

## MITOCW | 5. Application of QM modeling: Solar thermal fuels (II)

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**JEFFREY C.** All right. So we are here. I'm highlighting two, because I really want to keep talking about solar thermal fuels, mostly because it really captures a key problem that only quantum mechanics can solve. OK? So I really want to hit that home hard.

Also, because it's the topic of your next homework, and also because I'm biased. I'm more excited about this than this. But I want to tell you a little bit about hydrogen storage too, and why I think that's a perfect problem for atomic-scale computational modeling. OK? So we're going to do a lot more of solar thermal fuels, picking up where we did before, and then a little bit of hydrogen storage.

Now, before we do that, I want to keep blending in some reinforcement of key basic concepts that we have touched on, and we need to make sure we feel good about them. So we're going to feel good today about energy levels, first bullet of the outline, feeling good. It's a good way to start, I think. I didn't need to put that there, because you would have felt good anyway. Right? But there it is in writing.

We're going to feel good about energy levels, and then we're going to keep talking about solar fuels. And we'll do a few calculations, more calculations on the nanoHUB together. Right? Again, no better way to pass time. OK? And then we'll talk about hydrogen storage. That's our plan.

Now, like I said, I want to keep reinforcing-- I did this, and it put me off balance. It's excitement. That's a little bit more than my usual even. It's also, I think, just old age. I think sometimes, you get a little off balance. Anyway, now, point is that I think probably I like watch the NBA so much, because I still don't want to give up the idea that I could someday be in the NBA myself.

So I'm not letting go of that dream, but anyway, I want to go back to one of my original excitements here about materials design which is one of the things I really want to make sure we capture in this class, designing materials and computers. Right? So I want to take carbon, and I just have two or three slides here. So I want to touch on what I think is a really exciting example of materials design, and you all know this. Right?

You know carbon can do this and this, and many of you know that carbon can do-- well, where are my fullerenes? Well, there's some nanotubes. There's fullerenes inside of nanotubes, p-pods. Right? Now, there's all kinds of forms of carbon that there didn't used to be, or there used to be, but we didn't see them, and we couldn't control them. OK? And I want to give you a really, I think, interesting analysis of one thing you can do with carbon. OK?

And then another thing you can do with it, when you design it, when you can do materials design. So this is what we do with carbon now that we find in oil. Right? We burn it, and there's 1.73 megawatt hours of energy when you burn a barrel of oil. Right? I didn't show you this example. Did I? OK. Because I think it's a really neat one.

So that's how much energy is in a barrel of oil, and it's a lot of energy. That's a really nice-- oil is amazing. It's like this incredible energy-dense, safe, transportable, storage system. Right? It's solar powered. Right? You all know that it's made by the sun, but it's not renewable, which is a problem, but it's a really beautiful fuel.

Now, oil has a lot of carbon in it which is what's burning there and giving you that energy release. But there are other things you can do with that material, and one thing you can do is you can make these other forms of carbon from the oil. In fact, that's how we make a lot of our plastics. OK? We make a lot of plastics using oil.

If I take 1%, just 1% of the carbon in these 159 liters of oil, just 1% of it, and I make that into plastic, then because I know how to design carbon to be something else, like fullerenes, I can make polymers and fullerenes out of that same element carbon and put them together-- gesundheit, whoever that was-- and make solar cells, new kinds of solar cells, in fact, solar cells made out of mostly carbon. If I take 1% of that carbon that was in here, and I turn it into this, which we now know how to do, then I can make really bad solar cells. 5% efficient, not so good, die in one year, not so good. right?

The efficiency goes down. Most solar cells, you get a 20-year warranty. This one, one-year warranty, then efficiency is gone. Even in that case, this solar cell over that one year of really crappy efficiency will give me 10,000 times as much energy than by burning the carbon, 10,000.

Now, these are hand-waving arguments that are back-of-the-envelope calculations, but when you've got five orders of magnitude to play with, things are good. Right? And this is an example in the energy space. This is why I get so excited about designing materials, and this in particular, this is only 100 nanometers thick. Right?

The solar cell's thicker, because it's packaged but the active layer, the part of the material that's making the sun turn into electrons and holes, something we're going to talk about in our next example, in a few weeks. That part is 100 nanometers thick. That's atomic scale. That's the atomic scale.

You can't pack that many polymers and fullerenes into 100 nanometers. Things at the atomic scale and the quantum mechanical aspects of that material are critical, and designing that material is something you can do using atomistic modeling. So this is what I mean. You want to give elements completely new possibilities, and you can see the power of doing that. It changes the way we know how to use those elements, and I think that's just a very powerful concept.

OK. Any questions about that example. So that's my little my material design example of the day, if you will. We should make like a calendar, each day a new--

OK. Now, I want to pause and feel our oneness with energy levels and basis sets. So this is, again, going back to some important key elements of the computations, and then we're going to come back to the calculations and the example of the solar thermal fuels. OK? Now these are things that we have talked about, but they're so important that I want to talk about them again and make sure there's no questions. Make sure that we are all on the same page and know what these things mean. OK? So I want to give you, this is my attempt at summarizing our beautiful path to the energy level. OK? So let's make sure we're with it. All right?

So it all started back in the day in lecture one with the Schrodinger equation. Does everybody recognized that? Now, that is the equation we're solving. When you click Simulate to calculate the energy versus separation in say, I don't know,  $n=2$ , then the equation that's being solved in a computer is this one, the Schrodinger equation. Now, what are you getting out of that equation? Well, what you're getting are what? These, what are these?

**AUDIENCE:** Wave functions.

**JEFFREY C. GROSSMAN:** OK. Thank you, and why do I want those? What do they tell me?

**AUDIENCE:** Probability.

**JEFFREY C. GROSSMAN:** OK. Yeah. They tell me the probability, and they tell me more than that which is what we need to make sure we understand. So you see, solving that equation gives me wave function, and the wave functions, well, they're waves. Right? They have some shape to them.

They may change in time. Do we care about that? Not in this class, not in this class, in this class, it's all time independent. So we're doing like a snapshot, but they may change in time. But they certainly vary in space, and that is  $\psi$ . Right?

Now, what we talked about is how these wave functions themselves, we don't know how to draw physical meaning from. That doesn't mean that they're meaningless, and this is a really important point that we have to feel good about. OK? So I'm going to come back to that, but we know that when you square them, we know what they mean, and that's this. Right?

So what are these? Do you guys remember what these are?

**AUDIENCE:** Orbitals.

**JEFFREY C. GROSSMAN:** Orbitals, such a bad name, but anyway, because why is it a bad name?

**AUDIENCE:** Because they don't really orbit.

**JEFFREY C. GROSSMAN:** Yeah, totally, but anyway, these are orbitals. So these are those wave functions squared for what? Who knows what-- but what system is this? These are the atomic orbitals of a hydrogen atom, one electron, one proton. OK? You can solve that analytically.

Now, so we said, OK, well, this gives us like an electron sitting in one of these little wiggles. OK? We said that they go up in energy. They have different energies. That's really important. Each wave function you solve for has a different energy. Right?

So you get these functions, and they have different energies, and there it is for hydrogen. There's the energy for hydrogen. It just depends on  $1$  over the principle quantum number squared. Right? Remember, we talked about how it's quantized? But these little wiggles, when you square them, they give you the picture of where that electron is going to be, where it's likely to be. And we looked at how the shapes got more complicated, and what are these type of orbitals?

**AUDIENCE:** P

**JEFFREY C. GROSSMAN:** p? And then it goes to other things, d and then f. And then we said, OK, that's nice. That's great, but also there's this thing called spin. OK? And somebody remind me what spin is.

**AUDIENCE:** Property of the material.

**JEFFREY C. GROSSMAN:** Property of what thing in particular? Yeah?

**AUDIENCE:** It's some intrinsic angular momentum that a particle has.

**JEFFREY C.** OK.

**GROSSMAN:**

**AUDIENCE:** Regardless of its motion.

**JEFFREY C.** And if that particle happens to be an electron, what are your options?

**GROSSMAN:**

**AUDIENCE:** In the first one?

**JEFFREY C.** Yes.

**GROSSMAN:**

**AUDIENCE:** Plus or minus.

**JEFFREY C.** Plus or minus. It can only be-- or as we like to say up or down or as we like to draw this or that. Lots of ways of doing this, but I think you get the point. And then we talked about poly which gave us rules for how electrons can be together in one of these orbitals. OK?

**GROSSMAN:**

So you have wave functions that wiggle. We don't know how to interpret what they mean, but we know that their square gives you the probability distribution of that electron. And we know that these electrons also have another important quantity associated with them, a spin, and the spin can only be one of two values, up or down. OK?

That is the information we need to go to energy levels. OK? To this point, this is a review, but it's about to be-- well, maybe something some of you know, but it's about to be a little different. OK? So I want to make sure we all understand this.

Once I know that you can have two kinds of spin, and once I know that you get energies out of this equation, then the answer to the energy levels, to what energy levels are, is there are these things that you fill. There are these things that you fill with electrons. How do you fill them?

I keep blocking the screen, but it's fun to go in there. It makes me feel important maybe. I don't know. Never mind.

How do you fill them? I'll use this. Oh, yeah. What do you do here? What's going on? I want to fill these orbitals. Do I fill this one

**AUDIENCE:** You start at the lowest end and work to the highest.

**JEFFREY C.** Yeah, and when do I stop?

**GROSSMAN:**

**AUDIENCE:** When you run out of electrons.

**JEFFREY C.** When you run out of electrons. How many electrons did I have?

**GROSSMAN:**

**AUDIENCE:** 29.

**JEFFREY C.** It depends on the atom or molecule which is where we are now or solid. Now, that is really in a way-- the reason  
**GROSSMAN:** I'm focusing on it is this is the key quantum mechanical nature thingy, property of materials, I want you to come away with being able to understand and calculate in this class. OK? It's these energy levels. This is the most important thing I want you to come away with from this class. Why?

Well, we can calculate other things, and I've talked about that. We can calculate energies. We can calculate binding energies. We can calculate all kinds of things, but these energy levels are purely quantum mechanical. Right?

There where those electrons want to be in energy, and they matter so much to the properties of materials. So I want to focus on these and connect them to real exciting problems. OK? And make sure that you understand where they come from and also how to calculate them and what they can mean.

So that's where we are. So that's why I keep drawing things like this. You see me just drawing this. Right? Now, what did I draw? I don't know. I drew a bunch of levels. Right? If I'm a little more careful, and I do this, now what am I drawing? What is that?

**AUDIENCE:** Energy diagram.

**JEFFREY C.** Energy diagram. OK, good. What is it though? Do we know?

**GROSSMAN:**

**AUDIENCE:** Like there's no electrons in there.

**JEFFREY C.** OK, and it's the solution to which problem? Actually, this is infinite square well. So that's not the hydrogen atom,  
**GROSSMAN:** but those are the energy levels you get for the solution of the hydrogen atom. OK?

Now, if I ask you what this is though without putting any electrons down, we don't know, but what if I do this? Now, what is it? Hydrogen, what about now?

**AUDIENCE:** Lithium.

**JEFFREY C.** Lithium, what is this? Oh, I love this one.

**GROSSMAN:**

**AUDIENCE:** Carbon.

**JEFFREY C.** Carbon, carbon, it's a beautiful material. I love carbon. OK? I almost feel like you need a little moment. When you  
**GROSSMAN:** draw the energy levels of carbon, you need a little moment of respect.

Now, but you see, this is what we did. We solved for these wiggles. We got energies, and we put them in order from lowest to highest. And then we said how many electrons do we have? Six, OK, fill them, and then there are rules that we talked about about how you fill them.

Now, why am I going through this? Well, because that is only good for what kind of material? That is only a correct picture for what kind of material? Atoms, that's an atomic picture.

We solve for the atom, and this is true-- and remember, I said that we can solve for the hydrogen atom and see the whole periodic table. Right? Powerful stuff, but this is only an atom. These are how you would fill the energy levels of an atom, and we've talked about this. But see now, we're going onto other things, where you bring atoms together, and you form molecules.

This is not a chemistry class. So I'm not going to spend a lot of time telling you about sigma orbitals, pi orbitals, bonding orbitals, antibonding orbitals. That's not what we're about, but I do need you to understand that, when you bring atoms together, the orbitals from those atoms come together and form new orbitals. They form molecular orbitals. OK?

Now, in this case, you're seeing the H<sub>2</sub> molecule, and this is from this website. There's lots of great websites that talk about molecular orbital theory. OK? And in this case, you brought two s electrons together, see, from a hydrogen atom over here and a hydrogen atom over there, and they drew those energy levels.

And then they brought them together, and it turns out, when you bring to 1s levels together to form a molecule, you get two new levels. Right? And the chemists love names, and so they gave this one a sigma 1s, and that's a sigma star 1s. Those are just two new levels that are formed, when you bring these atomic levels together.

Now, all the same rules-- and one of them, ah, two points-- one of them is a bonding orbital. See, this actually looks like I brought two circles together, and they overlapped. That's a bonding orbital. OK?

Another one of them, though, is an antibonding orbital. All right? And an antibonding orbital is higher in energy. So it's going to come up higher. Its energy is going to be higher than the bonding orbital, when you bring two orbitals together.

And often, an antibonding orbital will actually have a node, which means there's zero chance of any electron being in between, exactly in between. That doesn't sound very binding-y. Right? Doesn't have a lot of appeal for bonding, if there's like a plane of no existing.

Now, why would that be possible? Doesn't it seem from this picture-- I took to 1s orbitals, and I brought them together. Right? How can I get a node between them?

**AUDIENCE:** Is it [INAUDIBLE]

**JEFFREY C.** Not quite. What is it?

**GROSSMAN:**

**AUDIENCE:** Coulomb repulsion.

**JEFFREY C.** Yeah. It is actually. It does have to do with Coulomb repulsion, but there's something more basic here at play.

**GROSSMAN:** How is it that I can bring two spheres, probability spheres like this together and have two orbitals that form, one of which has a node in between, and one of which is like really nicely happy bound.

**AUDIENCE:** [INAUDIBLE]

**JEFFREY C.** Not quite, any other? Yeah?

**GROSSMAN:**

**AUDIENCE:** It looks like the infinite square well there. You've got the ground state that doesn't have any nodes and then the first excited state does, the same deal.

**JEFFREY C. GROSSMAN:** Exactly. Well, so that's exactly right. We're not bringing together probability distributions. OK? That is not the right way to think about it. I won't stand in front anymore.

We're not bringing together probability distributions. We're bringing together wave functions, and then when those come together, they form a probability distribution or two, in the case I just showed you. And we all know that, when waves come together, they can do what and what?

**AUDIENCE:** Construct and deconstruct.

**JEFFREY C. GROSSMAN:** Exactly. They can construct, and they can deconstruct one another. Sounds like they're going to have like a philosophical discussion. So that's what's happening. We're bringing the wave function together, when we bring atoms together and molecules together.

We're bringing their size together. Oh, size, you can't get away from size being so important, and we're solving for the collective  $\psi$ . And when you bring waves together, they have phase, and they can form constructive and destructive interference, as we talked about in lectures one and two, and that's what's happening here. And then you square those, and you get new orbitals which have those properties. OK?

So this is the simplest example which is  $H_2$  molecule, and then we fill those orbitals. And when we fill these orbitals, when we draw them for a molecule, very often, I'll lose this notation, because there isn't-- and I'm not going to go through this notation, mostly because I can't remember past sigma and pi. But there's a whole lot of notation out there for molecular orbitals, and it depends on the symmetry and the group symmetry of the molecule you're working with, and there are rules and all that stuff.

But all we're going to need in this class is to know that, when you have a molecule, and you calculate this wave function which gives you the wiggles. And then you square it, you get the distributions, and that helps set the energy levels. It tells you where those energy levels are going to be, that will just draw them like this. Right?

Now, this is how I'll draw molecules, the energy levels of molecules, and again this is it. This is one of the most important properties I want to focus on, because this is everything. This is where those electrons are in energy space, and I can plot them. I can look at their energy, and there's all kinds of important information here. OK? And so what this means is usually I'll leave a space here. Does anybody know what this is called?

**AUDIENCE:** Gap.

**JEFFREY C. GROSSMAN:** Right. This is the gap, because that's how many electrons I had in my molecule. Not my atom, but in my molecule. So I do the same thing. I calculate energy levels, I fill them up, and I stop. I apply some rules, like you wouldn't have one level with two electrons up, Pauli exclusion. Right?

And then I stop, and then there's another level beyond that. Oh, that's important. So we're going to talk about that today. There's another level beyond that that's not filled, but the distance in energy between these is called the gap, and it's really important.

And the energy gap is what determines all kinds of properties about a material. It determines how it absorbs light. It determines how it conducts charge. It can determine things about its magnetic properties, certainly transport properties.

And what's going to happen, and that's why I really want to make sure we all understand this for a molecule. What's going to happen is, when we go to solids-- on Thursday, we're going to start talking about moving to solids-- this is going to happen. These are no longer simple lines. These go like this, and that's really cool.

That happens because you're putting them in a periodic arrangement. That's called a band structure. It doesn't happen for molecules. They're just little flat lines, like they are in atoms. OK?

So are we all good with this? Are there questions? Energy levels, energy levels, need to know about energy levels. No questions? Yeah?

**AUDIENCE:** So when you put up every central gas and you calculated all the total energy, if you like have big molecules--

**JEFFREY C.** Yeah.

**GROSSMAN:**

**AUDIENCE:** --you got huge gap and it's harder to identify that.

**JEFFREY C.** Which one? What's harder to identify?

**GROSSMAN:**

**AUDIENCE:** Ammonia. Because if you have one more unit, for example--

**JEFFREY C.** One more.

**GROSSMAN:**

**AUDIENCE:** --some group.

**JEFFREY C.** OK. So you put an electron here? Or what do you mean?

**GROSSMAN:**

**AUDIENCE:** So when you calculated the wave function--

**JEFFREY C.** Yeah.

**GROSSMAN:**

**AUDIENCE:** --how did you know the electron wave function for this type of ammonia?

**JEFFREY C.** Well, that's-- Yeah. So that's where really lecture three covers that. Where basically, you need to use an approximation to the Schrodinger equation, and that approximation that we're using in this class is called density function theory. But then you simply what goes into that equation is the approximations you choose, and the positions of the atoms and the number of electrons.

And once you have that, you basically are solving for the psi. You're solving for these. Right? And you get them and their energies out, and it's in the outputs of the nanoHUB runs. OK?

Now, one last thing before we go back to solar fuels that I want to make sure we feel our oneness with are these basis functions. So this is a slide from another lecture, an older lecture, but I just want to be sure we understand what we're doing here. OK? So we said we needed to make size for our materials. We need the code to give us  $\psi$ .

Now, for a hydrogen atom, these are analytic functions. Right? They're like sines, cosines, but for more complex material, a complex atom, they can look like this. They can be really complicated. OK?

So but a computer can't just draw lines. Right? A computer can't do that. It needs to have some mathematical representation for that function, and that's what a basis set is. But as I stressed last week, this is a new sort of not a problem, but it's a parameter that is not present in classical simulations. But it's one you have to be very carefully aware of, and you have to know when you've converted it. OK?

And the question came up last week of when is a basis set converged? OK? And what do I mean? Well, I can make a basis out of anything-- Gaussians, exponents, plane waves. I can make a basis out of wavelets which are really interesting hat-like functions.

But I can take any function, and if I add enough of them in the right places, and they have the right width and size, I can recreate a curve. That's what we're doing, but I want to have as few as possible. OK? So this is a basis set study that somebody did and randomly put on the web, which I randomly found and didn't credit, which I should have.

Anyway, this is the number of basis functions going this way, number of basis functions, and that's the energy. And you can see that the energy is going to change, as you increase the number of basis functions, and there's this thing called the basis set limit. Sometimes it's called the complete basis set limit, and that complete basis set limit is basically just saying, hey, I've represented my wave function now numerically correctly.

So infinite number of basis functions should give you that. We don't have enough computer time to have that many basis functions, because it gets really long and slow. So we don't do that. Usually, we do calculations out here, and maybe we extrapolate. OK? Or we just do a few cases, and we say, well, my results are converged.

But when is a basis set converged? It's a really important point of quantum mechanical-- hey, that would be like a good quiz question. Right? Like it's a really important part of quantum mechanical simulations are always a quiz question. It's not a bad one. Is it converged here, or is it converged here? You know what answer I'm looking for.

**AUDIENCE:** Depends on the problem.

**JEFFREY C. GROSSMAN:** It depends. I love that answer for this class. It depends, because here, I'm plotting the total energy of the whole system, but is that what I want? Is that what I'm calculating? I don't know, maybe, but what if I'm actually calculating this?

What if I'm calculating the gap between the highest occupied and lowest occupied level? Well then, I should plot that versus the basis set, and that, this line, the total energy may converge like this. Whereas, if I do the gap, it kind of goes-- maybe it's here, and then I get another value here, and then everything is fully converged all the way in.

So the gap value converged there. You don't know. Different properties will converge differently, and you start to get a feel for it, as you do more calculations. I'm not expecting you to get to that point in this class, but I want you to understand this. It's really important. OK? So basis sets must be converged. That's one point.

This can lead to big tables. Chemists love big tables. So it's actually a perfect fit. So you see papers like this. Oh, you can go to [bse.pnl.gov](http://bse.pnl.gov), and let's see, maybe I can just go there really quickly.

And you can see, oh, look at that. There's the nanoHUB. We're coming. We're coming, and look at this. Oh, this is beautiful. See, many basis sets have been made over the years. Right?

And so here, they are. Look at all these basis sets for different-- and you see, I can scroll down here. Look at these basis sets. You have a few of these to choose from in the nanoHUB, but look at how many there are.

These are all published basis sets, and you can go to a place like this. And you can click on one, like 3-21G\*, and you can click on-- well, I don't think that-- and you can say what code am I going to use? Right? And then, you can say get the basis sets, and there they are.

And there are the papers, where basically, they're trying to say what is the fewest number of Gaussians that we can use to represent these atoms? So basis sets are fit to atomic orbital wave functions. OK? And this is just a certain form, where you have the exponent of the Gaussian and a coefficient of the Gaussian. And I'm not going to go into details, because we don't need them. OK?

There's a lot of work on basis sets. There's also a lot of papers that were published in the 1970s and also '80s using basis sets, like this, that show really good answers using like Hartree-Fock theory or density functional theory even but for the completely wrong reason. Because they used a level of theory that wasn't accurate and a basis set that wasn't converged, because the computers couldn't go to larger basis sets, and so the errors canceled. So there are many papers with really nice agreement with experiment from theory that are complete nonsense, because they're using very inaccurate theory and really bad basis sets. And so the errors cancel, and you get beautiful results.

It's something that we need to be aware of and understand in this class, but we're not going to go into great detail in all these different basis sets. But you can go there, and there's just a lot of information there. And you can play around, and you can make big tables like this. I don't recommend that you do this.

But this was a study, this is like the kind of thing-- I think that some people really like big tables. This one goes on and on and on, by the way. It never stops. It almost never stops.

And you see, different levels theory here. These ones we haven't talked about. That's LDA, Hartree-Fock and then different basis sets. You see? And some property, the binding energy and some other properties that they care about. OK?

Yeah. Not expecting you to do that, but I want you to be aware of how big of a concern this is in quantum mechanical calculations. Any questions about basis sets? Basis sets. The last theory point, last question I want to ask, so we asked, with basis sets, how do we know when we're converged? Well, it depends.

When you add more basis functions or do a larger basis and things don't change, you've converged. But there's another bigger question, which is how do we know when the calculation is right, that we talked about here. Now, this is very important, and it goes to the point I just made. Just because you agree with experiment, if you're not doing your calculations carefully, it can be still dangerous. OK?

But let's suppose that you have done your calculations carefully, and you have converged your basis set. And you have checked everything else about your code, and you're asking the question of which of these structures of carbon-- remember, I really like carbon. Which of these three structures-- a ring, a kind of bowl, or a cage-- gives you-- is most stable for 20 atoms? That's a pretty simple question. Right?

This is the question I asked as a second-year grad student, a few years ago now. Who laughed? Sam? And it was really cool, because see, you could try one level of theory and work really hard to converge it completely. And you'd get, for example with LDA-- something you can do on the nanoHUB-- you would get that the cage, this guy, is the lowest energy. This means the most stable.

And then you would do another level of theory, Hartree-Fock or this other thing that you also have, this is called the GGA. It's another flavor of density function theory, and you would get exactly the opposite. You would get that the ring is the most stable, and the cage is the least stable.

So what's going on? What's going on? Two different DFT functionals gave me completely different answers, and I've converged everything.

**AUDIENCE:** Two more functionals.

**JEFFREY C. GROSSMAN:** Two more functionals. Now, that's actually a really good idea, and it's actually what people do. OK? In fact, you see, if you go to-- I think I left this web page open. Here's one of the codes that does density functional theory and other quantum chemistry calculations. It's called Gaussian.

And if you look in their 2009 version, this is a code you have to pay for. There's lots of codes that are free, by the way. NWChem, if anybody wants to play with a code, download it, that does quantum chemistry, that's a pretty darn good one that's free which you can download, and there are others. I'm happy to provide a list.

But look at the number of functionals you have to choose from. OK? Here's a little bit about density functional theory and the methods, and then here are the functionals. exchange functionals. You see S, XA, B, PW, G96, PBE. That's one of the ones on the nanoHUB. Right?

And correlation functionals, VWN, LYP, B95, and so what you wind up getting-- and then it goes on, standalone functionals, hybrid functionals. OK? Here's some more. User defined functionals, you can actually make up your own. Right? So here's a short list of some of the keywords you can enter and get different functionals out. So now, what do I do?

**AUDIENCE:** All of them.

**JEFFREY C. GROSSMAN:** All of them. Well, sadly, I think some researchers do that. So here's the broader point. OK? Density functional theory is an approximation in the way that we use it in our codes. The actual theory itself could be exact, but the way that it has to be implemented requires this approximate functional, as you learned in lecture three. OK?

What functional do I use? Well, some of these have been well tested for broad classes of materials and are known to do well for certain properties, certain materials, and known to do not as well for others, but it's mostly empirical in terms of our understanding. It's because it's been tried for many systems. OK?

And so in a way, we're a little bit back to the classical world. In the sense that density functional theory is a beautiful theory, but to make it practical, you have to make approximations that make it so that you have almost an empirical nature to it, or a semi-empirical nature which is what you have in classical force fields. Right? In classical force fields, the potential is as good as the complexity of the potential and what you fit it to. Right?

Density function theory is, I think, much more powerful, in the sense that you can really solve for the electronic structure, but we have the same kind of problem in density functional theory. So the functionals that I've given you on the nanoHUB are some of the most popular ones, but you always need to be aware-- [NON-ENGLISH]-- of the fact that we're making an approximation. And yes, one way to check is to try two functionals, and if they don't disagree too much, you may be OK. That's not the most gratifying way to do it.

Another way would be to compare with experiment, and that's actually the most gratifying way. Once you converge everything else, if your functional agrees with experiment for the kind of problem you're trying to solve, then that's a pretty good indication that it's an accurate solution to the Schrodinger equation, but you are making a approximations. OK? And that is something that we won't-- as you can see, I don't give you much options on the nanoHUB, because I don't really want to go there, but I do want you to be aware of this.

We are not solving quantum mechanics exactly. We cannot, and with density functional theory, there are some systems. So in my graduate days, I worked on a method that goes beyond density functional theory inaccuracy. So it's a very accurate method, very slow but very accurate.

And so I was purposefully looking for systems where DFT fails, and I was very happy with this one, where you basically don't know the answer. You can try functionals, and you'll get all kinds of different results. So the only thing you can do in that case is go to a higher accuracy method. OK?

What I found out is that this method here is the most accurate one, that actually none of the functions were right, and the bowl was the most stable. So it's pretty cool. It was exciting. What can I say? I was a physicist at the time, so you know. I won't say anything more.

OK. Now, let's go back to our first application example. Does everybody remember this from last week? OK. So let me make sure we know why. OK. I want to make sure we understand why this is such an important problem for quantum mechanics. OK?

So sun shines on a molecule, the molecule changes shape, and that changed shape is a higher energy. So if you draw the reaction, if you draw the reaction coordinate for this system, it looks like this. OK? So that would be the trans state and the cis state, and this is the higher energy that that forms, and it stores that much energy in the molecule. OK?

Now, what we found is that there's all these molecules that do this, but they're not very good solar fuels. OK? So there's lots of them that do this trans to cis photoisomerization. So the sun makes it go, or light makes it go, from one state to another. None of them are good solar fuels on their own, but we found this way of making them in general into good ones.

And this is a slide I skipped last week, so I want to just very quickly explain this again. Because it's really important to understand why we're so excited about this. If you put these molecules that switch back and forth onto a template, and the template can be anything, but here it's a nanotube. But if you put them onto it, and you covalently bind them-- that means you attach them really strongly, so they're not going to come off. Then, what you've done is you've packed them in a way that they're not able to get out of.

So you've packed them together, and they're not allowed to get out, because they're covalently bound. Some self-assembly work is weakly bound. Some is not. Here, it's really strongly bound. So they're really forced into this packing.

Now, what does that mean? Well, look up here for a minute. It's a little busy, but look at that cyan curve, the light blue. This is the spacing that they're packing on on this template.

This is it, 4.2 angstroms. OK? And that's also exactly the minimum of that molecule, when it's in the T state, here. When it's in the T state, it's happy at that spacing. It's happiest. Right?

But when it's in the cis state, you see the cis state has a different spacing that it wants to be at. That's the red curve. Right? These are the kinds of curves you should be getting in your homework for problem two.

That's the curve for the cis state, and you can see that it's a happy place is much further out, but it can't be much further out. It does not have that flexibility anymore. So you've constrained it to always be in the trans, happy place, in terms of its spacing.

Now, what that means is that, you can see right away, what that means is that, when it's in the cis state, the energy of the cis state is going to be higher. So already, what you've done is you've made this state go up, because you've sterically inhibited it just by forcing it to be this close and never further apart. In the gas phase or in solution, when it goes back and forth between trans and cis. It's always going to find its happy place. They're not going to worry about this, but here they can't.

But as I mentioned last week, much more importantly even, when you're in this highly confined geometry, this highly constrained rigid packing, what you can do now is you can play chemistry between them. So I can actually create functional groups on these molecules that bond them to each other and to themselves in different ways, depending on whether they're in the cis or the trans state. OK? And what that does is that allows me to lower this and lower this. That's the key. OK?

So now, because the key is, remember, goal is to increase this and this barrier. Going back, we want to be able to tune it separately. And you can see that, if you just look at this reaction coordinate, if I increase  $\Delta H$ , it looks like I'm going to probably decrease the activation barrier which is not a good thing. Because that's related to the stability of the fuel, when it's charged, the lifetime.

These molecules on their own last in the charged state for a few minutes. That's not very useful. So what we'd like to do is to be able to change both, and this trick allows us to do that.

We push this up from steric inhibition, but we pull it back down from reactions. We pull this, from interactions, we pull this down even more, because we can customize the interactions that happen between these molecules and within the molecule. So that's the key. That's the magic sauce. Right?

Now, all that is fine, except that, as I-- OK. So we have this new class of materials we're very excited about. We're making them in the lab. We're designing them on a computer. They're going to save the world, or maybe they'll just de-ice windows, but anyway, that's very exciting.

Now, all of that can be done using classical force fields. You can calculate  $\Delta H$ . You could try to get a good model of potentials for these molecules. You could maybe try different potentials and see when it agrees with experiment and all that and try to explore this phase space using classical force fields. That is accessible.

You may not-- *gesundheit*-- you may not be accurate. You may have some worries about validating the potentials and all that, but you can do this with classical force fields. You can get energies as a function of these twists in the bonds and try to engineer it this way, but you cannot talk about the optical properties.

You cannot do that using classical potentials. You need the electrons, and this goes back to our energy levels. OK? So now, it will come in to play here. We're going to go back to energy levels.

You see, I can make a really dense energy fuel, a really highly energy dense fuel, but if it doesn't absorb the sunlight efficiently, then I can never charge it. Right? So that's a critical part of this. If it doesn't absorb sunlight well, it's useless to me. OK?

Now, so this is the thing that we've been talking about, but that part can be looked at with potentials, if you wanted. This part here, where you absorb the light, cannot. So here's the light that comes down to Earth. Right? We talked about this. That's the solar flux.

And the key point here is that-- I keep that? We don't need that anymore. The key point here is that those molecules have energy levels, like this and like this, and they have a gap. Right? These are what we call occupied, and these are unoccupied. Unoccupied levels, occupied levels, I just don't want to draw the arrows, and that's the energy gap.

Now, why does the energy gap matter with respect to this picture? Yeah? At the same time-- one, two, no. Go ahead.

**AUDIENCE:** Because all the absorption are at certain frequencies-- or certain light coming in at frequencies with great enough energy that surpass the energy gap.

**JEFFREY C.** Why? That's really good. That's exactly right.

**GROSSMAN:**

**AUDIENCE:** So it's too low. It's not enough energy to shut it off from occupied to unoccupied.

**JEFFREY C.** Yeah.

**GROSSMAN:**

**AUDIENCE:** I mean, too low of energy.

**JEFFREY C.** Too low of an energy, right? So this is energy going-- this is wavelength going that way. So energy goes this way.

**GROSSMAN:** OK? Right? So there is going to be some minimum energy below which you can no longer absorb light. The molecule is transparent.

That is the energy gap. That's this energy gap here. Any energy that that molecule receives that's from those photons-- and this is the energy. Wavelength, as we know same, as the energy.

Any photons it receives from the sun that's less than this just go right past. They cannot get absorbed. If I don't absorb a photon, I don't do this. I don't switch. OK? So this is important.

Now, the question is what do I want? Well, do I want the material to have a very high gap or a very low gap? Out here would be a very low energy gap, and over here, it would be a very high energy gap. What do you guys think I want here? How would I get-- and I'm going to collect energy only above the gap.

So if my energy gap is here, it's only going to be this part of the sun I can collect. So where do you think I want my gap to be? Over here? That's definitely what you would think.

Why not just make this material have almost no gap? Right? If it had almost no gap, then if this were the gap, then any little bit of sunlight would excite electrons up, and you'd absorbed the photon. Why is that not a good solar fuel?

**AUDIENCE:** They fall easily.

**JEFFREY C.** Say that again.

**GROSSMAN:**

**AUDIENCE:** They fall back down easily.

**JEFFREY C.** Well, they certainly could fall back down, and actually usually, they'd be absorbed say up here, and they'd usually trickle down to here anyway to the LUMO state. That's called thermalization. They could also fall back down to the homo state and re-emit a photon. That's absolutely right, but there's another reason.

**AUDIENCE:** Lower energy density.

**JEFFREY C.** Yeah. Why?

**GROSSMAN:**

**AUDIENCE:** There's a band gap in the partial delta H.

**JEFFREY C.** Yeah. That's it. So what are we doing in storage materials? What are we doing with electrons in batteries, in solar thermal fuels? What are we doing with those electrons?

**AUDIENCE:** Storing them.

**JEFFREY C.** We are storing them. Yes, but what are we doing to make them-- what are we doing when we convert them?

**GROSSMAN:** Maybe I should say it that way. Same thing happens in a solar cell. I'm doing something to these electrons.

**AUDIENCE:** Putting them on a shelf.

**JEFFREY C.** Yeah. You know I love that analogy. Yeah? It's like pumping hydro. Hydro pumping is one of the best technologies we know of to store energy. It's even creating a little stir here in the third row, because he has read the reports, and he knows that there are certain areas where that's the only game in town, pumped hydro, a beautiful technology. It works.

You pump water up a hill. When you got too much energy, and you let it roll back down when you need it. Right? Now, that's all we're doing with electrons. That's it. It's the same exact thing.

We're pumping electrons up a hill. We're using light to do it here. For a battery, when you plug your electric car in, you're using current and electrons, potential, voltage to do it, but you're driving electrons up the hill. And then you're trying to keep them up there, and then let them come back when you need them, when you need them to release energy. OK?

Now, if my gap is really low, you see, the hill, it's never going to get to the top. Here's my hill. OK? If my gap is only this much in energy, then I'm just going to roll around here, and I'm never going to get any amount of storage. Right? So you want this to be as large as possible, because that's how much energy you store. But the gap can't be any smaller than this, or you're not going to give those electrons enough energy to get up the hill to go there, so the material can go there. Yeah?

**AUDIENCE:** So let's see you have some material with some small gap, and you just have it exposed to sunlight and then compare it with some material with a large gap. Wouldn't they both on average collect the same number of high-energy photons anyway?

**JEFFREY C.** Yes.

**GROSSMAN:**

**AUDIENCE:** So with the low-gap material, you'd get some with height that collect higher--

**JEFFREY C.** Great question.

**GROSSMAN:**

**AUDIENCE:** High energy photons, and then they have some excited state. And then the ones with the high gap will also have that excited state, but the ones with the low gap will also have these lower, excited states.

**JEFFREY C.** Yes. Yes.

**GROSSMAN:**

**AUDIENCE:** On top of that?

**JEFFREY C.** It's a great question, and what you're talking about is such a cool idea in solar PV called hot carrier. What you'd like to do is get those excited, really high energy electrons out in solar cells, before they come back down. In this case, they come back down.

See in this case, they thermalize, and the reaction happens in the lowest excited state. But it also happens in solar cells, because there are no hot carrier solar cells today. It's a great theory. It's a great idea.

So this is the idea, and there's a lot of active research in this area. And it's basically the idea of multijunction cells which are cells that work, and in fact, the highest efficiency solar cells to date are multijunction, triple-junction solar cells. Where basically, you have different band gaps together, and those different band gaps do exactly what you say. OK? They let you take some electrons out here, and then you have another material with a higher gap, and you can take them out here. And then you have another material with an even higher gap, and you can take those electrons out there. OK?

And see because otherwise, what happens? Otherwise, all the electrons will-- in each case-- all the electrons cascade down to here. They all wind up in that conduction band or that LUMO state, if it's a molecule. No matter what, that's just the dramatic and traumatic loss of solar materials. Right? Solar conversion, solar capture, those electrons thermalize, because that process of thermalization is so fast, that it's very hard to beat.

The way you beat it in multijunction solar cells-- 42% maybe is the record, something like that. The way you beat it is you literally just stick a level in there. So it's sort of a cheat, but that's the only way to do it that we know technologically today.

If there were other ways of extracting electrons out at their higher energies, you could do wonders in solar capture and storage. In the molecule, the electron thermalizes down, and the reaction goes in that lowest excited state. So that gap has to be bigger than  $\Delta H$ . OK? Does everybody see that? It's a very good question.

So it's this beautiful, constrained optimization problem. I love those, because constrained optimization problems, I want this to be really big, but I want this to stay not less than an electron volt. But then if this is really big, I can't absorb any of the light. Right? If I made  $\Delta H$  huge, then I'd have to have a gap that was like here, and I'd get almost no solar efficiency.

These are beautiful problems for materials design and for computation, because they're constrained, but they're not that constrained. And using computers, you can get your way out of that, those constraints, sometimes. OK? And that's what's, I think, really exciting. That's what your homework is going to be about, and so let's calculate one of these. OK? Because that is the key to the optical efficiency. Yeah?

**AUDIENCE:** So is the gap thinner than the just  $\Delta H$  or  $\Delta H$  plus the base?

**JEFFREY C. GROSSMAN:** That's a very good question, and--

**AUDIENCE:** He told me to ask.

**JEFFREY C. GROSSMAN:** Yeah. Yeah. It's a very good question. So in general, most of these kinds of photoactive molecules-- I've already talked to a chemist, so I'm well armed. Most of these photoactive molecules need the gap plus the activation barrier, because in the excited state, you'll get a similar barrier. It's not clear that's always true though, and so that puts more constraints on this. So it's even less of the spectrum you can absorb, basically. Right?

If you want to store 1 1/2 electron volts, and you need an electron volt of an activation barrier, that's a 2 1/2 eV-gap minimum. Which means you're closing in on the UV, which means your optical efficiency is probably at most 5%, 8%, 10%, at most. Right? That doesn't mean it's a deal breaker at all. But there are also cases where you do change the barrier in the exciting state, and so we're looking into that.

Now, I want another concept here to come across which is really important. OK? And that is nothing more than these levels smoothed out, and it's called the density of states. OK? So if you do a calculation of one of these molecules-- let me go back to here. Oh, yeah. You know we love this. Have you all rated this say a 10 out of 10? Come on. You know it's a 10 experience.

**AUDIENCE:** Someone gave it a 9.5?

**JEFFREY C. GROSSMAN:** No. That's an average. OK. I want to start using-- we're going to use a different tool for our next homework. We're going to use DFT for solids, surfaces, and molecules. It's called SIESTA. It's another free software that you can download.

And it's solving the same equations, but it uses different approximations, different basis sets, and so forth. OK? But here, and you see that basis sets are called different things, but I've still tried to help by saying really bad, mediocre, and OK, in terms of the quality. OK? Again, that's not the focus in this class.

Let's look at it, and we're going to do a molecule here-- Uh-oh, there we go-- a molecule. And I'm going to upload one, and you're going to get these. We'll give these with the homeworks. We'll put them on Stellar.

So here's a trans state. Let's do the phenyl. Here's a trans state. We're going to upload it and simulate. OK?

And this is doing just what the other code does. It's doing this self-consistent cycle, where it's solving for the wave function. OK? And it's getting the wave functions of all these levels for the molecule I just entered. So it's going to give me all these levels. That's what I want.

Now, the way this plots it though is in something called the density of states, and all that is, as we'll see in a minute, is you take these, and you turn it on the side. OK? So let's take a look. Is it done? Yes.

There it is. Oh, this is a beautiful solar fuel. It's actually got two photo-switchable molecules hanging off the same azobenzene ring. But anyway, and this-- where is the-- there we go. OK.

So the key outputs, so it tells you some things, and then you can go to Density of States, and this is a very important property. OK? This is the way that we like to look at energy levels, especially in solids. So we're going to be looking at DOS plots when we get to solids. OK? But in molecules, you can look at the DOS plot as well, and basically, what it is it's just these levels turned on their side. So if there's a bunch of levels near each other, you'll get a higher peak in the DOS.

You want to think about it as averaging over the likelihood of finding states at these energies. Has anybody seen a DOS plot? How many of you have seen a DOS plot, a density of states? One or two? That's OK. They're energy levels turned on their side. Right?

Now, when we do solids, it gets really fun. It gets really fun when we do solids, because when we do solids, like I said, these things go like this in a space yet to be determined. And then you turn those on their sides, and you still get the same kind of DOS plot.

But for molecules, this is what it would look like. So there's a little smoothing going on, but you're also representing how many states you have near these energies. So that's why it's called the density of states. Right? Gesundheit.

Does everybody see that this is that energy gap? This is it. That's the energy gap, but there's more in the density of states. OK? So the energy gap, now I can-- watch this-- I can go back, and I can magically put on some functional groups and go to the amino benzene case, and I can do that simulation.

How many people really want to hear about hydrogen storage or don't care? Be honest. Really want to hear about hydrogen storage? In the back.

Because I really want to make this point, because also, this will be the basis of your homework. But I can also take the first 10 minutes of Thursday and talk about hydrogen storage. Hydrogen storage, nobody cares about hydrogen storage anymore, do they? In the back, we have one hydrogen storage.

The hydrogen economy, it was a big myth. Well, it's not a myth, but it's a long way off. That we'd all be-- I'm not sure I would use that-- that we'd all be driving hydrogen-powered cars in this decade was a little bit of an exaggeration, to say the least.

So here's this guy. Now, what I did is I decorated it. I did some, like I thought-- oh, by the way, your computation is only as good as what's up here. Right? So you need to think about what you want to simulate, and here, we thought, well, we had this one. OK? We had this one, and it's not quite the same angle, but it's close. OK?

So these guys are going to switch, when the sun shines on them, and store some energy and switch back. But I decided that I wanted to try to do something about the strain in this state. Again, you're trying to lower, remember-- you're trying to lower these states, or change them, figure out how to tune them. Right?

So what I did is we put a group in there. You can see, you put a group in here which is going to cause some bonding, when it's in the trans state. And you put another group here which causes some bonding between those OH groups and the nitrogen, and that adds to the energy. It lowers the energy. Right?

Now, as I said, we do that with quantum mechanics, because it's actually not that big of a problem, but that doesn't tell me whether-- I may have made this a great solar thermal fuel that can never absorb light. And so you got to go, and you've got to look at these things, like the density of states. OK? And so here they are together, and you can see that in-- so that's one. OK. So one is now bold, and you can see that my modifications have done some interesting things. My chemical modifications have really changed where those energy levels are.

Now, remember, they're getting filled from here. Remember the filling. Right? You draw from the bottom, the most energy favorable ones, all the way up, and then you fill them up, and you stop filling here. Right? You stop filling here, and that's your gap, and you can see that the gap has changed considerably. So the gap has changed considerably, and that changes what kind of sunlight that molecule can absorb.

Now, what's nice about having the density of states is that, you see, I'm getting-- in all of the energy levels-- is I'm getting more than just the gap. Right? I'm getting other things. I'm getting shapes and peaks, and here's a double peak. There's a single peak. Here's a little narrow peak, but there's a really broad thing with like three peaks and a shoulder. Right?

That matters too. That matters a whole lot. OK? And the reason is that to a very, very crude approximation, you can consider these peaks in where the states are in energy as the places where this molecule will be able to absorb light. OK? And so you can match this up with the solar spectrum. Right?

Because what you want is for the molecules to be able to absorb light, where there's a lot of light. And you don't really care about them absorbing light. You don't necessarily need them to have huge peaks, where there's no sunlight. Right? So now, you have an interesting comparison of where these molecules tend to absorb light and where the light is. OK? So let's go back to this and make sure we know where I'm going. OK?

So see, we talked about-- just another five minutes or so I think to finish this discussion. We talked about how, well, you don't want-- there are constraints on just thinking about how big of a gap you want. Because it's a constrained optimization problem with this thing and this thing and this stuff. Right? We just talked about that.

Now, I'm going to tell you there's another problem, and that is that this state is also photoactive. So this state can absorb light which makes it go back. Well, that's a bummer. Right? That is a bummer.

Now, what that means is that, when I shine light on this material, I will never get it all to convert. I will never charge all of the material and make it all go from here to here, because there's constantly a competition at play. Some of it will be going this way, and some of it will be going that way. And what holds the key to determining how much of which one is made? What holds the key?

**AUDIENCE:** The ratio of  $\Delta H$  plus EA.

**JEFFREY C. GROSSMAN:** Well, actually, but the  $\Delta H$  and EA are out of the picture for now, because I'm only talking about the absorption efficiency. What type of photons it could absorb and what else? What type of photons it can absorb and? Yeah?

**AUDIENCE:** How many of those types of photons--

**JEFFREY C. GROSSMAN:** Exactly.

**AUDIENCE:**

**AUDIENCE:** Your solar cell.

**JEFFREY C. GROSSMAN:** Exactly, and this. Right? So you're given this much photons on planet Earth. You're give given the yellow, if you go up a little bit. Right? We're not going to charge our fuels in space. So this is what you got, the red, and that's where the photons are in energy, in wavelength energy, same thing.

Now, I'm giving you the fact that some molecules-- let's go back here. I can't just delete one, can I? I'm going to do one more simulation while I talk. I wish it wouldn't show my picture everywhere. I'm going to do the cis state. OK?

You see, some molecules in their cis state, they're still photoactive, which means they go back here, when you shine light on them. What that means is that there's going to be a stationary state. When I hold the fuel out in the sun, the light is converting this into this, as well as this into this with some efficiency in both directions. And there will be a stationary state that gives me a percentage, or a yield, or as it's called in the literature a quantum yield, of charged material.

How much is it? Well, in isolated azobenzene, when you don't do anything to it, it's 25%. I can only charge 25% of this stuff in the photo-stationary state, when I hold it out in the sun. And you can see why this is such an important part of the problem, I will remind you, a purely quantum mechanical part of the problem.

Because if I increase this, I work so hard to increase this by a factor of three or four, and then I can only charge a fourth of it, that's a whole factor of four hit. If you can only charge a fourth of it at a time, it's four times less useful. So it's effectively changing this by four times back. Right? So this is critical. How much of this can you charge? Right? And that comes from the quantum mechanics.

Now, the way that you get it is by looking at-- and I'll go through the equations on the next line a minute. So here it is now in the charged state. OK? So it's flipped. It's done its flip.

You can see, it's rotated those nitrogen bonds. It's a beautiful thing, kind of an emotional moment in a way. And you go back to here, and you look at your DOS, and now this is kind of hard to see. Isn't it?

One of these is the cis state that I just mentioned, and it's different. I can't see, because there's two trans states here and one cis state. I don't think there's any way to just do simulations two and three, but I think you know what I'm talking about.

There's a density of states for the trans. These levels here turn on their side, and there's a density of states for the cis state. And matching that with the solar flux is what will give you the photo-stationary state. It will give you the quantum yield of the material. OK? That will be your second homework.

So this, let's see, this is two ways that you could do it. OK? One way is you could just assume that all of the photons higher in energy than the gap are absorbed and lead to a switch. And if you do that, then the fraction of the molecules in the cis state, if you let them be  $x$ , you can show that it's just going to be a simple integral over the solar spectrum, that this  $I$  function, up to the gap times  $x$ . That's how many are in the cis state. Gesundheit. [NON-ENGLISH] Equals the number that are in the trans state,  $1 - x$ , times the integral over the number of photons that convert the trans. OK?

That's just stationary-- that's just telling you that the change in the concentration of cis is the same. It's like a reaction kinetics equation, the rate of going from one state to another times the number in that state equals the same as the other way. That's all we've done here.

But it gets more interesting if you use the density of states, because now, you have the absorption-- what I'm calling the absorption. Again, it's a crude approximation for the absorption, but let's just call it that-- of the cis state as a function of the wavelength, convoluted with, or times, the solar spectrum. Where you have states in both is where it matters. Right? Where you have states in both is where you hit the integral, and it's when those are taken together that you can calculate more accurately than just using the gap.

You can calculate the photo-stationary yield, and you get this all from those energy levels, those beautiful energy levels that we started this lecture talking about. OK? That yield is so important, because it can kill your-- great idea for improving  $\Delta H$  can get killed if the yield isn't good. OK? Maybe I'll spend 10 minutes on hydrogen storage.

Nobody raised their hands, but we'll do another poll. And we're going to start moving now-- you'll have a homework on this. It'll be lots of fun, and then on Thursday, we're going to move into solids.