FIRST ORDER NON-DEGENERATE PERTURBATION THEORY

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Post date: 24 September 2021.

All the quantum systems we've seen so far are special in the sense that we could obtain exact solutions for the wave function and energy levels. Needless to say, such systems are the exception rather than the rule, so we need methods for handling more realistic cases.

Of course, we could jump straight to numerical solutions of the Schrödinger equation, and this is, in fact, done in many cases. However, there are several techniques by which we can find approximate solutions to systems where the hamiltonian is a relatively minor modification of an exactly-solved system. We'll have a look at first order perturbation theory for non-degenerate systems here. (That's the simplest case, if you're wondering.)

The idea is that we begin by assuming that we have a complete set of solutions to the equation

$$H_0\psi_{n0} = E_{n0}\psi_{n0} \tag{1}$$

The notation gets a bit clumsy here, but the subscript 0 indicates that this is an exactly-known system, and the subscript n refers to the energy level, as usual. We're assuming that the system is non-degenerate, that is, that there is exactly one state for each energy.

Now suppose we introduce a perturbation into the hamiltonian, so we now have

$$H = H_0 + \lambda V \tag{2}$$

where λ is a real value, assumed small, and V is a time-independent function. We would like to solve

$$H\psi_n = E_n\psi_n \tag{3}$$

but in most cases, this won't be possible, at least exactly.

We make the assumption at this point that the energies and wave functions can be expanded in powers of λ:

$$E_n = E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \dots \tag{4}$$

$$\psi_n = \psi_{n0} + \lambda \psi_{n1} + \lambda^2 \psi_{n2} + \dots \tag{5}$$

The subscripts $n0$, $n1$ and so on indicate the nth energy level and the 0th, 1st, etc order term in the expansion. We can plug these expansions back into the original equation to get

$$(H_0 + \lambda V)\left(\psi_{n0} + \lambda \psi_{n1} + \lambda^2 \psi_{n2} + \dots\right) = \left(E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \dots\right)\left(\psi_{n0} + \lambda \psi_{n1} + \lambda^2 \psi_{n2} + \dots\right) \tag{6}$$

Equating individual powers of λ we get

$$H_0 \psi_{n0} = E_{n0} \psi_{n0} \tag{7}$$

$$H_0 \psi_{n1} + V \psi_{n0} = E_{n0} \psi_{n1} + E_{n1} \psi_{n0} \tag{8}$$

$$H_0 \psi_{n2} + V \psi_{n1} = E_{n0} \psi_{n2} + E_{n1} \psi_{n1} + E_{n2} \psi_{n0} \tag{9}$$

The first of these is just the original unperturbed equation. The second equation can be fiddled a bit as follows. Using the bra-ket notation $\psi_{ni} = |ni\rangle$, we can multiply both sides by $\langle n0|$ and get

$$\langle n0| H_0 |n1\rangle + \langle n0| V |n0\rangle = \langle n0| E_{n0} |n1\rangle + \langle n0| E_{n1} |n0\rangle \tag{10}$$

Since H_0 is hermitian, we can swap it to the bra end in the first term and then use $\langle H_0 n0| = E_{n0}$, and since the E_{ni}s are just constants, they come out of the brackets on the right, and since $|n0\rangle$ is normalized, we get

$$E_{n0} \langle n0 |n1\rangle + \langle n0| V |n0\rangle = E_{n0} \langle n0 |n1\rangle + E_{n1} \tag{11}$$

$$E_{n1} = \langle n0| V |n0\rangle \tag{12}$$

That is, the first-order correction to the energy is given by the expectation value of the perturbation to the hamiltonian in the *unperturbed* wave function ψ_{n0}.

To get the first order correction to the wave function, we expand ψ_{n1} in terms of the complete set of eigenfunctions of H_0:

$$\psi_{n1} = \sum_j c_{nj} \psi_{j0} \tag{13}$$

We can plug this into the first order equation above and get

$$H_0 \sum_j c_{nj} \psi_{j0} + V \psi_{n0} = E_{n0} \sum_j c_{nj} \psi_{j0} + E_{n1} \psi_{n0} \tag{14}$$

Since the ψ_{j0} form an orthonormal set, we can use $H_0\psi_{j0} = E_{j0}\psi_{j0}$ and take the inner product with ψ_{k0} for some specific index k. If we choose $k \neq n$, then

$$c_{nk}E_{k0} + \langle k0|\, V\, |n0\rangle = c_{nk}E_{n0} \tag{15}$$

$$c_{nk} = \frac{\langle k0|\, V\, |n0\rangle}{E_{n0} - E_{k0}} \tag{16}$$

If $k = n$, then

$$c_{nn}E_{n0} + \langle n0|\, V\, |n0\rangle = c_{nn}E_{n0} + E_{n1} \tag{17}$$

$$E_{n1} = E_{n1} \tag{18}$$

Thus the $k = n$ term tells us nothing new. In fact, we can just leave out this term from the expansion, since the contribution of the $k = n$ term is already present in the original unperturbed wave function, which is *entirely* ψ_{n0}. Thus the first-order perturbation to the wave function is

$$\psi_{n1} = \sum_{j\neq n} \frac{\langle j0|\, V\, |n0\rangle}{E_{n0} - E_{j0}}\psi_{j0} \tag{19}$$

Note that the assumption of non-degeneracy is crucial here, since if $E_{n0} = E_{j0}$ for some $j \neq n$, we would be dividing by zero.

Example 1. We consider the case of a delta-function perturbation in the centre of the infinite square well. That is, we introduce

$$V = \alpha\delta\left(x - \frac{a}{2}\right) \tag{20}$$

The exact wave functions in the unperturbed square well are

$$\psi_{n0} = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \tag{21}$$

The energy perturbation is

$$E_{n1} = \langle n0|\, V\, |n0\rangle \tag{22}$$

$$= \frac{2\alpha}{a}\sin^2\frac{n\pi}{2} \tag{23}$$

For odd n this is $E_{n1} = 2\alpha/a$, while for even n $E_{n1} = 0$. The latter result is due to the fact that for even n $\psi_{n0}(a/2) = 0$ so the delta function isn't seen.

We can work out the perturbation in the wave function for the case $n = 1$. We have

$$\psi_{11} = \sum_{j \neq 1} \frac{\langle j0 | V | 10 \rangle}{E_{10} - E_{j0}} \psi_{j0} \tag{24}$$

The unperturbed energy levels are

$$E_{j0} = \frac{(j\pi\hbar)^2}{2ma^2} \tag{25}$$

so

$$E_{10} - E_{j0} = \left(1 - j^2\right) \frac{\pi^2\hbar^2}{2ma^2} \tag{26}$$

The matrix elements are

$$\langle j0 | V | 10 \rangle = \langle j0 | \alpha\delta\left(x - \frac{a}{2}\right) | 10 \rangle \tag{27}$$

$$= \frac{2\alpha}{a} \sin\frac{\pi}{2} \sin\frac{j\pi}{2} \tag{28}$$

$$= \frac{2\alpha}{a} \sin\frac{j\pi}{2} \tag{29}$$

Putting it all together, we get

$$\psi_{11} = \frac{m\alpha}{\pi^2\hbar^2} \sqrt{\frac{a}{2}} \left[\sin\frac{3\pi x}{a} - \frac{1}{3} \sin\frac{5\pi x}{a} + \frac{1}{6} \sin\frac{7\pi x}{a} + \ldots \right] \tag{30}$$

So the complete wave function is

$$\psi = \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a} + \frac{m\alpha}{\pi^2\hbar^2} \sqrt{\frac{a}{2}} \left[\sin\frac{3\pi x}{a} - \frac{1}{3} \sin\frac{5\pi x}{a} + \frac{1}{6} \sin\frac{7\pi x}{a} + \ldots \right] \tag{31}$$

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