17.3 Degenerate perturbation theory

Obviously, the expressions we derived blow up in the case of degeneracies, where $E_n^0 = E_m^0$ for some $n \neq m$. So what do we do in that case?

Problems like that occur also if some states of $\hat{H}^0$, although not degenerate, have almost the same energy. While not blowing up term by term, the series in that case cannot be expected to converge. So whenever $\dfrac{\langle m^0 | \hat{H}' | n^0 \rangle}{E_n^0 - E_m^0}$

is large for some m, we have a problem.

To illustrate the resolution of this problem, let us start with just 2 (nearly) degenerate states. In general the perturbation will break their degeneracy. The problem of the formulation of perturbation theory used so far originates in the fact that, as we let $\lambda \to 0$ and slowly turn off the perturbation, the limiting states in general do not agree with the unperturbed basis states $|m^0\rangle$ that we started out with, but represent some linear combination of them which resides in the same degenerate subspace of $\hat{H}^0$. Our first goal is to find this linear combination and then build our perturbative expansion on these states.

- So suppose, the unperturbed Hamiltonian has the eigenstates $|n^\circ\rangle$ $(n=1,2,3,\ldots)$, with

$$\hat{H}^\circ |n^\circ\rangle = E_n^\circ |n^\circ\rangle$$

and that we number them in such a way that the 2 degenerate (or nearly degenerate) states are $|1^\circ\rangle$ and $|2^\circ\rangle$, with $E_1^\circ = E_2^\circ$ or $E_1^\circ \approx E_2^\circ$.

- Construct the projection operator

$$\hat{P}_{12} = \hat{P}_1 + \hat{P}_2 = |1^\circ\rangle\langle 1^\circ| + |2^\circ\rangle\langle 2^\circ|$$

that projects any Hilbert-space state onto this (quasi-) degenerate subspace of $\hat{H}^\circ$.

- In this subspace, we define the truncated Hamiltonian

$$\hat{\bar{H}} \equiv \hat{P}_{12}\,\hat{H}\,\hat{P}_{12} = \hat{P}_{12}(\hat{H}^\circ + \lambda\hat{H}')\hat{P}_{12} =$$

$$= \left(|1^\circ\rangle\langle 1^\circ| + |2^\circ\rangle\langle 2^\circ|\right)\left(\hat{H}^\circ + \lambda\hat{H}'\right)\left(|1^\circ\rangle\langle 1^\circ| + |2^\circ\rangle\langle 2^\circ|\right)$$

$$= E_1^\circ |1^\circ\rangle\langle 1^\circ| + E_2^\circ |2^\circ\rangle\langle 2^\circ| + \lambda\hat{P}_{12}\hat{H}'\hat{P}_{12}$$

- Next, we solve the eigenvalue problem of the truncated Hamiltonian (in the 2-dimensional quasidegenerate subspace) exactly:

$$\hat{\bar{H}}\,|\bar{i}\rangle = \bar{E}_i^{(0)}|\bar{i}\rangle \quad , \; i=1,2$$

Let's work this out in the basis $\{|1^\circ\rangle, |2^\circ\rangle\}$:

$$\langle k^\circ | \hat{\bar{H}} | \bar{i} \rangle = \bar{E}_i^{(0)} \langle k^\circ | \bar{i} \rangle \qquad (i, k = 1, 2)$$

$$\sum_{j=1}^{2} \langle k^\circ | \hat{\bar{H}} | j^\circ \rangle \langle j^\circ | \bar{i} \rangle = \bar{E}_i \langle k^\circ | \bar{i} \rangle$$

which can be written as the matrix equation

$$\begin{pmatrix} \langle 1^\circ | \hat{\bar{H}} | 1^\circ \rangle & \langle 1^\circ | \hat{\bar{H}} | 2^\circ \rangle \\ \langle 2^\circ | \hat{\bar{H}} | 1^\circ \rangle & \langle 2^\circ | \hat{\bar{H}} | 1^\circ \rangle \end{pmatrix} \begin{pmatrix} \langle 1^\circ | \bar{i} \rangle \\ \langle 2^\circ | \bar{i} \rangle \end{pmatrix} = \bar{E}_i^{(0)} \begin{pmatrix} \langle 1^\circ | \bar{i} \rangle \\ \langle 2^\circ | \bar{i} \rangle \end{pmatrix}$$

$$(i = 1, 2)$$

Here $$\langle k^\circ | \hat{\bar{H}} | j^\circ \rangle = E_1^\circ \langle k^\circ | 1^\circ \rangle \langle 1^\circ | j^\circ \rangle + E_2^\circ \langle k^\circ | 2^\circ \rangle \langle 2^\circ | j^\circ \rangle$$

$$+ \lambda \sum_{m,n=1}^{2} \langle k^\circ | m^\circ \rangle \langle m^\circ | \hat{H}' | n^\circ \rangle \langle n^\circ | j^\circ \rangle$$

$$= E_1^\circ \delta_{k1} \delta_{j1} + E_2^\circ \delta_{k2} \delta_{j2} + \langle k^\circ | \lambda \hat{H}' | j^\circ \rangle$$

So the matrix equation looks like

$$\begin{pmatrix} E_1^\circ + \langle 1^\circ | \lambda \hat{H}' | 2^\circ \rangle & \langle 1^\circ | \lambda \hat{H}' | 2^\circ \rangle \\ \langle 2^\circ | \lambda \hat{H}' | 1^\circ \rangle & E_2^\circ + \langle 2^\circ | \lambda \hat{H}' | 2^\circ \rangle \end{pmatrix} \begin{pmatrix} \langle 1^\circ | \bar{i} \rangle \\ \langle 2^\circ | \bar{i} \rangle \end{pmatrix} = \bar{E}_i^{(0)} \begin{pmatrix} \langle 1^\circ | \bar{i} \rangle \\ \langle 2^\circ | \bar{i} \rangle \end{pmatrix}$$

$$(i = 1, 2)$$

The eigenvalues $\bar{E}_i$ are obtained as solutions of the secular equation

$$\det \begin{pmatrix} \langle 1^\circ | \lambda \hat{H}' | 2^\circ \rangle + E_1^\circ - \bar{E} & \langle 1^\circ | \lambda \hat{H}' | 2^\circ \rangle \\ \langle 2^\circ | \lambda \hat{H}' | 1^\circ \rangle & \langle 2^\circ | \lambda \hat{H}' | 2^\circ \rangle + E_2^\circ - \bar{E} \end{pmatrix} = 0$$

with solutions

$$\boxed{\bar{E}^{(0)}_{1,2} = \frac{1}{2}\left\{E_1^0 + E_2^0 + \langle 1^0|\lambda\hat{H}'|1^0\rangle + \langle 2^0|\lambda\hat{H}'|2^0\rangle \pm\sqrt{\left[E_2^0 + \langle 2^0|\lambda\hat{H}'|2^0\rangle - (E_1^0 + \langle 1^0|\lambda\hat{H}'|1^0\rangle)\right]^2 + 4|\langle 1^0|\lambda\hat{H}'|2\rangle|^2}\right\}} \quad (*)$$

Plugging these values back into the matrix equation we can determine the eigenstates $|\bar{1}\rangle, |\bar{2}\rangle$ of $\hat{H}$ (i.e. their representation in the $\{|1^0\rangle, |2^0\rangle\}$ basis).

- We see from (*) that for $\lambda \to 0$ the eigenvalues $\bar{E}_i$ correctly approach

$$\bar{E}^{(0)}_{1,2} \xrightarrow[\lambda\to 0]{} \frac{E_1^0 + E_2^0}{2} \pm (E_2^0 - E_1^0) = E^0_{1,2} \qquad \text{which are (almost) degenerate}$$

However, for $\lambda \neq 0$, the degeneracy is broken unless $\langle 1^0|\hat{H}'|1^0\rangle = \langle 2^0|\hat{H}'|2^0\rangle$ <u>and</u> $\langle 1^0|\hat{H}'|2^0\rangle = 0$

This breaking of the degeneracy amounts to a <u>large</u> correction of the energy difference $E_1 - E_2$ and thus cannot be treated perturbatively, but must be dealt with exactly.

- We can now use the new "unperturbed" basis $\{|\bar{1}\rangle, |\bar{2}\rangle, |3^0\rangle, |4^0\rangle, \dots\}$ to do standard pertubation theory. To this end we write

$$\hat{H} = \hat{H}^0 + \lambda\hat{H}' = \underbrace{\left(\hat{H}^0 + \hat{P}_{12}\lambda\hat{H}'\hat{P}_{12}\right)}_{\bar{H}^0} + \lambda\left(\hat{H}' - \hat{P}_{12}\hat{H}'\hat{P}_{12}\right)$$

$$= \bar{H}^0 + \lambda\overline{H'}$$

The new "unperturbed Hamiltonian"

$$\overline{H}^0 = \hat{H}^0 + \hat{P}_{12}(\hat{H} - \hat{H}^0)\hat{P}_{12} = \hat{\overline{H}} + \left(\hat{H}^0 - \hat{P}_{12}\hat{H}^0\hat{P}_{12}\right)$$

is diagonal in the subspace $\{|\bar{1}\rangle, |\bar{2}\rangle\}$ (where it reduces to $\hat{\overline{H}}$).

The new "perturbation"

$$\hat{\overline{H}}' = \hat{H}' - \hat{P}_{12}\hat{H}'\hat{P}_{12}$$

reduces to zero in the subspace $\{|\bar{1}\rangle, |\bar{2}\rangle\}$.

So perturbation theory in $\lambda\hat{\overline{H}}'$ involves no more terms with small energy denominators $E_1^{(0)} - E_2^{(0)}$, and the problem has been solved.

- If the space of degenerate energy eigenvalues is larger, $E_i^{(0)}$ $(i = 1, 2, \dots, d)$, we repeat the same procedure with $\hat{P}_{12}$ replaced by a projector $\hat{P}_d$ on the d-dimensional degenerate subspace. We diagonalize the truncated Hamiltonian

$$\hat{\overline{H}} = \hat{P}_d \hat{H} \hat{P}_d$$

exactly in this d-dim. subspace, by solving

$$\hat{\overline{H}}\,|\bar{i}\rangle = \overline{E}_i^{(0)}\,|\bar{i}\rangle \quad (i = 1, \dots, d) \;\Rightarrow \det\left(\overline{H}_{d\times d} - \overline{E}\,\mathbb{1}_{d\times d}\right) = 0$$

where $\overline{H}_{d\times d}$ is the matrix representing $\hat{H}$ in the basis $\{|1^0\rangle, |2^0\rangle, \dots, |d^0\rangle\}$ spanning this subspace.

The roots $\bar{E}_i^{(0)}$ of this secular equation are the perturbed energies up to first order order. However, they are often much more accurate than this statement suggests since the interactions between the d states $\{|1^\circ\rangle, \dots |d^\circ\rangle\}$ are already taken into account <u>exactly</u>, i.e. to all orders in $\lambda \hat{H}'$.

<u>Example</u> Stark effect in the 2^{nd} hydrogen level.

- The second $(n=2)$ state of hydrogen is 4-fold degenerate: $|200\rangle, |211\rangle, |210\rangle, |2,1,-1\rangle \equiv \{|2lm\rangle\}$
- Denote by $\hat{P} = |200\rangle\langle 200| + |211\rangle\langle 211| + |210\rangle\langle 210| + |21-1\rangle\langle 21-1|$ the projector on this degenerate subspace.
- Construct $\hat{H} = \hat{P}\hat{H}\hat{P} = \hat{P}\hat{H}^\circ\hat{P} + \hat{P}\hat{V}\hat{P}$ where $\hat{V} = e\mathcal{E}\hat{Z}$

$$= E_2^\circ \hat{P} + \hat{P}\hat{V}\hat{P}$$

In the unperturbed degenerate basis $\{|2lm\rangle\}$ it is represented by

$$\hat{H} \leftrightarrow E_2^\circ \begin{pmatrix} 1 & & & 0 \\ & 1 & & \\ & & 1 & \\ 0 & & & 1 \end{pmatrix} + \begin{array}{c} \begin{array}{cccc} |200\rangle & |210\rangle & |211\rangle & |21-1\rangle \end{array} \\ \begin{pmatrix} 0 & \Delta & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{l} \leftarrow |200\rangle \\ \leftarrow |210\rangle \\ \leftarrow |211\rangle \\ \leftarrow |21-1\rangle \end{array}$$

Due to the dipole selection rule, $e\mathcal{E}\hat{Z}$ has matrix elements only between states $l_2 = l_1 \pm 1$ together with $m_1 = m_2$. Since for $l=0$ only $m=0$ exists, nonzero matrix elements all have $m_1 = m_2 = 0$; so only $\langle 210|e\mathcal{E}\hat{Z}|200\rangle$ and $\langle 200|e\mathcal{E}Z|210\rangle$ are nonzero:

$$\Delta = \langle 200|e\mathcal{E}\hat{Z}|210\rangle = -3e\mathcal{E}a_0 = \langle 210|e\mathcal{E}\hat{Z}|200\rangle \quad \text{(real)}$$

The eigenstates of $\hat{H}$ are

$$\left\{ \frac{|200\rangle + |210\rangle}{\sqrt{2}}, \frac{|200\rangle - |210\rangle}{\sqrt{2}}, |211\rangle, |21,-1\rangle \right\}$$

The corresponding "1st-order" eigenergies are

$$E_2^0 - 3e\mathcal{E}a_0, \quad E_2^0 + 3e\mathcal{E}a_0, \quad E_2^0, \quad E_2^0$$

(so the $n=2$ state splits into 3 levels). The levels $|211\rangle$ and $|21-1\rangle$ remain degenerate, but they are not mixed by the interaction. All corrections to these levels arise from matrix elements

$$\frac{|\langle nlm|e\mathcal{E}\hat{Z}|21,\pm1\rangle|^2}{E_2^0 - E_n^0}$$ with $n \neq 2$, so they involve no small energy denominators.

The "second-order" energy shifts are

$\frac{|200\rangle+|210\rangle}{\sqrt{2}}$: $$E^2_{2,1} = -\frac{R_y}{4} - 3e\mathcal{E}a_0 + \frac{1}{2}\sum_{\substack{k,l \\ k\neq 2 \\ l=0,1,2}} \frac{|\langle kl0|e\mathcal{E}\hat{Z}|(|200\rangle+|210\rangle)|^2}{-R_y\left(\frac{1}{4}-\frac{1}{k^2}\right) - 3e\mathcal{E}a_0}$$

$\frac{|200\rangle-|210\rangle}{\sqrt{2}}$: $$E^2_{2,2} = -\frac{R_y}{4} + 3e\mathcal{E}a_0 + \frac{1}{2}\sum_{\substack{k,l \\ k\neq 2; l=0,1,2}} \frac{|\langle kl0|e\mathcal{E}Z|(|200\rangle-|210\rangle)|^2}{-R_y\left(\frac{1}{4}-\frac{1}{k^2}\right) + 3e\mathcal{E}a_0}$$

$|21\pm1\rangle$: $$E^2_{2,3/4} = -\frac{R_y}{4} + \sum_{\substack{k,l \\ k\neq 2; l=0,2}} \frac{|\langle kl\pm1|e\mathcal{E}\hat{Z}|21\pm1\rangle|^2}{-R_y\left(\frac{1}{4}-\frac{1}{k^2}\right)}$$