Time-Independent Degenerate Perturbation Theory

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Suppose we have a problem, described by the hamiltonian H_0, for which we know the exact solution. Furthermore, suppose that the eigenstates may be degenerate, that is, different states may have the same energy. More precisely, suppose that we know the exact solution of

$$H_0 \, |\psi_{mr}^{(0)}\rangle = E_m^{(0)} \, |\psi_{mr}^{(0)}\rangle \qquad (1 \leq r \leq g_m)$$

Note that different energies may have different degrees of degeneracy. For example, if $g_1 = 4$, $g_2 = 1$, and $g_3 = 2$, then there are 4 unperturbed states with energy $E_1^{(0)}$, only one unperturbed state with energy $E_2^{(0)}$ (that is, this unperturbed state is non-degenerate), and 2 unperturbed states with energy $E_3^{(0)}$. Thus, the formalism here includes that of non-degenerate perturbation theory. Note also that $E_m^{(0)}$ in the expression above does *not* have an r index, since the g_m states $|\psi_{mr}^{(0)}\rangle$ (with $1 \leq r \leq g_m$) all have the same energy.

So, by assumption, we've already solved the eigenvalue problem above and we already know *all* the $|\psi_{mr}^{(0)}\rangle$ states and their energies $E_m^{(0)}$.

Now suppose we're faced with a new problem, described by the hamiltonian $H = H_0 + \lambda \, H'$, for which we do *not* know the exact solution. Here, H' is some *known* Hamiltonian and λ is some real parameter, assumed to be small (small as in $|\lambda| \ll 1$).

Since λ is small, we expect the solution to the new problem to be close to the solution of the original (unperturbed) problem. Moreover, since λ is a parameter, the new eigenenergies and eigenstates will be dependent on its value. In other words, we're faced with solving the following problem:

$$(H_0 + \lambda \, H') \, |\psi_{mr}(\lambda)\rangle = E_{mr}(\lambda) \, |\psi_{mr}(\lambda)\rangle \qquad (1 \leq r \leq g_m)$$

Note that the eigenenergies of the perturbed problem, $E_{mr}(\lambda)$, do depend on the second index. This corresponds to the assumption that the degeneracy is lifted (or broken) by the perturbation, that is, the eigenstates $|\psi_{mr}(\lambda)\rangle$ and $|\psi_{ms}(\lambda)\rangle$ no longer have the same energies, if $r \neq s$.

As already mentioned, we expect the solution to this new problem to be close to the solution of the unperturbed problem, meaning that both the eigenenergies and eigenstates can be written as power series expansions in λ. More specifically,

$$E_{mr}(\lambda) = E_m^{(0)} + \lambda\, E_{mr}^{(1)} + \lambda^2\, E_{mr}^{(2)} + \ldots$$

Note that we're making the assumption that $E_{mr}^{(1)}$ *does* depend on the second index, meaning that the degeneracy is lifted by the perturbation already at first order. It doesn't have to be that way; it could be that $E_m^{(1)}$ is *still* independent of r and that the degeneracy is lifted by the second-order terms, or third-order, or.... You get the idea.

Now, how can we expand $|\psi_{mr}(\lambda)\rangle$ in a way that's similar to the one above? The easiest, best, and standard way is first to express this state vector as a linear superposition of the *unperturbed* states. That's possible because the unperturbed states form a basis (in fact, an orthonormal basis, meaning that $\langle\psi_{mr}^{(0)}||\psi_{ns}^{(0)}\rangle = \delta_{mn}\,\delta_{rs}$). Thus,

$$|\psi_{mr}(\lambda)\rangle = \sum_n \sum_{s=1}^{g_n} c_{mn,rs}(\lambda)\,|\psi_{ns}^{(0)}\rangle\,.$$

Note that the coefficients $c_{mn,rs}(\lambda)$ must be functions of λ since the left-hand-side is a function of λ but the unperturbed states $|\psi_{ns}^{(0)}\rangle$ aren't (the unperturbed problem knows nothing about λ). *Now* we can expand the coefficients into a power series in λ just as we did with the energies. But before we do that, let's separate the contribution made by the various $|\psi_{ms}^{(0)}\rangle$ states to the sum above:

$$|\psi_{mr}(\lambda)\rangle = \sum_{s=1}^{g_m} c_{mm,rs}(\lambda)\,|\psi_{ms}^{(0)}\rangle + \sum_{n\neq m}\sum_{s=1}^{g_n} c_{mn,rs}(\lambda)\,|\psi_{ns}^{(0)}\rangle\,.$$

Now we're ready to perform a series expansion. What do we expect to obtain if we change λ back to zero? In that limit, it's reasonable to expect that we should fall back to the original unperturbed state from which we started, namely, $|\psi_{mr}^{(0)}\rangle$. But things aren't so simple. Since the energy level $E_m^{(0)}$ is assumed degenerate, the most we can say is that we'll end up in a state that's a combination of states of the same energy as the original state we started from. Therefore, we must write:

$$\begin{array}{rclcccccl} c_{mm,rs}(\lambda) & = & c_{mm,rs}^{(0)} & + & \lambda\, c_{mm,rs}^{(1)} & + & \lambda^2\, c_{mm,rs}^{(2)} & + & \ldots \\ c_{mn,rs}(\lambda) & = & & & \lambda\, c_{mn,rs}^{(1)} & + & \lambda^2\, c_{mn,rs}^{(2)} & + & \ldots \qquad (n \neq m) \end{array}$$

Why is it that the second set of coefficients (those with $n \neq m$) do not have a λ-independent term? Because in the limit $\lambda \to 0$, we expect no contribution from states other than those of energy $E_m^{(0)}$ (that is, no contribution from states with $n \neq m$). Note that, in non-degenerate perturbation theory, we have the freedom to set the zero-order term $c_{mm,rs}^{(0)}$ to 1 because there is only one such term for each value of m (that is, $r = s = 1$ *only*) and it can be proved that its value is a complex number of magnitude 1, which doesn't contribute to the expectation value of measurable operators. Here, we're not generally allowed to do so because of degeneracy.

We're now ready to obtain an approximate solution to the perturbed problem. Our goal is to obtain the various contributions to the energy ($E_{mr}^{(1)}, E_{mr}^{(2)}$, *etc*) and the various coefficients $c_{mm,rs}^{(0)}, c_{mm,rs}^{(1)}, c_{mm,rs}^{(2)}$, *etc* and $c_{mn,rs}^{(1)}, c_{mn,rs}^{(2)}$, *etc* (for $n \neq m$). How do we do that? By throwing the expansions back into the perturbed problem,

$$(H_0 + \lambda\, H')\, |\psi_{mr}(\lambda)\rangle = E_{mr}(\lambda)\, |\psi_{mr}(\lambda)\rangle\,,$$

and collecting terms of equal powers of λ:

$$(H_0 + \lambda\, H') \Big[\sum_{s=1}^{g_m} c_{mm,rs}(\lambda)\, |\psi_{ms}^{(0)}\rangle + \sum_{n \neq m} \sum_{s=1}^{g_n} c_{mn,rs}(\lambda)\, |\psi_{ns}^{(0)}\rangle + \dots \Big] \;=$$
$$\Big(E_m^{(0)} + \lambda\, E_{mr}^{(1)} + \lambda^2\, E_{mr}^{(2)} + \dots \Big) \Big[\sum_{s=1}^{g_m} c_{mm,rs}(\lambda)\, |\psi_{ms}^{(0)}\rangle + \sum_{n \neq m} \sum_{s=1}^{g_n} c_{mn,rs}(\lambda)\, |\psi_{ns}^{(0)}\rangle + \dots \Big]\,.$$

Now, recall that $c_{mm,rs}(\lambda)$ has a λ-independent term but $c_{mn,rs}(\lambda)$ ($n \neq m$) is already at least first-order in λ. Thus, the expression above breaks down into the following:

- λ-independent terms:

$$\begin{aligned}
H_0 \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle \;&=\; E_m^{(0)} \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle \qquad \Rightarrow \\
E_m^{(0)} \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle \;&=\; E_m^{(0)} \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle \qquad \Rightarrow \qquad \text{no information}
\end{aligned}$$

- λ terms:

$$H_0 \sum_{s=1}^{g_m} \lambda\, c_{mm,rs}^{(1)}\, |\psi_{ms}^{(0)}\rangle + \lambda\, H' \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle + H_0 \sum_{n \neq m} \sum_{s=1}^{g_n} \lambda\, c_{mn,rs}^{(1)}\, |\psi_{ns}^{(0)}\rangle \;=$$
$$E_m^{(0)} \sum_{s=1}^{g_m} \lambda\, c_{mm,rs}^{(1)}\, |\psi_{ms}^{(0)}\rangle + \lambda\, E_{mr}^{(1)} \sum_{s=1}^{g_m} c_{mm,rs}^{(0)}\, |\psi_{ms}^{(0)}\rangle + E_m^{(0)} \sum_{n \neq m} \sum_{s=1}^{g_n} \lambda\, c_{mn,rs}^{(1)}\, |\psi_{ns}^{(0)}\rangle\,.$$

  This can be simplified to the following, taking into consideration that $|\psi_{ms}^{(0)}\rangle$ is an eigenstate of H_0 with eigenvalue $E_m^{(0)}$ and noticing that every term is multiplied by a factor of λ:

$$\sum_{s=1}^{g_m} c^{(1)}_{mm,rs}\, E^{(0)}_m\, |\psi^{(0)}_{ms}\rangle + \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, H'\, |\psi^{(0)}_{ms}\rangle + \sum_{n\neq m}\sum_{s=1}^{g_n} c^{(1)}_{mn,rs}\, E^{(0)}_n\, |\psi^{(0)}_{ns}\rangle \quad = \\ E^{(0)}_m \sum_{s=1}^{g_m} c^{(1)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + E^{(1)}_{mr} \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + E^{(0)}_m \sum_{n\neq m}\sum_{s=1}^{g_n} c^{(1)}_{mn,rs}\, |\psi^{(0)}_{ns}\rangle\,.$$

Next, suppose we multiply on the left by the state $\langle\psi^{(0)}_{kq}|$, where k and q are arbitrary indices (well, q has to satisfy $1 \leq q \leq g_k$). Since $\langle\psi^{(0)}_{kq}||\psi^{(0)}_{mr}\rangle = \delta_{km}\,\delta_{qr}$, we get:

$$\sum_{s=1}^{g_m} c^{(1)}_{mm,rs}\, E^{(0)}_m\, \delta_{km}\,\delta_{qs} + \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{kq}|\, H'\, |\psi^{(0)}_{ms}\rangle + \sum_{n\neq m}\sum_{s=1}^{g_n} c^{(1)}_{mn,rs}\, E^{(0)}_n\, \delta_{kn}\,\delta_{qs} \quad = \\ E^{(0)}_m \sum_{s=1}^{g_m} c^{(1)}_{mm,rs}\, \delta_{km}\,\delta_{qs} + E^{(1)}_{mr} \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \delta_{km}\,\delta_{qs} + E^{(0)}_m \sum_{n\neq m}\sum_{s=1}^{g_n} c^{(1)}_{mn,rs}\, \delta_{kn}\,\delta_{qs}\,.$$

Performing the summations where possible, thanks to the δ's, we obtain:

$$c^{(1)}_{mm,rq}\, E^{(0)}_m\, \delta_{km} + \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{kq}|\, H'\, |\psi^{(0)}_{ms}\rangle + \sum_{n\neq m} c^{(1)}_{mn,rq}\, E^{(0)}_n\, \delta_{kn} \quad = \\ E^{(0)}_m\, c^{(1)}_{mm,rq}\, \delta_{km} + E^{(1)}_{mr}\, c^{(0)}_{mm,rq}\, \delta_{km} + E^{(0)}_m \sum_{n\neq m} c^{(1)}_{mn,rq}\, \delta_{kn}\,.$$

Since the state $\langle\psi^{(0)}_{kq}|$ was arbitrary, we have two possibilities: either $k = m$ or $k \neq m$. The first one gives us:

$$c^{(1)}_{mm,rq}\, E^{(0)}_m + \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{mq}|\, H'\, |\psi^{(0)}_{ms}\rangle + \sum_{n\neq m} c^{(1)}_{mn,rq}\, E^{(0)}_n\, \delta_{mn} \quad = \\ E^{(0)}_m\, c^{(1)}_{mm,rq} + E^{(1)}_{mr}\, c^{(0)}_{mm,rq} + E^{(0)}_m \sum_{n\neq m} c^{(1)}_{mn,rq}\, \delta_{mn}\,.$$

Now note a small miracle: both summations disappear since we're summing over $n \neq m$ but δ_{mn} requires that $n = m$. Moreover, the term $c^{(1)}_{mm,rq}\, E^{(0)}_m$ appears on both sides of the equation and also disappears, resulting in:

$$\sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{mq}|\, H'\, |\psi^{(0)}_{ms}\rangle = E^{(1)}_{mr}\, c^{(0)}_{mm,rq}\,,$$

which we can re-write as follows:

$$\sum_{s=1}^{g_m} c^{(0)}_{mm,rs} \left[\langle \psi^{(0)}_{mq} | \, H' \, | \psi^{(0)}_{ms} \rangle - E^{(1)}_{mr} \, \delta_{qs} \right] = 0 \, .$$

Let's now try to understand what this equation is saying. Recall that the λ-independent terms gave us no information, but they contained the unknown quantities $c^{(0)}_{mm,rs}$, which seemed to indicate that we wouldn't be able to determine them. But now we see that we *can* determine them, by solving the problem above. But, wait... The $E^{(1)}_{mr}$ values are also unknown. How can we solve for all these unknowns? It seems we don't have enough equations, but we do! The problem above has a non-zero solution for the $c^{(0)}_{mm,rs}$ coefficients if and only if the determinant of the matrix whose elements appear inside the square brackets above vanishes:

$$\det \left[\langle \psi^{(0)}_{mq} | \, H' \, | \psi^{(0)}_{ms} \rangle - E^{(1)}_{mr} \, \delta_{qs} \right] = 0 \, .$$

This is nothing but another eigenvalue problem, namely, that of diagonalizing the matrix whose elements are $\langle \psi^{(0)}_{mq} | \, H' \, | \psi^{(0)}_{ms} \rangle$. To see that more clearly, define the column vector

$$\mathbf{u}^{(m)}_r \equiv \left(c^{(0)}_{mm,r1} \quad c^{(0)}_{mm,r2} \quad c^{(0)}_{mm,r3} \quad \cdots \quad c^{(0)}_{mm,rg_m} \right)^t$$

and the matrix $\mathbf{A}^{(m)}$ whose elements are $\mathbf{A}^{(m)}_{qs} \equiv \langle \psi^{(0)}_{mq} | \, H' \, | \psi^{(0)}_{ms} \rangle$. Then, the equation resulting from the λ terms is nothing but:

$$\mathbf{A}^{(m)} \, \mathbf{u}^{(m)}_r = E^{(1)}_{mr} \, \mathbf{u}^{(m)}_r \, ,$$

an eigenvalue problem! As mentioned already, this eigenvalue problem will have a non-zero solution for the vectors $\mathbf{u}^{(m)}_r$ provided that

$$\det \left(\mathbf{A}^{(m)} - E^{(1)}_{mr} \, \mathbf{I} \right) = 0 \, ,$$

which is the result claimed above. Note that there are g_m eigenvalues (the $E^{(1)}_{mr}$'s) and g_m eigenvectors (the $\mathbf{u}^{(m)}_r$'s) since $1 \leq r \leq g_m$. Once we've solved for the eigenvalues $E^{(1)}_{mr}$ and the eigenvectors $\mathbf{u}^{(m)}_r$ (that is, for the $c^{(0)}_{mm,rs}$ coefficients), we can proceed to the $k \neq m$ case (recall that all of the above analysis was done assuming that the arbitrary state $\langle \psi^{(0)}_{kq} |$ wasn't so arbitrary after all but had $k = m$). Before we do that, however, let's see how this result changes if we didn't have any degeneracy. In that case, $g_m = 1$ and we'd obtain the simple result:

$$E^{(1)}_{mr} = \langle \psi^{(0)}_{mq} | \, H' \, | \psi^{(0)}_{ms} \rangle \, , \qquad \text{with } r = q = s = 1 \, ,$$

which you'll recognize as our old non-degenerate result for the first-order correction to the energy.

Now let's get back at the degenerate case, with $k \neq m$. Recall the result:

$$c^{(1)}_{mm,rq}\, E^{(0)}_m\, \delta_{km} + \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{kq}|\, H'\, |\psi^{(0)}_{ms}\rangle + \sum_{n\neq m} c^{(1)}_{mn,rq}\, E^{(0)}_n\, \delta_{kn} \quad = \quad E^{(0)}_m\, c^{(1)}_{mm,rq}\, \delta_{km} + E^{(1)}_{mr}\, c^{(0)}_{mm,rq}\, \delta_{km} + E^{(0)}_m \sum_{n\neq m} c^{(1)}_{mn,rq}\, \delta_{kn}\,.$$

When $k \neq m$, this simplifies to:

$$\sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{kq}|\, H'\, |\psi^{(0)}_{ms}\rangle + c^{(1)}_{mk,rq}\, E^{(0)}_k = E^{(0)}_m\, c^{(1)}_{mk,rq}\,.$$

Or, simpler still,

$$c^{(1)}_{mk,rq} = \frac{\sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, \langle\psi^{(0)}_{kq}|\, H'\, |\psi^{(0)}_{ms}\rangle}{E^{(0)}_m - E^{(0)}_k} \qquad (m \neq k)\,.$$

So, there, we've managed to obtain the zero- and first-order terms of the expansion of $c_{mk,rs}(\lambda)$ and the first-order correction to the energy, $E^{(1)}_{mr}$. Now, on to the second-order terms...

- λ^2 terms:

$$H_0 \sum_{s=1}^{g_m} \lambda^2\, c^{(2)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + \lambda\, H' \sum_{s=1}^{g_m} \lambda\, c^{(1)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + H_0 \sum_{n\neq m} \sum_{s=1}^{g_n} \lambda^2\, c^{(2)}_{mn,rs}\, |\psi^{(0)}_{ns}\rangle + \lambda\, H' \sum_{n\neq m} \sum_{s=1}^{g_n} \lambda\, c^{(1)}_{mn,rs}\, |\psi^{(0)}_{ns}\rangle \quad =$$
$$E^{(0)}_m \sum_{s=1}^{g_m} \lambda^2\, c^{(2)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + \lambda\, E^{(1)}_{mr} \sum_{s=1}^{g_m} \lambda\, c^{(1)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + \lambda^2\, E^{(2)}_{mr} \sum_{s=1}^{g_m} c^{(0)}_{mm,rs}\, |\psi^{(0)}_{ms}\rangle + E^{(0)}_m \sum_{n\neq m} \sum_{s=1}^{g_n} \lambda^2\, c^{(2)}_{mn,rs}\, |\psi^{(0)}_{ns}\rangle + \lambda\, E^{(1)}_{mr} \sum_{n\neq m} \sum_{s=1}^{g_n} \lambda\, c^{(1)}_{mn,rs}\, |\psi^{(0)}_{ns}\rangle\,.$$

By following the same procedure of multiplying on the left by an arbitrary state $\langle\psi^{(0)}_{kq}|$ and then considering what happens when $k = m$ and when $k \neq m$, we'll be able to obtain the second-order term of the expansion of $c_{mk,rs}(\lambda)$ and the second-order correction to the energy, $E^{(2)}_{mr}$. I'll leave that as an exercise for you...

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