First-Order Perturbation Theory
& The Linear Stark Effect

Suppose our Hamiltonian $H$ contains a major part $H_0$ whose eigenvalues 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 $E_n$. So

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

in which $\lambda$ is a small dimensionless parameter.

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

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

To first order

$$E_{n\lambda}(\lambda) \approx E_n^0 + \frac{\lambda}{2} E_{n\lambda}^1 \quad (4)$$

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,
\[ \langle m_1 | H_1 | m_1 \rangle = E_n(x) = E_n^0 + \chi^2 \langle m_1 | V | m_1 \rangle. \] (6)

What could be simpler?

What about the degenerate case?

Suppose we have \( g_n \) states \( | m_i \rangle \) that are e-vecs of \( H_0 \) with the same eigenvalue \( E_n^0 \)
\[ H_0 | m_i \rangle = E_n^0 | m_i \rangle. \] (7)

Since \( \chi \) is a small parameter, we expect that to first order in \( \chi \), the e-vecs \( | m_\alpha \rangle \) of
\[ (H_0 + \chi V) | m_\alpha \rangle = (E_n^0 + \chi E_{m_\alpha}) | m_\alpha \rangle \] (8)
be \( g_n \) linear combinations of the states \( | m_i \rangle \)
\[ | m_\alpha \rangle = \sum g_{m_\alpha} | m_i \rangle \chi m_i | m_\alpha \rangle \] (9)

so that
\[ (H_0 + \chi V) \sum_{i=1}^{g_n} | m_i \rangle \chi m_i | m_\alpha \rangle = (E_n^0 + \chi E_{m_\alpha}) \sum_{i=1}^{g_n} | m_i \rangle \chi m_i | m_\alpha \rangle. \] (10)

Hence
\[ \langle m_k | (H_0 + \chi V) \sum_{i=1}^{g_n} | m_i \rangle \chi m_i | m_\alpha \rangle = (E_n^0 + \chi E_{m_\alpha}) \sum_{i=1}^{g_n} \langle m_k | m_i \rangle \chi m_i | m_\alpha \rangle \] (11)
or since the eigenstates \( |ni\rangle \) of \( H_0 \) are orthogonal,

\[
\langle n_k | n_i \rangle = \delta_{ki} \quad (12)
\]

and since

\[
\langle n_k | H_0 = E_0 \langle n_k | \quad (13)
\]

\[
E_0 \langle n_k | n_{k' \alpha} \rangle + \sum_{i} \langle n_k | V_{1} | n_{i} \rangle \langle n_{i} | n_{k' \alpha} \rangle = (E_0 + E_{1 \alpha}) \langle n_k | n_{k' \alpha} \rangle, \quad (14)
\]

The \( E_0 \) terms cancel, as does \( \lambda \), so

\[
\sum_{i} \langle n_k | V_{1 \alpha} | n_{i} \rangle \langle n_{i} | n_{k' \alpha} \rangle = E_{1 \alpha} \langle n_k | n_{k' \alpha} \rangle, \quad (15)
\]

If \( \Psi_\alpha \) is a column vector with entries

\[
\Psi_{nk} = \langle n_k | \alpha \rangle \quad (16)
\]

and \( V_\alpha \) is the \( g \times g \) matrix with entries

\[
V_{nk} = \langle n_k | V_{1 \alpha} \rangle \quad (17)
\]

then we must solve

\[
V_\alpha \Psi_\alpha = E_{1 \alpha} \Psi_\alpha. \quad (18)
\]
The, e, vals, \( E' \), must satisfy
\[
0 = 1 \, V_n - E' \, a \, I = \det (V_n - E' \, a \, I). \tag{19}
\]
which is a polynomial equation with \( q \) \( \equiv \) roots. Here \( I \) is the \( q \times q \) 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 \( E \), parallel to \( z \), so that
\[
V = -q \, E \, z \tag{20}
\]
and
\[
H_0 = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{21}
\]
The eigenstates are \( |n\lambda\, m\rangle \) with
\[
H_0 \, |n\lambda\, m\rangle = E_n \, |n\lambda\, m\rangle \tag{22}
\]
and
\[
E_n = -\frac{1}{2} \mu \, c^2 \, \frac{e^2}{m^2}. \tag{23}
\]
Even the strongest laboratory electric fields are tiny compared to the field felt by the lower state of the H-atom.

The ground state is not degenerate so

$$E_1' = \langle 1001(-3Ez)1100 \rangle = 0 \quad (24)$$

vanish because

$$0 = \int \hat{A} \cdot \hat{e} \, \, d^3r \quad (25)$$

More generally, under space reflection or parity

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

while $z$ changes sign

$$P \, P_\perp = -z \quad (27)$$

so all diagonal matrix elements vanish.

Here's a proof:

$$\langle n\ell m|z|n\ell m \rangle = \langle n\ell m|P \, P_\perp|n\ell m \rangle \quad (28)$$

$$= (-1)^\ell \, (-1) \, \langle n\ell m |z| n\ell m \rangle = -\, \langle n\ell m |z| n\ell m \rangle$$

implies

$$\langle n\ell m |z| n\ell m \rangle = 0 \quad (29)$$
There are four $n=2$ states $|12\,0\rangle$, $|12\,1\rangle$, $|12\,-1\rangle$, and $|12\,1\rangle$ and some of their matrix elements with $\mathbb{Z}$ are non-zero.

$$
\langle 12 \, | m \rangle \langle 2 \, 12 \rangle = \int d\Omega \, Y^*_m(\hat{r}) Y^{0}_{12}(\hat{r}) (=0)
$$

$$
= R^{m m} \quad (30)
$$

in which $z \propto Y^{0}_{12}$ and $\langle z | 12 \rangle \propto Y^{0}_{12} \langle z$.

So the $4 \times 4$ matrix $V_z$ has non-zero matrix elements only between the $|12\,0\rangle$ & $|12\,0\rangle$ states:

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

The states $|12\,\pm 1\rangle$ have no change in energy, but the states

$$
|12\,\rangle = \frac{1}{\sqrt{2}} (|12\,0\rangle + |12\,0\rangle) \leftrightarrow \chi \\
|12\,-\rangle = \frac{1}{\sqrt{2}} (|12\,0\rangle - |12\,0\rangle) \leftrightarrow -\chi
$$

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