11.4: Non-Degenerate Perturbation Theory

Let us now generalize our perturbation analysis to deal with systems possessing more than two energy eigenstates. Consider a system in which the energy eigenstates of the unperturbed Hamiltonian, H_0, are denoted

$$H_0\,\psi_n = E_n\,\psi_n, \tag{11.4.1}$$

where n runs from 1 to N. The eigenstates are assumed to be orthonormal, so that

$$\langle m|n\rangle = \delta_{nm}, \tag{11.4.2}$$

and to form a complete set. Let us now try to solve the energy eigenvalue problem for the perturbed Hamiltonian:

$$(H_0+H_1)\,\psi_E = E\,\psi_E. \tag{11.4.3}$$

It follows that

$$\langle m|H_0+H_1|E\rangle = E\,\langle m|E\rangle, \tag{11.4.4}$$

where m can take any value from 1 to N. Now, we can express ψ_E as a linear superposition of the unperturbed energy eigenstates:

$$\psi_E = \sum_k \langle k|E\rangle\,\psi_k, \tag{11.4.5}$$

where k runs from 1 to N. We can combine the previous equations to give

$$(E_m - E + e_{mm})\,\langle m|E\rangle + \sum_{k\neq m} e_{mk}\,\langle k|E\rangle = 0, \tag{11.4.6}$$

where

$$e_{mk} = \langle m|H_1|k\rangle. \tag{11.4.7}$$

Let us now develop our perturbation expansion. We assume that

$$\frac{e_{mk}}{E_m - E_k} \sim \mathcal{O}(\epsilon) \tag{11.4.8}$$

for all $m \neq k$, where $\epsilon \ll 1$ is our expansion parameter. We also assume that

$$\frac{e_{mm}}{E_m} \sim \mathcal{O}(\epsilon) \tag{11.4.9}$$

for all m. Let us search for a modified version of the nth unperturbed energy eigenstate for which

$$E = E_n + \mathcal{O}(\epsilon), \tag{11.4.10}$$

and

$$\langle n|E\rangle = 1,$$
$$\langle m|E\rangle = \mathcal{O}(\epsilon)$$

for $m \neq n$. Suppose that we write out Equation ([e12.45]) for $m \neq n$, neglecting terms that are $\mathcal{O}(\epsilon^2)$ according to our expansion scheme. We find that

$$(E_m - E_n)\,\langle m|E\rangle + e_{mn} \simeq 0, \tag{11.4.11}$$

giving

$$\langle m|E\rangle \simeq -\frac{e_{mn}}{E_m - E_n}. \tag{11.4.12}$$

Substituting the previous expression into Equation ([e12.45]), evaluated for $m = n$, and neglecting $\mathcal{O}(\epsilon^3)$ terms, we obtain

$$(E_n - E + e_{nn}) - \sum_{k\neq n} \frac{|e_{nk}|^2}{E_k - E_n} \simeq 0. \tag{11.4.13}$$

Thus, the modified nth energy eigenstate possesses an eigenvalue

$$E_n' = E_n + e_{nn} + \sum_{k \neq n} \frac{|e_{nk}|^2}{E_n - E_k} + \mathcal{O}\left(\epsilon^3\right) \tag{11.4.14}$$

and a wavefunction

$$\psi_n' = \psi_n + \sum_{k \neq n} \frac{e_{kn}}{E_n - E_k}\, \psi_k + \mathcal{O}(\epsilon^2). \tag{11.4.15}$$

Incidentally, it is easily demonstrated that the modified eigenstates remain orthonormal to $\mathcal{O}(\epsilon^2)$.

Contributors and Attributions

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