

• Last times: time independent, a.k.a. stationary state perturbation theory, continued $H = H_0 + H_1$, with $H_0 \sim \epsilon^0$ and $H_1 \sim \epsilon^1$, and that we can do an expansion order-by-order in the small parameter, making corrections to the H_0 case. Recall $E_{n,1} = \langle E_{n,0} | H_1 | E_{n,0} \rangle$ and

$$\langle E_{m \neq n,0} | E_{n,1} \rangle = \frac{1}{E_{n,0} - E_{m,0}} \langle E_{m \neq n,0} | H_1 | E_{n,0} \rangle, \quad \langle E_{n,0} | E_{n,1} \rangle = 0,$$

where the last condition is by a choice of overall phase. So

$$|E_{n,1}\rangle = \sum_m' \frac{|E_{m,0}\rangle \langle E_{m,0} | H_1 | E_{n,0} \rangle}{E_{n,0} - E_{m,0}} = \frac{P_{n\perp}}{E_{n,0} - H_0} H_1 |E_{n,0}\rangle$$

where \sum_m' means all states with $E_{m,0} \neq E_{n,0}$ and $P_{n\perp} \equiv 1 - |E_{n,0}\rangle \langle E_{n,0}|$. Note that $|E_{n,1}\rangle \equiv |n_1\rangle$ is not an eigenstate of either H_0 or H_1 ; it is the order ϵ correction to the eigenstate of H . To second order

$$E_{n,2} = \langle E_{n,0} | H_1 | E_{n,1} \rangle = \sum_m' \frac{|\langle E_{m,0} | H_1 | E_{n,0} \rangle|^2}{E_{n,0} - E_{m,0}}.$$

Note that this is always negative for the ground state. To the above order we have the expected result

$$E_n = \langle n | H | n \rangle = (\langle n_0 | + \langle n_1 | + \dots)(H_0 + H_1)(|n_0\rangle + |n_1\rangle + \dots).$$

$\langle n | n \rangle = \langle n_0 | n_0 \rangle = 1$ gives $\langle n_0 | n_2 \rangle + \langle n_2 | n_0 \rangle + \langle n_1 | n_1 \rangle = 0$, so $\langle n_2 | H_0 | n_0 \rangle + \langle n_0 | H_0 | n_2 \rangle + \langle n_1 | H_0 | n_1 \rangle = \langle n_1 | H_0 - E_{n,0} | n_1 \rangle = -E_{n,2}$, so to $\mathcal{O}(\epsilon^2)$ get $2E_{n,2} - E_{n,2} = E_{n,2}$.

• Wave function renormalization: $|n\rangle = |n_0\rangle + |n_1\rangle + \dots$ has $\langle n | n \rangle \equiv Z_n^{-1} = 1 + \langle n_1 | n_1 \rangle + \dots$, gives

$$Z_n = 1 - \sum_{m'} \frac{|\langle m_0 | H_1 | n_0 \rangle|^2}{(E_{n,0} - E_{m,0})^2} + \dots$$

The renormalized state is $|\hat{n}\rangle = Z^{1/2} |n\rangle$. Note that $Z_n = |\langle n_0 | \hat{n} \rangle|^2$ is the probability of finding the H eigenstate $|\hat{n}\rangle$ in the unperturbed H_0 eigenstate $|n_0\rangle$; so clearly $Z_n < 1$, as is clear also from the above. A general identity is

$$Z_n = \frac{\partial}{\partial E_{n,0}} (E_{n,0} + \langle n_0 | H_1 | n_0 \rangle + \sum_{m'} \frac{|\langle m_0 | H_1 | n_0 \rangle|^2}{E_{n,0} - E_{m,0}} + \dots) = \frac{\partial E_n}{\partial E_{n,0}}.$$

The fact that $Z_n < 1$ for the ground state fits then with the fact that the second order perturbation is negative.

- Stark effect: put an atom in an external electric field, treating eE_0 as a perturbation. Take $H_1 = eE_0z$ for an electric field along the \hat{z} axis (the electron charge here is $-e$). Then $E_{n,1} = eE_0\langle E_{n,0}|z|E_{n,0}\rangle$, which is zero by parity symmetry if the state is non-degenerate (e.g. in the ground state of the hydrogen atom). To second order,

$$E_{n,2} = e^2 E_0^2 \sum'_m \frac{|\langle E_{m,0}|z|E_{n,0}\rangle|^2}{E_{n,0} - E_{m,0}}.$$

It follows from the Wigner-Eckart theorem that $\langle n', \ell', m'|z|n, \ell, m\rangle \propto \delta_{m',m} \delta_{(\ell'-\ell)^2, 1}$. The second order shift can be understood as polarizing the system, and the change in energy is $-\frac{1}{2}\alpha E_0^2$ (you'll check this in HW examples).

For degenerate states, there is generally an effect already at first order; we need to use degenerate perturbation theory.

- Degenerate perturbation theory: especially interesting case, where H_1 splits the degenerate spectrum of H_0 . Suppose the H_0 eigenstates are $|n_{0,k}\rangle$, where k runs over the degenerate space of H_0 eigenvectors with eigenvalue $E_{n,0}$, say $k = 1 \dots K$. Now H_1 's matrix elements on this space of states is a $K \times K$ matrix. If we naively apply the above expressions, we run into problems with the denominator of e.g. $\langle E_{m \neq n,0}|E_{n,1}\rangle = \frac{1}{E_{n,0} - E_{m,0}} \langle E_{m \neq n,0}|H_1|E_{n,0}\rangle$ in the degenerate subspace. The solution is to diagonalize the H_1 matrix elements on this space, so we get 0/0 instead of 1/0. Also, diagonalizing H_1 in the degenerate space is needed for a smooth $\epsilon \rightarrow 0$ limit, since for any $\epsilon \rightarrow 0^+$ the states are not eigenstates unless they diagonalize H_1 . The eigenvalues of the H_1 matrix are the first order correction $E_{n,1,k}$ values. The expression for $|n, 1\rangle$ is similar to that in the non-degenerate case, where the \sum'_m is understood to be over states with $E_{m,0} \neq E_{n,0}$, i.e. excluding all of the states with energy $E_{n,0}$.

If some degeneracy remains at first order, one needs to diagonalize the matrix $V_{n',n} + \sum'_m V_{nm}V_{mn'}/(E_{n,0} - E_{m,0})$ where we take $H_1 \rightarrow V$ to reduce index clutter.

- Stark effect for $n = 2$ states continued, if the state is e.g. initially in the $|2S_0\rangle$ state, to first order in the small \vec{E} perturbation the energy is $-(e^2/2a_0)(\frac{1}{4} \pm 6E_0/(e/a^2))$ with equal probability for the two cases. Note that $e^2/a_0 = 5.15 \times 10^9 \text{V/cm}$ so the E_0 just has to be small compared with that huge value for perturbation theory to be a good approximation.

Stark effect for $n = 2$ states. H_1 is a 4×4 matrix, with non-zero element $\Delta = \langle 200|eEz|210\rangle = -3eEa_0$ and its transpose (Hermitian conjugate). This is diagonalized by $(|200\rangle \pm |210\rangle)/\sqrt{2}$, with eigenvalue $\pm\Delta$, along with $|21 \pm 1\rangle$ with eigenvalue 0. The split energy eigenstates are not parity eigenstates.