Perturbation Theory (from Landau & Lifshitz, Vol. 3)

Hamiltonian contains two terms: $\hat{H} = \hat{H}_0 + \hat{V}$,

where $\hat{V}$ is a small correction (or *perturbation*) to the *unperturbed* operator $\hat{H}_0$.

The solution of zero-order (unperturbed) Schrodinger equation is known: $\hat{H}_0 \psi^{(0)} = E^{(0)} \psi^{(0)}$

We seek the approximate solution of exact Schrodinger equation

$$\hat{H}\psi = (\hat{H}_0 + \hat{V})\psi = E\psi, \quad (3)$$

by expanding the exact wave function in the basis of unperturbed wave functions:

$$\psi = \sum_m c_m \psi_m^{(0)}$$

This gives after substitution to (3):

$$\sum_m c_m (E_m^{(0)} + \hat{V}) \psi_m^{(0)} = \sum_m c_m E \psi_m^{(0)}$$

Multiplying both sides by $\psi_k^{(0)*}$ and integrating we obtain

$$(E - E_k^{(0)}) c_k = \sum_m V_{km} c_m \quad (6)$$

where the matrix elements of perturbation

$$V_{km} = \int \psi_k^{(0)*} \hat{V} \psi_m^{(0)} \, dq.$$

Perturbation Theory (2)

We seek the solution of equation $(E - E_k^{(0)})c_k = \sum_m V_{km} c_m$ **(6)**
in the form of series:

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots, \quad c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \ldots, \quad \textbf{(7)}$$

Let us determine the corrections to the nth eigenvalue and eigenfunction, putting accordingly $c_n^{(0)} = 1$, $c_m^{(0)} = 0$ for $m \neq n$. To find the first approximation, we substitute in equation (**6**) $E = E_n^{(0)} + E_n^{(1)}$, $c_k = c_k^{(0)} + c_k^{(1)}$, and retain only terms of the first order. The equation with $k = n$ gives

the first-order energy correction $E_n^{(1)} = V_{nn} = \int \psi_n^{(0)*} \hat{V} \psi_n^{(0)} \, dq$

and the first-order correction to the wave functions is

$$c_k^{(1)} = V_{kn}/(E_n^{(0)} - E_k^{(0)}) \text{ for } k \neq n, \quad \psi_n^{(1)} = \sum_m{}' \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

Substituting (7) to (6) one obtains the second-order energy correction:

$$E_n^{(2)} c_n^{(0)} = \sum_m{}' V_{nm} c_m^{(1)}, \quad \Rightarrow \quad E_n^{(2)} = \sum_m{}' \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$