Degenerate stationary state perturbation theory

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Suppose we have a Hamiltonian, $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ where we may regard the effect of $\hat{V}$ as small compared to the unperturbed Hamiltonian $\hat{H}_0$; further suppose that the spectrum of the unperturbed Hamiltonian is degenerate

$$\hat{H}_0 \left|E_n^{(0)}, N_n, k\right\rangle = E_n^{(0)} \left|E_n^{(0)}, N_n, k\right\rangle$$

where N_n gives the number of states with energy $E_n^{(0)}$, hence the dimension of the n^{th} degenerate subspace, and k runs over the N_n states, spaning the subspace. For example, in the case of the hydrogen atom (neglecting spin), $N_l = 2l+1$ and $k = m$.

The expansion by powers of λ proceeds as for non-degenerate perturbations, giving the first order correction:

$$\left(\hat{H}_0 - E_n^{(0)}\right)\left|E_{n,k}^{(1)}\right\rangle = \left(E_{n,k}^{(1)} - \hat{V}\right)\left|E_n^{(0)}, N_\alpha, k\right\rangle$$

The key idea here is that we first build the corrections to the states out of the original eigenkets,

$$\left|E_{n,k}^{(1)}\right\rangle = \sum_{k=1}^{N_n} \alpha_k \left|E_n^{(0)}, N_n, k\right\rangle$$

This means that

$$\left(\hat{H}_0 - E_n^{(0)}\right)\left|E_{n,k}^{(1)}\right\rangle = \sum_{k=1}^{N_n} \alpha_k \left(\hat{H}_0 - E_n^{(0)}\right)\left|E_n^{(0)}, N_n, k\right\rangle = 0$$

Therefore,

$$\hat{V}\left|E_n^{(0)}, N_\alpha, k\right\rangle = E_{n,k}^{(1)}\left|E_n^{(0)}, N_\alpha, k\right\rangle$$

This is an eigenvalue equation on the N_n-dimensional degenerate subspace. The technique is to solve this eigenvalue problem first, choosing a new basis for the degenerate subspace which diagonalizes $\hat{V}$ there,

$$\begin{aligned}\left|E_{n,k}^{(0)}\right\rangle &= \sum_{k=1}^{N_n} \alpha_k \left|E_n^{(0)}, N_\alpha, k\right\rangle \\ \hat{V}\left|E_{n,k}^{(0)}\right\rangle &= E_{n,k}^{(1)}\left|E_{n,k}^{(0)}\right\rangle\end{aligned}$$

Now revisit the full problem. The matrix elements of the perturbing potential are now diagonal on the degenerate subspaces, but may still have arbitrary small components between different values of n,

$$\left\langle E_{n,k'}^{(0)}\right|\hat{V}\left|E_{n,k}^{(0)}\right\rangle = E_{n,k}^{(1)}\delta_{kk'}$$

but

$$\left\langle E_{n',k'}^{(0)}\right|\hat{V}\left|E_{n,k}^{(0)}\right\rangle \neq 0$$

However, the states $\left|E_{n,k}^{(0)}\right\rangle$ are no longer degenerate, so we may now apply non-degenerate perturbation theory in the new basis.