

First-Order Perturbation Theory & The Linear Stark Effect

Suppose our hamiltonian H contains a major part H_0 whose e-vecs we know

$$H_0 |n, i\rangle = E_n^0 |n, i\rangle \quad (1)$$

in which n labels the energy level and i the g_n different degenerate states of energy E_n^0 . So

$$H = H_0 + \lambda V \quad (2)$$

in which λ is a small dimensionless parameter.

We expect the n th level, if $g_n = 1$, or levels, if $g_n > 1$, to vary with λ as

$$E_{n\alpha}(\lambda) = E_n^0 + \Delta E_{n\alpha}(\lambda). \quad (3)$$

To first order

$$E_{n\alpha}(\lambda) \approx E_n^0 + \lambda E_{n\alpha}^1 \quad (4)$$

If $g_n = 1$, then

$$\langle n | H | n \rangle = \langle n | H_0 + \lambda V | n \rangle = E_n^0 + \lambda \langle n | V | n \rangle \quad (5)$$

That is,

$$\langle n | H | n \rangle = E_n(\lambda) = E_n^0 + \lambda \langle n | V | n \rangle. \quad (6)$$

What could be simpler?

What about the degenerate case?

So suppose we have $g_n > 1$ states $|n, i\rangle$ that are e-vecs of H_0 with the same eval E_n^0

$$H_0 |n, i\rangle = E_n^0 |n, i\rangle. \quad (7)$$

Since λ is a small parameter, we expect that to first order in λ , the e-vecs $|n, \alpha\rangle$ of

$$(H_0 + \lambda V) |n, \alpha\rangle = (E_n^0 + \lambda E_{n\alpha}^{\prime}) |n, \alpha\rangle \quad (8)$$

be g_n linear combinations of the states $|n, i\rangle$

$$|n, \alpha\rangle = \sum_{i=1}^{g_n} |n, i\rangle \chi_{ni} |n, \alpha\rangle \quad (9)$$

so that

$$(H_0 + \lambda V) \sum_{i=1}^{g_n} |n, i\rangle \chi_{ni} |n, \alpha\rangle = (E_n^0 + \lambda E_{n\alpha}^{\prime}) \sum_{i=1}^{g_n} |n, i\rangle \chi_{ni} |n, \alpha\rangle. \quad (10)$$

Hence

$$\langle nk | (H_0 + \lambda V) \sum_{i=1}^{g_n} |n, i\rangle \chi_{ni} |n, \alpha\rangle = (E_n^0 + \lambda E_{n\alpha}^{\prime}) \sum_{i=1}^{g_n} \langle nk | n, i\rangle \chi_{ni} |n, \alpha\rangle \quad (11)$$

or since the e-vectors $|ni\rangle$ of H_0 are orthogonal,

$$\langle nk | ni \rangle = \delta_{ki} \tag{12}$$

and since

$$\langle nk | H_0 = E_n^0 \langle nk | \tag{13}$$

$$E_n^0 \langle nk | m\alpha \rangle + \lambda \sum_{i=1}^{g_n} \langle nk | V | mi \rangle \langle mi | m\alpha \rangle = (E_n^0 + \lambda E_{n\alpha}^1) \langle nk | m\alpha \rangle. \tag{14}$$

The E_n^0 terms cancel, as does λ , so

$$\sum_{i=1}^{g_n} \langle nk | V | mi \rangle \langle mi | m\alpha \rangle = E_{n\alpha}^1 \langle nk | m\alpha \rangle, \tag{15}$$

If ψ_α is a column vector with entries

$$\psi_{\alpha k} = \langle nk | m\alpha \rangle \tag{16}$$

and V_n is the $g_n \times g_n$ matrix with entries

$$V_{ki} = \langle nk | V | mi \rangle, \tag{17}$$

then we must solve

$$V_n \psi_\alpha = E_{n\alpha}^1 \psi_\alpha. \tag{18}$$

The evals E'_m must satisfy

$$0 = |V_m - E'_m I| = \det(V_m - E'_m I). \quad (19)$$

which is a polynomial equation with g_m roots. Here I is the $g_m \times g_m$ identity operator.

When V has less symmetry than H_0 , it breaks the symmetry of H_0 and lifts some of the degeneracy.

The Stark effect nicely illustrates first-order perturbation theory. Consider a hydrogen atom in an external uniform constant electric field \vec{E} parallel to \hat{z} , so that

$$V = -qEz \quad (20)$$

and

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}. \quad (21)$$

The e-vecs are $|n \ell m\rangle$ with

$$H_0 |n \ell m\rangle = E_n |n \ell m\rangle \quad (22)$$

and

$$E_n = -\frac{1}{2} \mu c^2 \frac{\alpha^2}{n^2}. \quad (23)$$

Even the strongest laboratory electric fields are tiny compared to the field felt by the lower states of the H-atom.

The ground state is not degenerate

so

$$E_1' = \langle 100 | (-ge_z) | 100 \rangle = 0 \tag{24}$$

vanishes because

$$0 = N \int d^3r e^{-cr} z. \tag{25}$$

More generally, under space reflection or parity

$$P |nlm\rangle = (-1)^l |nlm\rangle \tag{26}$$

while z changes sign

$$P z P^{-1} = -z \tag{27}$$

so all diagonal matrix elements vanish.

Here's a proof:

$$\langle nlm | z | nlm \rangle = \langle nlm | P^{-1} P z P^{-1} P | nlm \rangle \tag{28}$$

$$= (-1)^{2l} (-1) \langle nlm | z | nlm \rangle = - \langle nlm | z | nlm \rangle.$$

implies

$$\langle nlm | z | nlm \rangle = 0. \tag{29}$$

There are four $n=2$ states $|200\rangle$, $|211\rangle$, $|210\rangle$, and $|2,1,-1\rangle$ and some of their matrix elements with \hat{z} are non-zero.

$$\begin{aligned} \langle 21m|\hat{z}|200\rangle &\propto \int dR Y_{1,m}^*(R) Y_{1,0}(R) Y_{0,0}(R) \quad (=0) \\ &= r \delta_{m0} \end{aligned} \quad (30)$$

in which $\hat{z} \propto Y_{1,0}$ and $\langle 2100\rangle \propto Y_{0,0} \propto 1$.

So the 4×4 matrix V_2 has non-zero matrix elements only between the $|210\rangle$ & $|200\rangle$ states:

$$V_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & rE \\ 0 & 0 & rE & 0 \end{pmatrix} \quad (31)$$

The states $|2,1,\pm 1\rangle$ have no change in energy, but the states

$$|2+\rangle = \frac{1}{\sqrt{2}} (|210\rangle + |200\rangle) \leftrightarrow rE$$

$$|2-\rangle = \frac{1}{\sqrt{2}} (|210\rangle - |200\rangle) \leftrightarrow -rE$$

shift by $\pm rE$. This is the linear Stark effect.