PROFESSOR: So we'll do the relativistic corrections. And all the corrections that I'll do today, I'll skip the easy but sometimes a little tedious algebra. It's not very tedious. Nothing that is pages and pages of algebra. It's lines of algebra. But why would I do it in lecture? No point for that.

So let's see what we can do. This is the relativistic correction, the minus p squared. So could we write this for the relativistic correction? We're going to do first order correction, relativistic, of the levels n l ml. Let's put a question mark. Minus 1 over 8 m cubed c squared psi n l ml p to the fourth.

Now recall that p to the fourth, the way it was given, is really p squared times p squared. You have four things that have to be multiplied. So it's not px to the fourth plus py to the fourth plus pz to the fourth is px squared plus py squared plus pz squared, all squared, just in case there's an ambiguity.

That seems reasonable. The first order corrections should be found by taking the states and finding this. But there is a big question mark. And this kind of question is going to come up every time you think about these things.

This formula, where I said the shift of the energy of this state is that state evaluated here, applies for nondegenerate perturbation theory. And if the hydrogen atom is anything, it's a system with a lot of degeneracies. So why can I use that, or can I use that?

We have the hydrogen atom. I just deleted it here. So here, if you have n, for degeneracies you fix n. For degeneracies, you fix some value of n. And now you have the degeneracies between the various l's, for each l between the various m's. A gigantic amount of degeneracy. Who allows me to do that?

I'm supposed to take that level three has nine states, remember? n square states. Well, we should do a 9 by 9 matrix here and calculate this. Nine sounds awful. We don't want to do that so we better think. So this is the situation you find yourself.

Technically speaking, this is a problem in the degenerate perturbation theory. We should do that. And you better think about this every time you face this problem because sometimes you can get away without doing the degenerate analysis, but sometimes you can't. Yes?

AUDIENCE: It's like rotationally symmetric. So you can mix terms with different [INAUDIBLE].

PROFESSOR: OK. So you're saying, basically, that this thing in this basis-- so we have nine states here. n equal 3. In these nine states, it doesn't mix them. So this is diagonal here. And what one is claiming by doing that is that this is a good basis, that delta H is already diagonal there. And don't worry, we can do it.

In fact, that is true. And the argument goes like that. We know that p to the fourth, the perturbation, commutes with l squared. We'll discuss it a little more. And p to the fourth commutes with lz as well. So these are two claims. Very important claims.

Remember, we had a remark that I told you few times few lectures ago. Very important. If you have a Hermitian operator that commutes with your perturbation for which the states of your bases are eigenstates with different eigenvalues, then the basis is good.

So here it is. l squared commutes with p to the fourth. Why? Because, in fact, p to the fourth commutes with any angular momentum because p to the fourth is p squared times p squared. And p squared is rotational invariant.

p squared commutes with any l. If that's not obvious intuitively, which it should become something you trust-- this is rotational invariant. p squared dot product doesn't depend on rotation. If you have a p and you square it or you have a rotated p and you square it, it's the same.

So p to the fourth commutes with any component of angular momentum. So these two are written like great facts, but the basic fact is that p squared with any li is 0. And all this follows from here.

But this is a Hermitian operator. This is a Hermitian operator. And the various states, when you have fixed n, you can have different l's. But when you have different l's, there are different eigenvalues of l squared. So in those cases, the matrix element will vanish.

When you have the same l's but different m's, these are different eigenvalues of lz. So the matrix element should also vanish. So this establishes rigorously that that perturbation, p to the fourth, is diagonal in that subspace. So the subspace relevant here is this whole thing. And in this subspace, it's completely diagonal.

Good. So generally, this kind of point is not emphasized too much. But it's, in fact, the most

important and more interesting and more difficult point in this calculations. We'll have one more thing to say about this. But let's continue with this.

I'll say the following. We use the Hermiticity of p squared to move one p squared to the other side. So Enl ml 1 is equal to minus 1 over 8m cubed c squared p squared psi nlm p squared psi nml-- nlm. OK.

We move this p to the fourth. It was p squared times p squared. One p squared is Hermitian. We move it here. And then, instead of calculating a billion derivatives here, you use the fact that p squared over 2m plus v of r on the wave function is equal to the energy of that wave function that depends on n times the wave function.

These are eigenstates. So p squared-- we don't want to take derivatives, and those expectation values can be replaced by a simpler thing. P squared on psi is just 2m En minus v of r psi. So Enlm 1 is equal to minus 1 over 8m cubed c squared.

Here we have, well, the m's. Two m's are out, so we'll put a 2 and an mc squared. Yep. En minus v of r psi En minus v of r psi nlm nlm. OK.

We got it to the point where I think you can all agree this is doable. Why? Because, again, this term is Hermitian, so you can put it to the other side. And you'll have terms in which you compute the expectation value on this state of E squared. E squared is a number, so it goes out, times 1, easy.

En cross terms with vr is the expectation of v of r in this state, is the expectation of 1 over r in a state. That's easy. It comes from the Virial theorem. Then you'll have the expectation of v squared in a state, and that's the expectation of 1 over r squared in a state. You've also done it.

So yes, getting all together, getting the factors right would take you 15 minutes or 20 minutes or whatever. But the answer is already clear. So let's write the answer.

And the answer is that Enl ml 1 relativistic is minus 1/8 alpha to the fourth. That's our very recognizable factor. mc squared 4n over l plus 1/2 minus 3.

Now, fine structure is something all of us must do at least once in our life. So I do encourage you to read the notes carefully and just do it. Just become familiar with it. It's a very nice subject, and it's something you should understand.

So here, again, I have to do a comment about basis, and those comments keep coming because it's an important subject. And I want to emphasize it. So what is the reason? The reason I wanted to comment is because in a second, I'm going to do the spin orbit term. And in that case, I would like to work with a coupled basis.

Here, I'm working with the uncoupled basis. And really, this thing is the expectation value of Hl relativistic in nl ml ms nl ml ms. This is really that. I wrote psi nl ml, so you should trust the first three labels. And ms goes for the ride. It's this spin.

The operator you're putting here, delta H relativistic, has nothing to do with spin. Could not change the spin of the states. This has to be diagonal in spin. So this number you've computed is nothing else than this overlap in the uncoupled basis. So this calculation was uncoupled basis matrix element. And we saw that it's diagonal.

In fact, this whole thing is nothing but the function of n and l. n and l. And independent of ml and ms. OK. That's what we've calculated.

So here is the question. We could consider this in the coupled bases nlj mj. nlj mj. And the question is, do I have to recalculate this in the coupled basis or not?

And here is an argument that I don't have to recalculate it. So I'm going to claim that this is really equal to that. Just the same. It's the kind of thing that makes you a little uneasy, but bear with me.

Why should it be the same? Think of this as fixed n and l because this depends on n and l. If we have the hydrogen atom here, you'd take one of these elements, one of these states-- this is a fixed n, fixed l. And we're looking at fixed n, fixed l.

Yes. There are lots of states here that have different ml and ms. But the answer doesn't depend on ml and ms. In this basis, we are also looking at that subspace, that multiplet, nl fixed. And they have reorganized the states with j and mj. In fact, with two values of j and several values of mj.

But at the end of the day, the coupled basis is another way to describe these states coming from tensoring the l multiplet with a spin 1/2. So it gives you two multiplets, but they are the same states. So the fact that every state here is some linear combination of states in the uncoupled bases with different values of ml and ms that add up to mj.

But this answer doesn't depend on ml and ms. So whatever linear combination you need, it doesn't change because the answer doesn't depend on ml and ms. So this must be the same as that.

I'll give another argument. Maybe a little more abstract, but clearer perhaps. Think of this. So this can be-- in the notes, I explain that by changing basis and explaining why exactly everything works out. But there is no need for that argument if you think a little more abstractly.

Think of this subspace. Because with fixed n and l, we have this subspace. In this subspace, the uncoupled basis makes the perturbation diagonal. But more than diagonal, it makes the perturbation proportional to the unit matrix, because every eigenvalue is the same. Because in this subspace, n and l is fixed. And yes, m and ms change, but the answer doesn't depend on that.

So this matrix, delta H, in this subspace is proportional to the unit matrix. And when a matrix is proportional to the unit matrix, it is proportional to the unit matrix in any orthogonal basis. A unit matrix doesn't get rotated. So it should be a unit matrix here as well, and it should be the same matrix. So this is the same pair.