DEGENERATE PERTURBATION THEORY - TWO STATES

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We've had a look at first order and second order perturbation theory for non-degenerate systems. In those systems, the first and second order corrections to the energy are

$$E_{n1} = \langle n0 | V | n0 \rangle \tag{1}$$

$$E_{n2} = \sum_{j \neq n} \frac{|\langle j0 | V | n0 \rangle|^2}{E_{n0} - E_{j0}} \tag{2}$$

If we try to apply these formulas to systems with degenerate energy levels, there is an obvious problem with E_{n2}. In a degenerate system, two or more distinct states have the same energy, so that $E_{n0} = E_{j0}$ for some $j \neq n$, thus the denominator in the sum will be zero for some of the terms.

There is, in fact, another problem that is a bit more subtle. In a degenerate system with, say, two orthonormal states $|a0\rangle$ and $|b0\rangle$ having the same energy E, any linear combination of these two states also has the same energy:

$$H_0 (\alpha |a0\rangle + \beta |b0\rangle) = E (\alpha |a0\rangle + \beta |b0\rangle) \tag{3}$$

Since there are infinitely many such states with the same energy, we have no way of determining which of these states should be used in calculating the matrix element $\langle n0 | V | n0 \rangle$ in the first order formula or the elements $\langle j0 | V | n0 \rangle$ in the second order formula.

Despite these problems, let's follow the same reasoning that we used in our original discussion of perturbation theory and see where it leads. Starting with the first order equation, we have

$$H_0 |n1\rangle + V |n0\rangle = E_{n0} |n1\rangle + E_{n1} |n0\rangle \tag{4}$$

Multiply through by $\langle a0|$

$$\langle a0|H_0|n1\rangle + \langle a0|V|n0\rangle = \langle a0|E_{n0}|n1\rangle + \langle a0|E_{n1}|n0\rangle \tag{5}$$
$$\langle H_0 a0|n1\rangle + \langle a0|V|n0\rangle = E_{n0}\langle a0|n1\rangle + E_{n1}\langle a0|n0\rangle \tag{6}$$
$$E_{n0}\langle a0|n1\rangle + \langle a0|V|n0\rangle = E_{n0}\langle a0|n1\rangle + E_{n1}\langle a0|n0\rangle \tag{7}$$
$$\langle a0|V|n0\rangle = E_{n1}\langle a0|n0\rangle \tag{8}$$

Now we can substitute

$$|n0\rangle = \alpha|a0\rangle + \beta|b0\rangle \tag{9}$$

to get

$$\alpha\langle a0|V|a0\rangle + \beta\langle a0|V|b0\rangle = \alpha E_{n1} \tag{10}$$

We can multiply 4 through by $\langle b0|$ to get another relation:

$$\alpha\langle b0|V|a0\rangle + \beta\langle b0|V|b0\rangle = \beta E_{n1} \tag{11}$$

Defining the shorthand notation

$$W_{ij} \equiv \langle i0|V|j0\rangle \tag{12}$$

we get the two relations

$$\alpha W_{aa} + \beta W_{ab} = \alpha E_{n1} \tag{13}$$
$$\alpha W_{ba} + \beta W_{bb} = \beta E_{n1} \tag{14}$$

What do we actually know in these two equations? We're assuming that we have solved the unperturbed system, so we should know $|a0\rangle$ and $|b0\rangle$, so that means we can work out the matrix elements W_{ij}. The constants α and β are related through normalization, so that $|\alpha|^2 + |\beta|^2 = 1$, and of course E_{n1} is what we're trying to find.

We can eliminate β as follows:

$$\beta W_{ab} = \alpha E_{n1} - \alpha W_{aa} \tag{15}$$
$$\beta = \frac{\alpha E_{n1} - \alpha W_{aa}}{W_{ab}} \tag{16}$$

Substituting this into 14 we have

$$\alpha W_{ba} + \frac{W_{bb}}{W_{ab}}(\alpha E_{n1} - \alpha W_{aa}) = \frac{E_{n1}}{W_{ab}}(\alpha E_{n1} - \alpha W_{aa}) \tag{17}$$

We now have α as a common factor in all terms, so assuming it's not zero, we get

$$W_{ab}W_{ba} - (E_{n1} - W_{aa})(E_{n1} - W_{bb}) = 0 \tag{18}$$

$$E_{n1}^2 - (W_{aa} + W_{bb})E_{n1} + W_{aa}W_{bb} - W_{ab}W_{ba} = 0 \tag{19}$$

From the definition of W_{ij}, we have $W_{ab}W_{ba} = |W_{ab}|^2$, so using the quadratic formula we get two possible values for E_{n1}:

$$E_{n1} = \frac{1}{2}\left(W_{aa} + W_{bb} \pm \sqrt{W_{aa}^2 + 2W_{aa}W_{bb} + W_{bb}^2 - 4W_{aa}W_{bb} + 4|W_{ab}|^2}\right) \tag{20}$$

$$= \frac{1}{2}\left(W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right) \tag{21}$$

Since the operand of the square root is intrinsically positive, we will always get two distinct values for E_{n1}. Thus the effect of the perturbation on two degenerate energy levels is to split them into two different states with different energies.

In fact, this formula works also in the case $\alpha = 0$, since in that case (from normalization) $\beta = 1$ and we get, from our pair of relations 14 above, $W_{ab} = 0$ and $E_{n1} = W_{bb}$, which is what we get from the quadratic solution if we take the minus sign for the square root. If we did the same calculation, except we eliminated α instead of β, we'd end up with the same formula. In that case, if we take $\beta = 0$, $E_{n1} = W_{aa}$ which is obtained from the quadratic formula by taking the plus sign.

Note that in general we won't know α or β a priori, so we'll have to work out the matrix elements W_{ij} for the pair of orthonormal degenerate states that we know from our analysis of the unperturbed system. If we discover in the process that $W_{ab} = 0$, then the two values for E_{n1} are W_{aa} and W_{bb}. That is, the order of calculation is: first, find $|a0\rangle$ and $|b0\rangle$, then calculate W_{ij} to get the two values for E_{n1}. We don't actually need to know α or β to find the perturbed energies.

However, it's clearly easier if we can find the special states for which $W_{ab} = 0$, since in that case the two energies are just $W_{aa} = \langle a0|V|a0\rangle$ and $W_{bb} = \langle b0|V|b0\rangle$, which happen to be the first order corrections for the *non*degenerate system.

In general, there will be a pair of 'special' unperturbed states that allow this, with each state having its own values of α and β. Let's define them as the plus and minus states, so

$$|\pm 0\rangle = \alpha_\pm |a0\rangle + \beta_\pm |b0\rangle \tag{22}$$

In this case, we're *not* assuming that the states $|a0\rangle$ and $|b0\rangle$ are special, so $\alpha_\pm$ and $\beta_\pm$ can be any values consistent with $|\alpha|^2+|\beta|^2=1$.

First, we can show that the special states are orthogonal. Using the orthogonality of $|a0\rangle$ and $|b0\rangle$, we have

$$\langle +0\,|-0\rangle = \alpha_+^*\alpha_- + \beta_+^*\beta_- \tag{23}$$

From our pair of relations above we have, assuming $W_{ab}\neq 0$ (which is valid since $|a0\rangle$ and $|b0\rangle$ are not special states)

$$\beta_\pm = \alpha_\pm \frac{E_{\pm,1}-W_{aa}}{W_{ab}} \tag{24}$$

so

$$\langle +0\,|-0\rangle = \alpha_+^*\alpha_-\left[1+\frac{(E_{+,1}-W_{aa})(E_{-,1}-W_{aa})}{|W_{ab}|^2}\right] \tag{25}$$

$$= \frac{\alpha_+^*\alpha_-}{|W_{ab}|^2}\left[|W_{ab}|^2+E_{+,1}E_{-,1}-W_{aa}(E_{+,1}+E_{-,1})+W_{aa}^2\right] \tag{26}$$

Using the quadratic formula, we have

$$E_{+,1}E_{-,1} = \frac{1}{4}\left[(W_{aa}+W_{bb})^2-(W_{aa}-W_{bb})^2-4|W_{ab}|^2\right] \tag{27}$$

$$= W_{aa}W_{bb}-|W_{ab}|^2 \tag{28}$$

$$E_{+,1}+E_{-,1} = W_{aa}+W_{bb} \tag{29}$$

Putting these results in the previous equation gives us

$$\langle +0\,|-0\rangle = 0 \tag{30}$$

Thus the two special states are always orthogonal.

Next, we can show that the off-diagonal elements of $\langle +0|\,V\,|-0\rangle$ are zero as well. Expanding out the brackets:

$$\langle +0|\,V\,|-0\rangle = \alpha_+^*\alpha_-W_{aa}+\alpha_+^*\beta_-W_{ab}+\beta_+^*\alpha_-W_{ba}+\beta_+^*\beta_-W_{bb} \tag{31}$$

Using our original pair of relations:

$$\alpha_+^*(\alpha_-W_{aa}+\beta_-W_{ab}) = \alpha_+^*\alpha_-E_{-,1} \tag{32}$$

$$\beta_+^*(\alpha_-W_{ba}+\beta_-W_{bb}) = \beta_+^*\beta_-E_{-,1} \tag{33}$$

$$\langle +0\,|-0\rangle = \alpha_+^*\alpha_-+\beta_+^*\beta_- = 0 \tag{34}$$

we can plug all these into the first equation and get

$$\langle +0|V|-0\rangle = 0 \tag{35}$$

Finally, we can find the diagonal elements $\langle \pm 0|V|\pm 0\rangle$ by repeating the analysis of the off-diagonal elements. For example, we can replace $|-0\rangle$ by $|+0\rangle$ and we get

$$\langle +0|V|+0\rangle = \alpha_+^*\alpha_+W_{aa} + \alpha_+^*\beta_+W_{ab} + \beta_+^*\alpha_+W_{ba} + \beta_+^*\beta_+W_{bb} \tag{36}$$

Using our original pair of relations:

$$\alpha_+^*\left(\alpha_+W_{aa} + \beta_+W_{ab}\right) = \alpha_+^*\alpha_+E_{+,1} \tag{37}$$

$$\beta_+^*\left(\alpha_+W_{ba} + \beta_+W_{bb}\right) = \beta_+^*\beta_+E_{+,1} \tag{38}$$

$$\alpha_+^*\alpha_+ + \beta_+^*\beta_+ = |\alpha_+|^2 + |\beta_+|^2 = 1 \tag{39}$$

we can plug all these into the first equation and get

$$\langle +0|V|+0\rangle = E_{+,1} \tag{40}$$

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