First-Order Perturbation Theory & The Linear Stark Effect

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

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

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

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

in which λ is a small dimensionless parameter.

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

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

To first order

$$E_{n i}(\lambda) \cong E_n^0 + \lambda E_{n\alpha}^1 . \qquad (4)$$

If $g_n = 1$, then

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

That is,

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

What could be simpler?

What about the degenerate case? Suppose we have $g_n > 1$ states $|n,i\rangle$ that are e-vecs of H_0 with the same eval E_n^0

$$H_0|n,i\rangle = E_n^0|n,i\rangle. \tag{7}$$

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

$$(H_0 + \lambda V)|n\alpha\rangle = (E_n^0 + \lambda E'_{n\alpha})|n\alpha\rangle \tag{8}$$

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

$$|n\alpha\rangle = \sum_{i=1}^{g_n} |ni\rangle\langle ni|n\alpha\rangle \tag{9}$$

so that

$$(H_0+\lambda V)\sum_{i=1}^{g_n} |ni\rangle\langle ni|n\alpha\rangle = (E_n^0 + \lambda E'_{n\alpha})\sum_{i=1}^{g_n} |ni\rangle\langle ni|n\alpha\rangle. \tag{10}$$

Hence

$$\langle nk|(H_0+\lambda V)\sum_{i=1}^{g_n} |ni\rangle\langle ni|n\alpha\rangle = (E_n^0 + \lambda E'_{n\alpha})\sum_{i=1}^{g_n} \langle nk|ni\rangle\langle ni|n\alpha\rangle \tag{11}$$

or since the e-vecs $|ni\rangle$ of H_0 are orthonormal,

$$\langle nk|ni\rangle = \delta_{ki} \qquad (12)$$

and since

$$\langle nk|H_0 = E_n^0\langle nk| \qquad (13)$$

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

The E_n^0 terms cancel, as does λ, so

$$\sum_{i=1}^{g_n}\langle nk|V|ni\rangle\langle ni|n\alpha\rangle = E_{n\alpha}^1\langle nk|n\alpha\rangle, \qquad (15)$$

If Ψ_α is a column vector with entries

$$\Psi_{\alpha k} = \langle nk|n\alpha\rangle \qquad (16)$$

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

$$V_{nki} = \langle nk|V|ni\rangle, \qquad (17)$$

then we must solve

$$V_n\Psi_\alpha = E_{n\alpha}^1\Psi_\alpha. \qquad (18)$$

The evals $E'_{n\alpha}$ must satisfy

$$0 = | V_n - E'_{n\alpha} I | = \det(V_n - E'_{n\alpha} I) . \tag{19}$$

which is a polynomial equation with g_n roots. Here I is the $g_n \times g_n$ 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 $\vec{\mathcal{E}}$ parallel to $\hat{z}$, so that

$$V = -q \mathcal{E} z \tag{20}$$

and

$$H_0 = \frac{p^2}{2\mu} - \frac{e^2}{r} . \tag{21}$$

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

$$H_0 | n \ell m \rangle = E_n | n \ell m \rangle \tag{22}$$

and

$$E_n = -\tfrac{1}{2} \mu c^2 \frac{\alpha^2}{n^2} . \tag{23}$$

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

$$E_1' = \langle 100 | (-q\mathcal{E} z) | 100 \rangle = 0 \qquad (24)$$

vanishes because

$$0 = N \int d^3r \, e^{-cr} \, z. \qquad (25)$$

More generally, under space reflection or parity

$$P \, |n\ell m\rangle = (-1)^{\ell} \, |n\ell m\rangle \qquad (26)$$

while z changes sign

$$P z P^{-1} = -z \qquad (27)$$

so all diagonal matrix elements vanish.
Here's a proof:

$$\langle n\ell m | z | n\ell m\rangle = \langle n\ell m | P^{-1} P z P^{-1} P | n\ell m\rangle \qquad (28)$$

$$= (-1)^{2\ell} (-1) \langle n\ell m | z | n\ell m\rangle = - \langle n\ell m | z | n\ell m\rangle$$

implies

$$\langle n\ell m | z | n\ell m\rangle = 0. \qquad (29)$$

There are four $n=2$ states $|200\rangle$, $|211\rangle$, $|21,0\rangle$, and $|2,1,-1\rangle$ and some of their matrix elements with z are non-zero.

$$\langle 21m| z|200\rangle \propto \int d\Omega \, Y_1^{m*}(\Omega) Y_1^0(\Omega) Y_0^0(\Omega)$$

$$= \gamma \, \delta_{m0} \qquad (30)$$

in which $z \propto Y_1^0$ and $\langle \Omega|00\rangle \propto Y_0^0 \propto 1$.

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

$$V_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma\mathcal{E} \\ 0 & 0 & \gamma\mathcal{E} & 0 \end{pmatrix} \qquad (31)$$

The states $|21\pm1\rangle$ have no change in energy, but the states

$$|2+\rangle = \frac{1}{\sqrt{2}}\left(|210\rangle + |200\rangle\right) \longleftrightarrow \gamma\mathcal{E}$$

$$|2-\rangle = \frac{1}{\sqrt{2}}\left(|210\rangle - |200\rangle\right) \longleftrightarrow -\gamma\mathcal{E}$$

shift by $\pm\gamma\mathcal{E}$. This is the <u>linear</u> Stark effect.