's definitely your Hamiltonian, but this equation now-- remember the many-body, multiparticle mess that we just showed you? Now we're back from that to this. What does that look like, it's reminiscent of, and for which material? It sort of looks back like hydrogen almost, right?

That's not as simple as hydrogen because V is now more complex, but it basically turned the problem back into a single-particle problem. So now that's the equation we solve once we go through the density functional theory approximation.

And you have to solve it in what's called a self-consistent way, which is to say you have to start with a guess for your density. You plug it into the equation, and you get out these wave functions. So you do get wave functions in density function theory, but they're essentially just a basis for the density. The conceptual framework is to work with the density.

So you start with the density. You plug it into here, and you solve this. The computer solves this, and it gets you a wave function. And then from that wave function you can get a new density because the density is, after all, just this sum over these things squared. We know that because we talked about how that's what density is, electron density.

So does everybody know what I'm talking about? Probability-- electron density is where it is. It's a probability distribution. And so that you get from that. You put it back in here. You do it again, and basically you stop when what?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: When you're about right. I love that answer. Tell me more. When do you stop? If it's a self-consistent loop, I guess for this. I put it in here. I get a new set of these. They give me a new this, and I put that back in there, and I get a new set. When should I stop?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: Yeah, when it doesn't change, when the answer doesn't change. And so that's what this is showing you here. Is it self-consistent means it didn't change, basically. You did this loop, and it didn't change.

And that's what it'll look like in the code. You'll see energies, total energies coming out of the system, and they'll be sort of converging to a value. And then the code will say, OK, it's close enough.

Now the other key thing is you have to write these phis. When you talk about a phi-- so this is the Schrodinger equation. And then you write the psi in terms of some set of orbitals. But to write an orbital-- I mean, if I want to write anything-- if I want to write anything on a computer-- that's my electron density. It's my orbital. I need to represent it mathematically somehow. The computer can't just take that.

So you need functions to represent these, and those are called basis functions. So those basis functions-- and you can use different kinds of basis functions. You can use Gaussians. You can just use-- if I want Gaussians, I would put a nice one there and then maybe some more ones here. Well, that wouldn't work. Anyway, you need a bunch of Gaussians centered in different places, and you add them up, and they'd give you that function back, approximately. So we have to represent these things with basis functions.

You can use plane waves, which are really good for solids. You can use plane waves for atoms as well. They're nice. Plane waves are nice for solids because they're periodic, which is what your wave function is.

Gesundheit. Gesundheit. The double.

You can use them for atoms and molecules as well, but you have to be a little careful because a plane wave goes through the whole cell of the simulation, but your molecule only takes up a small part of it. So with plane waves, you're actually sort of wasting those functions. But if you do it in a smart way, it's not so bad.

All right, so that's sort of-- I wanted to kind of touch on that. This is a really cool movie that Lynn found.

Why do we care? Well, this is the kind of thing you can do when you know where these electrons are for complex systems. This is a porphyrin ring. I think it's got zinc in the center from this group here. And you can actually show-- this is a computation, and you can actually show what happens to the electrons-- the density of electrons when you shine lasers on it.

Now it turns out that this is-- and there it is. So now you're going to push on the system with lasers, which cause a resonance, and it causes these electrons to start sloshing back and forth as you pump this porphyrin ring with lasers. So you can see the lasers down here. They're not actually real. It's a computation.

But what you see is very important. Look at that slosh. Look at that. Now that is really important. The sloshing of those electrons is really, really important for how this molecule absorbs light, and that's why it was studied because this is what we're going to end with today is where those electrons are determines the band gap of the molecule, and it determines its optical properties, what we talked about in the very beginning, something we really need when we're talking about photoactive materials like porphyrin. And porphyrin has many important properties, right? It's a beautiful molecule.

These are the kinds of molecules and these are the kinds of things you can get now using these approximations. You can get electron densities and then correlate those to something really important. And that's what we're going to do by the end of today and in our homeworks for solar thermal fuels.

Do you guys want me to post these videos on Steller? Do you guys look at the Stellar stuff? OK, I'll definitely do that then. I wasn't sure if anybody-- OK.

So any questions? So that was sort of a little review of where we are. Let's do a calculation. Actually, before we move on, let's just do a calc-- now that's a little embarrassing. Let's put that over here. That was taken a few years ago.

Now there's MIT. Oh yeah. It was out in Berkeley, yeah. Now let's see if this works. Aha!

Now the two tools that matter for quantum mechanics in this toolset are quantum chemistry-- and this is doing just what I said. It's doing what those quantum chemists like to do. It's messing with the wave function. And this is the density functional theory code we're going to use SIESTA, which is a cool name. And this is actually messing with the density. This is density functional theory. Although this now, like I said, the two communities have overlapped. This code now can also do density functional theory. But these are the two quantum-mechanics codes we're going to use.

And if you go-- let's say you go to here. I just want to just do one little calculation together. And what I want to do is the following. There's some inputs here that are worth-- oh, you're kidding me. I can't scroll. Unbelievable. Well, that's really frustrating. So there's no way-- it doesn't let me actually scroll down here. Oh, there. Thank you. OK, I'm good.

So here you see it's got water, and there are some things you can do-- that's right. So the cursor has to actually be over there. And here are some inputs. So we'll work with water.

That's the basis set. Low means like what? Do you think that's good or bad? Yeah, it's not very good. Medium and high, those are the three options. Now G means Gaussians.

The other person who won the Nobel Prize together with Kohn that year was Pople, and Pople won it for some really important work that he did relating to these basis sets, basically, and some important chemistry work he'd done. But that G stands for Gaussian, and the 3-21G is a set that he made which became incredibly important to helping quantum chemistry move forward. He made sets of basis sets.

And if you google "basis set order form," there's a website where you can enter any element, and there are hundreds and hundreds and hundreds of basis sets that have been developed and published, and these are some of them. And this is just-- you go from here to the next and the next one. You just add more functions, basically, and so the calculation gets longer.

When is it enough? When do I have enough of a basis set? That was one question I wanted to discuss. 10? Oh, I love that answer. I thought 10 was pretty good too.

It depends. That's the answer. Now what does it depend on?

AUDIENCE: What kind of calculation you're doing.

JEFFREY C GROSSMAN: And?

AUDIENCE: How accurate you want the results to be.

JEFFREY C GROSSMAN: How accurate you want your results to be, what calculation you're doing. What do you mean by what calculation you're doing?

AUDIENCE: If you just want energy or whether you want to get properties [INAUDIBLE].

JEFFREY C GROSSMAN: OK, so the property. It depends on the property you're calculating. How do you know when to stop? So I'm going to do a calculation with 3-21G, and I'm going to calculate the water molecule using the formalism you just saw. That's what this code is doing. And you're going to see a nice pretty picture of water. There it is. And then you have these key outputs.

And there's my total energy. My total energy of this water molecule is 2,056.56 electronvolts. Yes?

AUDIENCE: What's a basis set?

JEFFREY C GROSSMAN: Yeah. So a basis set is those functions that the computer needs to represent the wave functions. So if this is your wave function-- if your wave function looks like this-- let's say this is phi versus r.

By the way, does anybody know which wave function this is? That is a wave function. I didn't just make it up. It belongs to an element. It's the 1s orbital of hydrogen. You got it. That's the r dependence of the 1s orbital of hydrogen. It looks like an exponential.

So should I use an exponential to represent this in a computer? You bet except no, and the reason is that those are slow to calculate. Exponentials are kind of slow, exponential functions.

So early on exponentials were used, and then it was realized that you could actually represent this pretty darn well with Gaussians, like three or four Gaussians, and you'd kind of get it right. You'd never get this part here. You can't get a finite slope at zero with Gaussians, but you can come so close that it doesn't matter.

And so because Gaussians have advantages-- we won't go into details, but I'm happy to talk to anybody who wants. Gaussians have advantages in terms of computing integrals on computers so that you can actually use some of the formalism that's been developed to do integration with Gaussians and do it very quickly and efficiently. You cannot do it with exponentials. And because of that, the chemists early on started using Gaussians for their basic sets, and all these Pople sets, those are all Gaussians.

Now when you use plane waves, that's a different kind of function. That's a sine and cosine function. And so there you're using functions like this to reproduce your psi. Either way, what you're doing is you're going to add a bunch of functions together to try to make up your psi, and you've got to have enough to do it justice. And that was the question is how do you know when you've had enough?

It's a very important part and problem in quantum mechanics-- in computing with quantum mechanics that doesn't exist in classical potentials, right? See, classical potentials, this is not a convergence problem. You don't converge your basis set. You just have a potential, and you calculate it.

Here you have to represent psi mathematically somehow. Here you're doing it with Gaussians. With SIESTA, actually it's not plane waves. It's a different kind of function like Gaussians. But in a way, it doesn't matter. They should all converge to the same answer, right? You just have to understand that this is what's going on under the hood.

So again I ask, when is it enough? When do I have enough basis functions?

AUDIENCE: When you approximate your wave function well enough with your basis set.

JEFFREY C GROSSMAN: And how do I know if I've done that?

AUDIENCE: When you check for self-consistency. Is that [INAUDIBLE]?

JEFFREY C GROSSMAN: That's within a single calculation. How do I know I've used a good-enough basis set?

Well, let's go back. Let's go back a second to what Sam said. It depends on the property.

So now I'm going to tell you a property. I want to know the binding energy of a water molecule. How can I calculate that? Somebody tell me how I calculate that. I have the energy of the water molecule. Is that the binding energy? Yeah?

AUDIENCE: The atoms that are really far away, and then you calculate the energy. And then if they have energy with them close together minus the far away, that will [INAUDIBLE].

JEFFREY C GROSSMAN: Exactly. So the energy-- so the binding energy, E bind, is equal to the energy of the molecule minus the energy sum over the energy of the atoms. So that's the property I want to calculate. It could have been another property. Could have been-- let's say this is the gap. Yeah, it could have been the electronic gap of the material.

Now how do I know if I've used enough basis functions? This is really important. Yeah?

AUDIENCE: Experimental data.

JEFFREY C GROSSMAN: OK, good. See if it matches experimental data. Except there may be other reasons it doesn't match experimental data, not just the basis set. So how do I know if I've just converged the basis set?

AUDIENCE: Get the lattice parameters of it.

JEFFREY C GROSSMAN: OK or along those lines, but that's still comparing with experiment, which is always a good thing to do when you can.

Well, what if I just do this calculation and then I do another one with a higher basis set and it doesn't change? How about that? Well, it's the same as the self-consistent thing. Once the answer doesn't change, I've converged.

But this isn't part of a single calculation now. This is part of more than one calculation that you have to do.

So I'm going to go to a larger basis set like medium and do simulate. And then it's going to calculate this, and let's see what happened. The gap-- OK, there it is again. Thank you. The gap went to 19. Oh boy. So now my key output-- let's see, is 2,068.6 electrons-- electronvolts-- is the energy with this basis set. Everything else is the same. And with the first basis set, it's 2,056 electronvolts.

Am I converged? Trick question. You still don't know. Well, except there's something else to it that I'm trying to get out of you guys. It's not an easy-- it's not an easy thing to see, but it's really important because we're talking about something called convergence that you don't really have in your classical force fields. You just have a classical force field, and then you have another one or another one, right?

But here we're converging within one calculation, one level of theory. And so what counts-- you have to do this when you do simulations. But what counts here is not the total energy. Why? Because that's not the thing I'm trying to converge. I'm trying to converge this I said, the binding energy, which is a difference of energies. And it very well may be that the binding energy converges with a really bad basis set right away and doesn't change when I get my next basis set or my next one. Even though the total energies are changing, they're changing in such a way that the error cancels completely.

This is the thing. It depends-- that's why I love it depends. It depends is such a great answer-- on the property you're simulating, and you have to do convergence for the property you care about. It could have been the gap. 20.7 was the low basis, and the higher basis is 19.7. That's a whole EV difference in the electronic gap. That's a lot of difference. That doesn't sound very good.

Maybe we should go to-- let's say we care about the gap. Let's go to one higher. Use a higher basis set. And we see here now the gap, oh, it changed again. Uh oh. And so now it went to 18. So we had, with the highest basis set, 18, with the medium one, 19, and with the lowest one, 20. So you can see it's actually going down, which means the right answer is probably going to be even lower.

Does that look converged? Not to me. You actually need a higher basis set still. This tool won't allow it because it's not a very flexible tool, but that's OK. That's not the point.

So does everybody understand what I'm talking about when I say convergence? We will come back to convergence again when we do solids because there's another thing in solids you have to converge, not just your basis set but something else, which we'll come back to and I'm going to save it as a surprise, very exciting surprise.

So we know that it can calculate the binding energy of water. There's one more question I want to ask you about, this spin thing here. Default-- default means that it took a guess. And you can see that the guess it made for water is that it's a spin singlet.

Now we talked about this in lecture two. Does everybody know what a spin singlet means? So we're talking about electrons filling orbitals. Remember, we're solving for those electrons, and they fill orbitals like this. Remember Pauli exclusion and all that and filling-- OK?

Now if I-- this is the last question I want to ask. Then we'll go back to the lecture. Oxygen is 1s. Somebody tell me what else is in oxygen. How many electrons? Three? Eight. So 1, 2, 3, 4, 5, 6, 7, 8. Right? Good. Very good.

Now, is that a spin singlet? Does everybody remember what singlet, doublet, triplet-- so singlet, triplet, doublet is very important because it tells the computer how these electrons are filling these orbitals. So that's another really important part of these simulations.

A singlet means that overall you have the same number of spins pointing up as spins pointing down. Is that what I have for oxygen? Uh uh. So a doublet is when I have one more pointing up or down, and a triplet is when I have two extra electrons pointing up or down. Doesn't matter. So this is actually-- the oxygen atom is a triplet.

Now what about water? Well, it turns out water is a singlet. So the default guessed it correctly.

Let's do the oxygen atom. Well, the code will do whatever spin state you say. I'm going to say now that I just want oxygen. So there it is. I'm going to do it with the same basis. And now here it is, and oh, that's a beautiful picture of oxygen. And now you go to key outputs, and there's the energy.

OK, so I'm going to do my calculation of this binding energy. I just calculated the energy of the atom. Can I use that? What's wrong with that? Look at the top line. No, second from the top line. What did it do? It did a singlet. Uh oh. It did this. It defaulted incorrectly. Never trust tools. Always know what you're doing. That's my point.

And these are the key things you need to know. You need to know that the basis, and you've got to know about spin. You've got to know how those electrons filled their levels. And what this calculation did is it did this.

Did it get an answer? Sure. Is it oxygen? Well, yes. in some very strange, excited state of oxygen. But that's not the right state of oxygen. And, in fact, you can tell because remember this energy, 2,032.1? And now let's give it the right spin state. Let's make it a triplet, which we know oxygen is, and let's see what the energy is.

OK, go away. I know you're there. Yes, that's the oxygen atom. And now when I use the right spin state, it's 2,035.6. Do you see how much lower the energy went?

Because, see, the right oxygen is the way oxygen wants to be. It's the ground state of that atom. If I compare it with this excited state, it's three electronvolts higher in energy. The more negative, the more stable, the more energy that has, the more happy those electrons are.

So that means that the electrons and oxygen really want to be in a triplet state, and you better use that energy to do things like calculate the binding energy. So you've got to think about the spin state. So that was the other thing I wanted to mention in doing this, spin state and basis sets. Any questions? No questions?

In the last half hour or so, I want to get to-- oh, 35 minutes even-- I want to get to this first application that I'm really excited about. And I think you're kind of now in a place where we can actually think about these-- think about applications for molecules.

And that's an area-- I want to introduce solar chemical fuels to you, and then we're going to talk about why this kind of modeling is so important here and what we can do. And then you'll have a homework related to this.

OK, I love this. I love that materials are going to determine-- and then here we are down here. I love this too. I think I've shown this to you, right, but it never hurts to show this again because it's a cool picture, and this is where we live. We're past silicon, man. That's old. Never better against silicon. Never. It's still a really important material.

But on the left, plastics. Oh, what's that? That is, I think, a nanotube or a-- it's either a nanotube or some other sort of 2D material wrapped up into like a gear that I think has never been made. Maybe it's not a good picture, but it looked good, and I grabbed it in five seconds from Google. Anyway, I'm going to skip this. I'll talk about this later.

Solar, we get a lot of it, right? You guys have seen this. How many of you have seen this? There's a whole lot of solar. So this is a cool comparison. Look. It beats coal. I mean, forget about like we know the resource of solar beats things like tidal and tides, waves, geothermal, hydro, all the other renewables combined. But it beats coal. That's pretty cool.

Well, biomass would be if you take all the arable land. You've got to remember, these numbers-- and this is the author of this fairly recent study. But those numbers have many assumptions go into them, and so there's a lot of debate about what the right numbers are. To within a factor of 2 to 10, these are probably the right numbers.

But biomass, if you take the arable land where you're not going to cause a huge famine in the area and you kind of add that up, you try to consider water resources and other things. You can actually compute using, say, some crop or set of crops-- sugarcane, maybe other things, switchgrass-- how much energy could you generate in a year? And that's about it.

I think-- and I don't remember. There was a number with biomass that was 11 that I saw for a while in the study, but that was if you literally stop growing food for people and you just take all land that can be used to grow anything and you make fuel, and you're still at considerably less than other resources. I'm not saying biofuels isn't a really important direction. But I kind of like these comparisons.

There we are. We use not much compared to how much we have in the sun. These are the different ways you can use the sun. And I want to talk about this one now.

So I think you know about this. You take the sun, and you make a lot of heat. I'm going to actually start with this because it's related to this. Here we take sun and we make electrons. That's going to be our next homework-assignment example that we'll talk about when we do solids because from the band structure of a solid-- and the band structure is nothing more than this for solids. From the band structure of a solid, I can explain to you-- you can explain to your friends why silicon is so expensive-- why silicon is too expensive. And then you can also take the sun's energy and just try to make fuels directly out of it.

So what are solar thermal fuels? Well, like I said, I want to start with heat because heat is-- and this will be a fairly quick introduction. But heat is something-- it's one of the oldest technologies we know about in terms of how to use the sun. Paint the barrel black. Put it on the roof. Put water in it. It gets hot. It's a really simple technology. It works really well, and it's used all over the world.

You can also, if you want higher temperatures because you want to make electricity, you can go to large-scale plants because there you need large scale because you need to focus the sun's energy to get much higher temperatures like, say, 500 Celsius to drive some sort of cycle like a Stirling engine or something. If you do that, you can make electricity. Those are concentrated solar power plants.

Here's the distribution. That is actually interesting, right? This is how much-- there's sort of capacity and produced. But you can see that using solar thermal as heat is actually the second-most-utilized renewable resource in the world. But that's the painting the barrel black and putting it on your rooftop. That's not making electricity. So in the world this is actually a very heavily used alternative energy. That is almost completely unused in this country. I think in terms of countries that use the sun in this way, we're like number 17.

There are some places that are trying to make power with it but very few. It's a hard thing to do. I think 15 of the 20 existing CSP plants are in Spain. The Spanish love this. But you can just sort of see where it stands.

Anyway, the point is there are challenges with using the sun's energy in the form of heat. One of them is that you lose the energy, reradiation. As soon as you absorb heat, it starts going out way, so you've got to contain it. And it's still going to leak.

So in some of these plants, you actually pump in fossil-fuel-based energy. So you use the sun to concentrate on, say, a molten salt in a tower, so a phase change of material. You get it up to really high energy over the phase change. You all took 3012. Know many of you did, so you know about when I say phase change, you're going up this heat, this latent heat, and you're storing a bunch of energy that way.

And then you want to keep it up there. So you actually pump in fossil-fuel energy because it's reradiating heat out and losing energy, and you don't want it to slip back down. That's not a good thing.

And really importantly is this is not transportable. So you can't use heat from the sun except where you make it.

So that's where solar chemical comes in. Oh, there's that-- we're number-- well, we're after Macedonia. Anyway, Albania. We don't use solar thermal this way, and I don't understand why. It's a very inexpensive renewable resource.

Solar chemical-- so in solar chemical, what you do is you take a molecule-- in this case, it's azobenzene. And you shine a light on it, and it goes into a different state. Now the important thing is that-- so that's the charging. Charge it by the sun.

In this different state, it's storing energy, and that can be released. It can be released in the form of heat. So you've got a way of closed-cycle capturing and storing the sun's energy, triggering this state to release that energy in the form of heat.

It's transportable. It can be stored for as long as you want. It's renewable. It's cheap, and it's a closed cycle. That's the dream.

Now this was very heavily studied 30, 40 years ago. And the reason as a field it was abandoned is because for all the cases that were studied in the 1970s that do this closed loop, they degrade. So you get this cycle. You charge up your fuel from the sun. You use it as heat somewhere. You bring it back. You charge it again. You use it again. And after 10 cycles, half of your fuel is toluene. That's a problem.

Some thoughts on that?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: Yeah. That was a good one. It was actually well timed. And I like that kind of feedback.

The papers of the times were saying things like an energy-storage plant, although technically feasible, is not economically justified because there's an upfront cost for this fuel. And if it doesn't cycle, if it just degrades in 10 cycles, you can't justify the cost. So there's a lot of work on this, and those are the degradation products. I won't go into it, but I'll leave it in your notes.

A lot of work was done. Many papers were written, and a lot of experiments were done to fix this problem, but no magic bullet was found. So they would substitute things into molecules. They'd put metal atoms into the molecules. They'd do what are called push-pull substitutions. And no matter what they did to these things, if they made them more cyclical, like 10 to the third cycles, which isn't bad, then they'd be terrible in their energy density. If they made them really high energy density, then maybe they were really bad at absorbing sunlight. So no matter what they did, they couldn't fix this problem.

And this is where it's just such a great time to tackle it again. The reason is that if you wanted to do 100,000 calculations of solids when this material was being studied heavily-- if you wanted to screen 100,000 materials, it would take you 30 years in 1980 to do that, and today it takes a few days. Not on the nanoHUB necessarily-- maybe they're back to 30 years.

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: Depends where you compute. But we're just a whole generation later in what we can tackle with computational quantum mechanics.

Now I'm going to end by telling you why you need quantum mechanics. So this is a really cool time to work on this problem, and this wasn't available back then when it was such a big deal. And then, of course, there's the sort of advances we've made on the synthesis side, which I won't talk about because this is a class on computation.

So what we've done-- and this is research that we're doing-- is we've shown that there are new ways-- we've shown computationally that there are new ways to tackle the problem. We've shown that you can take a molecule that does this switch-- there are many molecules that do this.

How many of you have heard of photo switches? What have you heard of them being used for? Have you heard of them being used for anything? Well, they have been studied a lot but in what fields? You have a molecule that you shine light on, and it goes like this. And then you shine a different light on it or you just take the light off maybe, and it goes back-- photo switches. Where might that be useful?

AUDIENCE: It kind of reminds me of like LCD screens but it's a bit different.

JEFFREY C GROSSMAN: Yeah. Well, actually mechanical computing is a big deal or nanomechanical memory, optomechanical functions. There are actually many areas where these sorts of switching molecules like stilbene and azobenzene and stuff that the name is so long I can't write it here-- spiropyran-- these are very heavily studied, these optically activated switching, big deal. But they're all terrible solar thermal fuels. They're terrible. They don't store much energy, and they go back in a few minutes.

So what we've realized is that you can actually turn them into good ones, and the way you do that is you put them on a template. So you take a molecule that's one of these switches. There are many switches. You stick it on a template, and what happens is when you stick it on a template you have new chemistry that you can do, and that's really the key.

Now we're going to come back to you in a few minutes is this picture, so I wanted to just tell you what it is. This is what the molecule does. This is a reaction pathway. This is the energy curve for the molecule. So it's down here. You shine light on it, and it goes up over this barrier, and it drops you down here into a new state. In this case, it's azobenzene. It's going from trans to cis.

How many of you have heard of trans/cis, trans and cis isomers? So you know about photo switches then. Not all trans/cis states are photo accessible, but many are. That's all this is doing.

And then when you want to release the heat, you trigger it. And it goes over this barrier, like say with a catalyst, and it releases this much energy. So that's your storage energy. That's how much energy that molecule stored.

And this back-reaction barrier's related to the lifetime of the stored state. We're going to come back to this.

So these are-- what we did is some work that showed that you can put these onto nanotubes and you can make them into good switches, and I'm not going to go into the details. But basically you see this is the advantage of computational quantum mechanics today is that we can do chemistry in the computer on these switches and screen hundreds of ideas in a week. And we can calculate the things like how much energy they store or how stable they are in a matter of an hour on a computer. So this is the perfect time to try to tackle old problems like this that weren't solved a generation ago but that you can play with them with many different directions computationally.

And this is just an example. And don't worry about the details, but this was that photo switch. This is how much energy is stored on its own, this line up here. And now we can tweak it by putting it on this template and doing different chemistries. We can make it store three times as much energy. So we can triple the storage energy of these molecules just by playing with the chemistry when you put them on a rigid template. That's the idea.

At the same time, we can tune the barrier back, and we can have cases like this one where you triple the storage density and you increase the barrier to going back. And that's really important because you want to be able to tune those things separately because the back barrier is related to how long it stays in the charged state.

So that's the key, and so we've developed materials like this that are very competitive with the best lithium-ion batteries in terms of their energy densities. Any questions about these? I'm kind of going through this quickly, but I don't want to get bogged down by too much of the details.

So there are many template materials that you can put these on. You have to use a template or you can't get this new chemistry.

And there are many switches that let you go back and forth like this. And what we've shown is that this is sort of a large phase space. And so they're sort of a new chemistry platform out here for making these kinds of fuels.

When I went to the Sloan class, Energy Ventures, and talked about this, my thought was-- this is last fall-- I have this really cool material. It's going to save the world. We're going to replace coal plants. We're going to make electricity this way. Everything's going to be heated this way.

And they did a study on commercialization, and they came back and they said, no, you're not going to do any of that. What you're going to do is you're going to deice windows.

And at first I was actually not happy because I wanted to solve the world's energy problems. They looked at all these different applications. There's lots of ways to use heat. If you can store the sun's energy and release it as heat on demand, that's a big deal-- and do it over and over again. There are many places you can use.

But they said, no, this is going to be the best. So actually we started looking at that. Actually Sam started looking at that, and he built a whole test apparatus. And Sam, with our solar fields when they're made, he'll be able to deice a window for you in about five seconds, and that's pretty cool.

So you can embed this stuff inside of glass and have it passively absorb the sun's energy during the day. In the morning, trigger it, and it gives you 300 Celsius inside the glass. You don't need to melt much ice to get it to fall off.

So a lot of people-- and they talked with MBTA and others who would pay a whole lot of money to get something like that because there's a lot of money wasted on deicing. It actually turns out to be very interesting.

We also built a solar cooker in collaboration with the Slocum group, and that basically lets you cook with the sun's energy when the sun's not out because, again, you have this ability to take the sun's energy and release it as heat when you want it and then recharge it the next day. So we're really excited about this. Oh, and there's our solar cooker.

I love this. I'm going to take the last 15 minutes to talk about what we can do with what we can do. But this is the last thing I'll tell you about the solar fuels. I love this picture.

So these kinds of things are not good. This is a big deal. This causes more deaths in the third world than malaria and AIDS combined, wood-fired stoves. Women primarily and sometimes children spend 20 hours a week searching for wood. 20 hours a week of their time goes to getting wood for burning.

This is the alternative if you want to use the sun to cooking. And I love these because this is a restaurant in India, and you can see these come with specialized goggles and gloves. And you can see why because he's inside the oven. He's getting burned when he's cooking because you can focus on a point, but you're not going to be perfect. So there's a lot of sun hitting him. It's not a very comfortable way to cook. But also you can only cook when the sun's out.

So solar cookers, I think, could play a really big role if you can get them low cost-- these are over $600-- and if you can get them to be able to cook when it's more convenient. OK, so I won't go into those details.

This is the kind of thing we do in my group, and I get so excited about it. We design things in a computer. We make them, and we build prototypes, and it's sort of a full loop here to try to impact interesting energy problems.

Now this leaves me on the last part, which is what I want to talk about in the last 10 minutes of class. Which is, OK, that's a really cool energy problem. You have to agree with that. OK, you don't have to agree with that, but I think it's really cool energy problem. Where does computational quantum mechanics fit into this?

OK, so this is what it does. The fuel goes from here to here. This is the reaction coordinate. It goes from a low-energy state to a high-energy state when you shine the light on it.

Could I calculate-- now this is how much energy it's stored, which is related to the density of the fuel, the energy density of the fuel. Remember, that's something we had to kind of hike up by a factor of three or four. It's not really that good.

Could I have done that with classical potentials? Can I calculate this with classical potentials? What is this? How do I calculate this?

Here's my solar fuel, and this is the trans state, and this is the cis state. What is this difference? How would I calculate this energy difference? How would you do that calculation in a computer?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: No, no, no, this is calculationally. Is that a word? Yeah. Go ahead.

AUDIENCE: So they're both sort of local minima of the potentials.

JEFFREY C GROSSMAN: Yeah.

AUDIENCE: So you could theoretically run some DFT simulation on your trans configuration and run a DFT simulation on your cis configuration and then get out the sort of ground-state energies for the two and compare them.

JEFFREY C GROSSMAN: E cis minus E trans. You bet. That's it. That's all this is-- equals delta H.

Now tell me why you said DFT. Can't I use reacts or a Lennard-Jones potential to calculate that? Why not?

AUDIENCE: The trans and cis may have different types of bonds, so [INAUDIBLE] electrons.

JEFFREY C GROSSMAN: What if I had a super-duper good potential?

AUDIENCE: [INAUDIBLE] for electrons [INAUDIBLE].

JEFFREY C GROSSMAN: But why do I need-- but hang on. I mean, that would be true with all the first part of your class, right? Everything you did in the first part of class, like straining wires and stuff, captured energy of bonds. Yeah?

AUDIENCE: You need to be given the potential to use in order to do a classical simulation. So doing the quantum simulation, you just need to give the configuration of atoms, and then it--

JEFFREY C GROSSMAN: Which is nice.

AUDIENCE: --find the energy for you.

JEFFREY C GROSSMAN: Which is certainly very nice, but let's say I tell you that I'm giving you a really super-duper, really, really, really, honestly really good potential. And that's what it's called in the literature. I put the word honest in it. Could I calculate this with classical potentials? It's a difference of energies between two molecules. Can I calculate that with a classical force field? I'm seeing some of this and I'm seeing some of this.

Well, actually yes. You could calculate the energy difference between two molecules using classical force fields. What you have identified is the challenge of doing that, which is that it's only going to be as good as the potential. Can the potential accurately represent these two? Well, you compare with experiment. You compare with higher-level theories and you'll know. But what if it can? What if it can't? Well, then this is perfectly reasonable to do with classical force fields. I don't need electrons to calculate this. I just need the right energies, which is what classical force fields are trying to capture.

Now, there's a key here though. By the way, you could even get this using a good-- if the classical force fields were good enough, you could get the back-reaction barrier, the activation energy.

I want to make sure that we understand context here. When you do a simulation, when you do your computational materials research, it's not a one size fits all kind of thing, and it's not even a one problem, one method kind of thing. You can have one problem with different properties that require different methods.

And which is the right method to use? Well, very often the answer to that is whichever one is accurate enough for the problem at hand and fastest, and so that's where you have to know-- you have to test and know where you sit in accuracy phase space with a given method, and then you go ahead with it.

And if you can find a classical potential that seems to represent this class of materials well and you can validate that it's getting this, by all means use that because it's going to be a whole lot faster than DFT. However-- I should do that more because it kind of felt good. It actually kind of loosened my shoulder, made me look silly.

There are things here I can't do as classical potentials, not even if I really, really close my eyes and dreamt it. They wouldn't happen. What would that be?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: Yeah. So you're saying there's a hint here. This is what I'm shining on the molecule. Who's seen this before? Yeah, you're feeling it. This is the sun. This is how much energy comes to us from the sun. And you can see that it's dependent on the wavelength of the light. That's pretty cool, right?

And you know what's really cool are these big, huge gaps. See, this is if you go outside of the earth's atmosphere, you get this yellow line. But on the planet, we get this red curve. We get all those parts blocked out. You just don't get that frequency of light on the earth. And the reason is because you have these molecules in the atmosphere that are blocking that part of the sun's spectrum. Isn't that pretty cool? But this red is what we get on the planet.

And the question is how do these molecules do in capturing that energy? This is how we're going to charge them. This is how we're going to charge them up. Now that is related to something else that's not here. What might that be related to? The band gap, exactly. Exactly. That is related.

So this all comes back to where those electrons are. So remember, we filled these electrons up. I'm just making them-- just for simplicity, I'm not labeling them s, p because I'm not talking about a particular thing here. And then we filled them all up. There were 10 electrons, and we filled the levels with those electrons, and that was it. But there's another level up here, and there's many more levels up there that don't have electrons.

And this distance here in energy between the highest occupied and lowest unoccupied level, the HOMO/LUMOS, that's called the band gap. This is called the Highest Occupied Molecular Orbital, and this is the Lowest Unoccupied Molecular Orbital. And the difference between them is the gap, and that is so important for optical properties and electronic properties-- transport of electrons, absorption of sun. In this case, we care about the absorption of the sun much more than transport of electrons.

Now the reason that's so important is you see it goes back to the hydrogen atom. Somebody tell me a weirdness thing about looking out into space. What do you see when you look at the colors of hydrogen? They're discrete. Why?

AUDIENCE: [INAUDIBLE]

JEFFREY C GROSSMAN: Yeah because, remember, here's your electron. It can only be in these quantized levels. It can only be in 1s or 2s, and it cannot be in between. Remember that?

How does that relate to the absorption of sun by a solar fuel? Well, it's the same idea. You see, when you absorb sunlight-- see this H new? Sunlight came into this trans state, and it made it go up onto another energy surface. That got it to twist.

Now when it absorbed the sunlight, what really happened is that the sun's energy came into the molecule and it kicked an electron out of some happy place. It's just hanging out with its buddies, and a photon comes in, and that photon kicks it up here, and that's what does it. That's what makes the molecule change its shape, that electron getting kicked up into one of these other states.

Now the key here-- and this is what's related to the hydrogen atom-- is that you see you can't-- if you just shine-- so let me try to draw this a little bit more clearly. These are occupied levels, and these are unoccupied levels, and this is the gap. So these would be occupied, unoccupied.

You cannot shine light. If I only have enough energy from the photon to take an electron from here to here, well, you're in no man's land. You're just like that electron in the hydrogen atom trying to go in between a 1s and a 2s orbital. You can't do it. There is no state here. There's no wave function there for the electron to be it. And so there is a gap. That is the minimum energy it takes, right?

So how is that now related to this? Gap is related to absorption how? So this is actually wavelength. So the energy gap goes as 1 over this, right?

AUDIENCE: So for a molecule only has a certain range over which it can absorb light?

JEFFREY C GROSSMAN: Exactly. Actually, for now we're just saying it has a minimum energy below which it cannot absorb any light. No photon below this energy can do anything in terms of exciting these electrons up. So the photons have to be above that, which means they have to be-- if they have to be above a certain energy, then they have to be below a certain wavelength. So there's some-- does everybody see there's some lambda max where they're not going to absorb any more? So beyond some point here, they can't take any of that sun. That's it. Does everybody see that? They cannot absorb that sun.

Now would it be good-- if lambda max were up here, would that be OK? Seems like it, but there's a real problem with that, which I'll come back to probably next Tuesday. But what would happen if lambda max were here?

AUDIENCE: You're missing out on a lot.

JEFFREY C GROSSMAN: You're missing so much of the sun's energy. You just can't-- because of quantum mechanics, that darn quantum mechanics and that electronic thing that you cannot get from classical potentials, that electronic gap, you cannot absorb light beyond the gap. Which means if your gap is here in energy, all of this part of the sunlight is completely wasted.

So I'm going to spend a little time on this on Tuesday because there's some really cool questions about these photo switches that we're going to use quantum mechanics to model in the homework. And so I want to spend a little more time on this Tuesday, and then I'll talk a little bit about hydrogen storage. So we're going to pick up with this picture on Tuesday.