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ROBERT FIELD: Last time, we talked about photochemistry. And the crucial thing in photochemistry is that the density of vibrational states increases extremely rapidly-- extremely, extremely-- and especially for larger molecules. And this enables you to understand intermolecular vibrational redistribution, intersystem crossing, internal conversion. The matrix elements are different in each of these cases.

But what happens when the vibrational density of states gets large is that you have a special state, which is a localized state or something that you care about that you think you understand-- a bright state-- which is different from the masses. And because of the density of states, that bright state or that special state, gets diluted into an extremely dense manifold of uninteresting states. And as a result, the system forgets whatever the bright state wanted it to tell you. And so you get faster decay of fluorescence, not because the population goes away, but because the unique thing-- the bright state, the localized state-- the thing that you can prepare by excitation from the ground state, which is always localized, its character is dissipated. And so you get what's called statistical behavior.

Now I have a very strong feeling about statistical behavior, and that it's mostly a fraud. But the current limit for statistical behavior is when the density of states is on the order of 100 per wave number. That's the usual threshold for statistical behavior. As we know more, as we develop better experimental techniques, we're going to push that curtain of statistical behavior back. And we'll understand more about the short-time dynamics and whatever we want to do about manipulating systems. So statistical just means we don't know, but it's not what we expected. And it's usually boring.

OK. Today I'm going to talk about the discrete variable representation, which is really weird and wonderful thing, which is entirely inappropriate for a course at this level. But I think you'll like it. So in order to talk about the discrete variable representation, I'll introduce you to delta functions. And you sort of know what delta functions are. And then I'm going to say, well for any one-dimensional problem-- and remember, you can have a many-dimensional problem

treated as a whole bunch of one-dimensional problems. And so it really is a general problem. But if you have a one-dimensional potential, you can obtain the energy levels and wave functions resulting from that one-dimensional potential. Regardless of how horrible it is, without using perturbation theory, which is should make you feel pretty good. Because perturbation theory is labor intensive before you use the computer. The computer helps you, but this is labor free because the computer does everything.

At the beginning of the course, I said, you cannot experimentally measure a wave function. And that's true. but if you can deal with any potential and have a set of experimental observations, energy levels, which you fit to an effective Hamiltonian, you can generate the wave functions associated with the effective Hamiltonian directly from experimental observations. So it's not a direct observation, but you get wave functions. And you can have whatever complexity you want.

OK, so let's begin.

Delta functions.

So this is not the Kronecker delta. This is the delta function that is a useful computational trick. And it's more than that.

We write something like this.

OK, this is a delta function. And it says that this thing is non-zero when x is equal to x_i . And it's really big. And it's 0 everywhere else. And as a result, you can say that we get $x_i \delta(x - x_i)$. So that's an eigenvalue equation.

So we have the operator, x , operating on this function. And this function has the magical properties that it returns an eigenvalue and the function.

So this is more than a mathematical trick. It's an entry into a form of quantum mechanics that is truly wonderful.

So this is part one. Part two will be DVR-- discrete variable representation.

And the issue varies. Suppose we have a matrix representation of an operator.

Well, suppose we wanted some function of that operator. How do we generate that? And there are lots of cases where you care about such a thing. For example, you might want to know

about something like this-- $e^{-iHt/\hbar}$. This would tell you something about how a system propagates under the influence of a Hamiltonian, which is not diagonal.

This is kind of important. Almost all of NMR is based on this sort of thing. Also-- well, we'll get to it.

So extend DVR to include rotation. And then the last part will be-- can be determined for even the most horrible situations, like a potential that does something like this, or something like that.

Now we don't want to have a continuum. So I put a wall here. But this is a summarization from an unstable isomer to a stable isomer. This is multiple minima. Anything you want, you would never want to perturbation theory on it. And you can solve these problems automatically and wonderfully.

OK, so let's just play with delta functions. And a very good section on delta functions is in Cohen-Tannoudji, and it's pages 1468 to 1472, right at the end of the book. But it's not because it's so hard, it's just because they decided to put it there. And so we have notation-- $\delta(x - x_i)$. It's the same thing as $x - x_i$. So basically, if you see a variable at a specified value, it's equivalent to this, and this thing is 0 everywhere except when x is equal to x_i . So the thing in parentheses is the critical thing. And it has the property that if we do an integral from minus infinity to infinity, some function of x -- $\int_{-\infty}^{\infty} f(x) \delta(x - x_i) dx$. We get $f(x_i)$. Isn't that wonderful?

I mean, it's a very lovely mathematical trick. But it's more than that.

It says this thing is big when x is equal to x_i . It's 0 everywhere else. And it's normalized to 1 in the sense that, well you get back the function that you started with, but at a particular value. So it's infinite, but it's normalized. It should bother you, but it's fantastic and you can deal with this.

It's an eigenvalue equation. I mean, you can say, all right, we have $\delta(x - x_i) \delta(x - x_i)$.

And we can have delta functions in position, in momentum, in anything you want. And they're useful.

So suppose we have some function, $\psi(x)$, and we want to find out something about how it's composed. And so we say, well, we have $c_j \delta(x - x_j)$. This is the standard method for expanding a function.

OK, what we want is these expansion coefficients. And you get them in the standard way. And that is by-- normally, when you have a function, you write it c_k the function-- I'm sorry.

So here we have an expansion of members of a complete set of functions. And in order to get the expansion coefficients, you do the standard trick of integrating $\phi_j^* \psi_j dx$. OK, so this is familiar. This is not. But it's the same business. In fact, we've been using a notation incorrectly-- the Dirac notation. We normally think that if we have something like k and ψ_k of x , they're just different ways of writing the same thing.

But the equivalent to the Schrodinger picture is really $x \psi$. This is a vector, not a function. This is a set of vectors. And this is how you relate vectors to functions. We just have suppressed that. Because it's easier to think that the wave function is equivalent to the symbol here. It's not. And if you're going to be doing derivations where you flip back and forth between representations, you better remember this, otherwise it won't make sense.

This is familiar stuff, you just didn't realize you understood it. OK, and so now, often, you want to have a mathematical representation of a delta function. And so this thing has to be localized and it has to be normalized. And there are a whole bunch of representations that work really well. One of them is we take the limit, epsilon goes to 0 from the positive side, and $\frac{1}{2\epsilon} e^{-x/\epsilon}$. Well this guy, as epsilon goes to 0, this becomes minus infinity. And it's 0 everywhere except for x is equal to 0.

And so if we wanted to put $x - x_i$, then fine. Then it would be 0 everywhere except when x is equal to x_i . So that's one. That's a simple one.

Another one is limit as epsilon goes to 0 from the positive side of $\frac{1}{\pi \epsilon} \frac{\epsilon}{x^2 + \epsilon^2}$. This also has the properties of being an infinite spike at x equals 0. And it's also Lorentzian. And it has the full width. It'd have maximum-- or a half width it would have-- a full width at half maximum of epsilon. If you make the width as narrow as you want, well that's what this is. OK, there are a whole bunch of representations. I'm going to stop giving them because there's a lot of stuff I want to say, and you can see them in the notes.

OK, so what if we have something like x_i , that just is the same thing as saying $x - x_i$ is 0.

You can produce a delta function localized at any point by using this trick. OK, there are some other tricks that you can do with delta functions, which is a little surprising. And that's really for the future. Delta of minus x is equal to delta of x . It's an even function.

Derivative of a delta function is an odd function. Delta-- a constant times x is 1 over the absolute value of that constant, δx . A little surprising, but if you have x , which-- I better not say that. OK, we have now another fantastic thing-- g of x . So what is the delta function of a function?

Well it's a sum over j of the g ex and x of j times δx minus x_j .

This is something where you're harvesting the zeros of this function. OK, when this is 0 , we get a big thing. So the delta function of our function is a sum over the derivative-- the zeros of g of x . And at times, it's kind of neat.

OK, there's also stuff in Cohen-Tannoudji on Fourier transforms of the delta functions. I'm not going to talk about that. But one of the things is, if you have a delta function and x , and you take the Fourier transformer with it, you get a delta function of p , momentum. Kind of useful. It enables you to do a transform between an x representation and a position representation and a momentum representation. It's kind of useful.

OK, now we're going to get to the good stuff.

So for every system that has a potential, and where the potential has minima, what is the minimum potential? What is the condition for a minimum of the potential?

Yes?

AUDIENCE: The first derivative has to be 0 with respect to coordinates.

ROBERT FIELD: Right. And so, any time you have a minimum, the first term in the potential is the quadratic term. And that's the same thing as a harmonic oscillator. The rest is just excess baggage. I mean, that's what we do for perturbation theory. We say, OK, we're going to represent some arbitrary potential as a harmonic oscillator. And all of the bad stuff, all of the higher powers of the coordinate get treated by perturbation theory. And you know how to do it. And you're not excited about doing it because it's kind of algebraically horrible. And nobody is going to check your algebra. And almost guaranteed, you're going to make a mistake. (Exam 2!)

So it would be nice to be able to deal with arbitrary potentials-- potentials that might have multiple minima, or might have all sorts of strange stuff without doing perturbation theory. And that's what DVR does.

So for example, we want to know how to derive a matrix representation of a matrix. So often, we have operators like the overlap integral or the Hamiltonian. So we have the operator, the S matrix, or the Hamiltonian matrix. And often, we want to have something that is a matrix representation of a matrix.

For example, if we're dealing with a problem in quantum chemistry, where our basis set is not orthonormal, there is a trick using the S matrix to orthonormalize everything. And that's useful because then your secular equation is the standard secular equation, which computers just love. And so you just have to tell the computer to do something special before, and it orthonormalizes stuff. And you can do this in matrix language. And if you're interested in time evolution, you often want to have $e^{-iHt/\hbar}$. And that's horrible. But so we'd like to know how to obtain a matrix representation of a function of a matrix.

Well, suppose we have some matrix, and we can transform it to be $a_1, a_n, 0, 0$. We diagonalize it. And if a is real and symmetric, or Hermitian. We know that the transformation that diagonalized it has the property that t^\dagger is equal to the inverse. And we also know that if we diagonalize a matrix the eigenvectors that-- they say, if you want the first eigenvector, the thing that belongs to this eigenvalue, we want the first column of t^\dagger . And if you want to use perturbation theory instead of the computer to calculate t^\dagger , you can do that, and you have a good approximation. And you can write the vector, the linear combination of basis functions, that corresponds to t^\dagger as fast as you can write. And the computer can do it faster.

So if the matrix is Hermitian, then all of these guys are real. And it's just real and symmetric. Well then these guys are still numbers that you could generate, but they might be imaginary or complex.

Suppose we want some function of a matrix. So this is a matrix, this has to be a matrix too. It has to be the same dimension as the original matrix. So you can do this.

Well we can call that f twiddle.

But we don't want f twiddle. And so if we do this, we have the matrix representation of the function. So this is something that could be proven in linear algebra, but not in 5.61. You can do power series expansions, and you can show term by term that this is true for small matrices, but it's true. So if your computer can diagonalize this, then what happens is that we

have this-- we can write that f twiddle is the--

So this is the crucial thing. We've diagonalized this, so we have a bunch of eigenvalues of a . So the f twiddle is just the values of the function at each of the eigenvalues.

And we have zeros here.

And now we don't like this because this isn't the matrix representation of f . It's f in a different representation. So we have to go back to the original representation. And so that's another transformation. But it uses the same matrix. So if you did the work to diagonalize a , well then you can go back and undiagonalize this f twiddle to make the representation of f .

And so the only work involved is asking the computer to find t dagger for the a matrix. And then you get the true matrix representation of this function of a .

Is it useful? You bet.

Now suppose a is infinite dimension. And we know that this is a very common case. Because, even for the harmonic oscillator, we have an infinite number of basis functions. But what about using the delta function? We also have an infinite number of them.

So what do we do? We can't diagonalize an infinite matrix.

So what we do is we truncate it.

Now the computer is quite happy to deal with matrices of dimension 1,000. Your computer can diagonalize a 1,000 by 1,000 matrix in a few minutes, maybe a few seconds depending on how up to date this thing is. And so what we do is we say, oh, well let's just take a 1,000. So here is an infinite matrix. And here is a 1,000 by 1,000 block. That's a million elements. The computer doesn't care. And we're just going to throw away everything else.

We don't care. Now this is an approximation. Now you can truncate in clever ways, or just tell the computer to throw away everything above the 1,000th basis function. That's very convenient. The computer doesn't care. Now there are transformations that say, well you can fold in the effects of the remote basis states, and do an augmented representation. But usually, you just throw everything away. And now you look at this 1,000 by 1,000 matrix. And you get the eigenvalues.

And so this might be the matrix of x , or q if we're talking in the usual notation. This is the

displacement from equilibrium.

Well, it seems a little-- so we would like to find this matrix. Well, we know what that is. Because we know the relationship between x and a plus a dagger are friends. And so we have a matrix, which is zeros along the diagonal, and numbers here and here, and zeros everywhere else. It doesn't take much to program a computer to fill in as many one-off the diagonal, especially because they're square roots of integers. So that's just a few lines of code, and you have the matrix representation of x . Now that is infinite. And you're going to say, well, I don't care. I'm going to just keep the first 1,000. We know that we can always write-- so we have v of x , and this is a matrix now. And it's an infinite matrix. But we say, oh, we just want v of x to the 1000th, and we'll get v of 1,000. We have a 1,000 by 1,000 v matrix. And we know how to do this. We diagonalize that. Then we write at each eigenvalue of x , what v of x is at that eigenvalue.

And so now we have a v matrix, which is diagonal, but in the wrong representation for us. And then we transform back to the harmonic oscillator representation. And so everything is fine. We've done this. And we don't know how good it's going to be.

But what we do is we do this problem. So we have the Hamiltonian, which is equal to the kinetic energy, I'm going to call it k , plus v . We know how to generate the representation of v in the harmonic oscillator basis by writing v of x , diagonalizing x , and then undiagonalizing-- or then writing v at each of the eigenvalues of x , and then going back to the dramatic oscillator basis. We know k in the harmonic oscillator basis. It's just tri-diagonal, and it has matrix elements Δv equals 0 plus minus two. So now we have a matrix representation of k , which is simple, add a v which is-- computer makes it simple. Add any v you want, there it is. So that's a matrix, the Hamiltonian. You solve the Schrodinger equation by diagonalizing this matrix.

And so you have this h matrix, and it's for the 1,000-member x matrix, and you get a bunch of eigenvalues.

And so then you do it again. And maybe use a 900 by 900, or maybe you use a 1,100-- you do it again. And then you look at the eigenenergies of the Hamiltonian, e_1 , say, up to e_{100} . Now if you did a 1,000 by 1,000, you have reasonable expectation that the first 100 eigenvalues will be right. And so you compare the results you get for the 1,000 by 1,000 to the 900 by 900, or 1,100 by 1,100. And you see how accurate your representation is for the first 100. Normally,

you don't even care about the first 100. You might care about 10 of them.

So the computer is happy to deal with 1,000 by 1,000s. There's no least squares fitting, so you only do it once.

And all of a sudden, you've got the eigenvalues, and you've demonstrated how accurate they are. And so depending on what precision you want-- you can trust this up to the 100th, or maybe the 73rd, or whatever, to a part in a million, or whatever. And so you know how it's going to work. And you have a check for convergence.

So it doesn't matter. So the only thing that you want to do is you want to choose a basis set where we have-- x is the displacement from equilibrium.

OK, so this is the equilibrium value. This is the definition of the displacement.

And so you want to be able to choose your basis set, which is centered at the equilibrium value. You could do it somewhere else, it would be stupid. It wouldn't converge so well. And you want to use the harmonic oscillator, k over u .

You have a couple of choices before you start telling the computer to go to work. And you tell it, well I think the best basis that will be what works at the equilibrium-- the lowest minimum of the potential, and matches the curvature there. You don't have to do that. But it would be a good idea to ask it to do a problem that's likely to be a good representation.

And all this you've done. You get the energy level. So what you end up getting--

So you produced your Hamiltonian. And since it's not an infinite dimension Hamiltonian, we can call it an effective Hamiltonian. It contains everything that is going to generate the eigenvalues. And we get from that a set of energy levels-- e_{v_i} -- and a set of functions. So these guys are the true energy levels. And these are the linear combinations of harmonic oscillator functions that correspond to each of them. Who gives that to you?

And so then you say, well, I want to represent the Hamiltonian by a traditional thing. Like, I want to say that we have $\omega v + \frac{1}{2} \omega x^2$ equals $\frac{1}{2} \omega^2$, et cetera. Now we do a least squares fit of molecular constants to the energy levels of the Hamiltonian.

And there's lots of other things we could do, but-- so we say, well in the spectrum, we would observe these things, but we're representing them as a power series in $v + \frac{1}{2}$. Or maybe

in-- where we would have not just the energy-- the vibrational quantum number-- but the rotational constant. We could say the potential is v of 0 plus $b \times j(j+1)$. Well, that means we could extend this to allow the molecule to rotate. And we just need to evaluate the rotational constant as a function of x , and just add that to what we have here.

Another thing, you have t^\dagger and t for our problem. And you have, say, the 1,000 by 1,000, and maybe the 900 by 900 representations. You keep them. Because any problem you would have, you could use these for. So you still have to do a diagonalization of the Hamiltonian, but the other stuff you don't have to do anymore. Now maybe it's too bothersome to store a 1,000 by 1,000 t^\dagger matrix. It's a million elements. Maybe you don't, and you can just calculate it again. It takes 20 minutes or maybe less. And so this is a pretty good.

OK I've skipped a lot of stuff in the notes, because I wanted to get to the end. But the end is really just a correction of what I said was impossible at the beginning of the course.

We have in the Schrodinger picture $H\psi = E\psi$, right? That's the Schrodinger equation.

So this wave function is the essential thing in quantum mechanics. And I also told you, you can't observe this. So it's a very strange theory where the central quality in the theory is experimentally inaccessible. But the theory works. The theory gives you everything you need. It enables you to find the eigenfunctions, if you have the exact Hamiltonian. Or it says, well we can take a model problem and we can find the eigenvalues and wave functions for the model problem.

We can generate an effective Hamiltonian, which is expressed in terms of molecular constants.

We can then determine the potential. And we can also determine ψ . All of them.

So what I told you was true, but only a little bit of a lie in the sense that you can get as accurate as you want a representation of the wave function, if you want it. And DVR gives it to you without any effort. And so it doesn't matter how terrible the potential is, as long as it is more or less well behaved. I mean, if you had a potential, which--

Even if I had a v potential-- the discontinuity here-- you would still get a reasonable result from DVR.

What it doesn't like is something like that, because then you have a continuum over here. And the continuum uses up your basis functions pretty fast.

I mean, yeah, it will work for this. But you don't quite know how it's going to work, and you have to do very careful convergence tests, because this might be good. But up here, it's going to use a lot of basis functions.

So for the first time in a long time, I'm finishing on time or even a little early. But DVR is really a powerful computational tool that, if you are doing any kind of theoretical calculation, you may very well much want to use something like this rather than an infinite set of basis functions and perturbation theory.

It's something where you leave almost all of the work to the computer. You don't have to do much besides say, well what is the equilibrium value? And what vibrational frequency have I got to use for my basis set? And if you choose something that's appropriate for the curvature at the absolute minimum of the potential, you're likely to be doing very well. Now other choices might mean you don't get the first 100, you only get the first 50. But you might only care about the first 10. Or you could say, I'm going to choose something which is a compromise between two minima, and maybe I'll do better. But it doesn't cost you anything in the computer. Your computer is mostly sitting idly on your desk, and you could have it doing these calculations. And there is no problem where you can't use DVR. Because if you have a function of two variables, you do a two-variable DVR.

It gets a little bit more complicated because, if you have two DVRs, now you're talking about a million-- 1,000 by 1,000-- two of them, and couplings between them. And so maybe you have to be a little bit more thoughtful about how you employ this trick. But it's a very powerful trick. And there are other powerful tricks that you can use in conjunction with quantum chemistry that enable you to deal with things like-- I've chosen a basis set, which is not orthonormal. And my computer only knows how to diagonalize an ordinary Hamiltonian without subtracting an overlap matrix from it. And so if I transform to diagonalize the overlap matrix, well then I can fix the problem. And so there is a way of using this kind of theory to fix the problem, which is based on choosing a convenient way of solving the problem, as opposed to the most rigorous way of doing it.

OK, so I'm hoping that I will have a sensible lecture on the two-level problem for Wednesday. I've been struggling with this for a long time. And maybe I can do it. If not, I'll review the whole

course. OK, see you on Wednesday.