Quantum Mechanics 2

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Degenerate Perturbation Theory

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Perturbation Theory

We have seen in [perturbation] that given a perturbed Hamiltonian

$$H = H_0 + H_I$$

the lower-ordered corrections to energy and eigenkets are given by

$$E_n^{(1)} = \langle n^{(0)} | H_I | n^{(0)} \rangle$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle n^{(0)} | H_I | k^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$C_{nm}^{(1)} = \frac{\langle m^{(0)} | H_I | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$C_{nm}^{(2)} = \sum_{k \neq n} \frac{\langle m^{(0)} | H_I | k^{(0)} \rangle \langle k^{(0)} | H_I | n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \frac{\langle m^{(0)} | H_I | n^{(0)} \rangle \langle n^{(0)} | H_I | n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)^2}$$

Except for the first one, all others blow up if $E_n^{(0)} = E_k^{(0)}$. So the said formalism does not work for degenerate systems.

Degenerate States

Just as we have excised out n from the summation in non-degenerate perturbation theory, to avoid the situation where the denominator $E_n^{(0)} - E_k^{(0)}$ is zero, we can expand the kets to be excluded in the summation to all states that are degenerate with $|n^{(0)}\rangle$.

If we denote $\{|n^{(i)}\rangle\}$ as the degenerate states, we now write

$$|n\rangle = N(\lambda)\left[\sum_i \alpha_i |n^{(i)}\rangle + \sum_{k\neq n} C_{nk}(\lambda) \sum_i \beta_i |k^{(i)}\rangle\right]$$

The first-order perturbation terms thus become

$$H_0 \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i |k^{(i)}\rangle + H_I \sum_i \alpha_i |n^{(i)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i |k^{(i)}\rangle + E_n^{(1)} \sum_i \alpha_i |n^{(i)}\rangle$$

Energy and Kets

Taking the inner product with $\langle n^{(j)}|$

$$\sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \sum_i \beta_i \langle n^{(j)}|k^{(i)}\rangle + \sum_i \alpha_i \langle n^{(j)}|H_I|n^{(i)}\rangle$$
$$= E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \sum_i \beta_i \langle n^{(j)}|k^{(i)}\rangle + E_n^{(1)} \sum_i \alpha_i \langle n^{(j)}|n^{(i)}\rangle$$

and applying the orthonormalization

$$\langle n^{(j)}|k^{(i)}\rangle = \delta_{nk}\delta_{ij}$$

we get

$$\sum_i \alpha_i \langle n^{(j)}|H_I|n^{(i)}\rangle = E_n^{(1)} \alpha_j$$

which is an eigenvalue equation, from which $E_n^{(1)}$ and α_j can be determined.