Appendix A Time-independent Perturbation Theory

- Want to solve $\hat{H}\psi = E\psi$ in Quantum Mechanics
- Often, we cannot solve it exactly.
- In many problems, we can write:

$$\hat{H} = \underbrace{\hat{H}_0} + \underbrace{\hat{H}'}_{\text{perturbation}}$$

$$\hat{H}_0 \psi_{0n} = E_{0n}\psi_{0n} \quad \text{(eigenfunctions and eigenvalues assumed known)}$$

Q: knowing the solutions to $\hat{H}_0$, how can we obtain an approximate solution to $\hat{H}$, especially when we know that $\hat{H}'$ is only a minor correction to $\hat{H}_0$?

(a) Key results of perturbation theory for non-degenerate energy levels

$$\hat{H}_0 \psi_{0n} = E_{0n}\psi_{0n}$$ n labels different eigenstates of $\hat{H}_0$

- Focus on one of the eigenvalues, say, E_{0n} of $\hat{H}_0$.
- Let's say that there is only one eigenfunction ψ_{0n} associated with E_{0n}, i.e. E_{0n} is non-degenerate or having degeneracy $= 1$.

Question: What is the correction to E_{0n} and ψ_{0n} when $\hat{H}' \neq 0$?

Key-point: $\hat{H} = \hat{H}_0 + \hat{H}'$

- ψ_{0n} is not an eigenstate of $\hat{H}$
- But if $\hat{H}'$ is only a small change from $\hat{H}_0$,

we expect that

$\left\{\begin{array}{l} E_n \text{ of } \hat{H} \text{ is not too far from } E_{0n} \text{ of } \hat{H}_0 \\ \text{and } \psi_n \text{ of } \hat{H} \text{ is not too far from } \psi_{0n} \text{ of } \hat{H}_0. \end{array}\right.$

where $\hat{H}\psi_n = E_n \psi_n$

$\therefore$ we expect: (non-degenerate E_{0n})

$$\left\{\begin{array}{l} E_n = E_{0n} + (\text{corrections due to } \hat{H}') \\ \psi_n = \psi_{0n} + (\text{corrections due to } \hat{H}') \end{array}\right.$$

Perturbation theory gives the results:

$$E_n \cong \underbrace{E_{0n}}_{\substack{\text{zeroth order} \\ \text{in } \hat{H}'}} + \underbrace{\int \psi_{0n}^* \hat{H}' \psi_{0n} \, dV}_{\text{1st order in } \hat{H}'} + \underbrace{\sum_{m \neq n} \frac{\left| \int \psi_{0m}^* \hat{H}' \psi_{0n} \, dV \right|^2}{E_{0n} - E_{0m}}}_{\text{2nd order in } \hat{H}'} \quad (*)$$

(since E_{0n} is non-degenerate $\Rightarrow$ denominators will not vanish)

$$\psi_n \cong \underbrace{\psi_{0n}}_{\substack{\text{zeroth} \\ \text{order in } \hat{H}'}} + \underbrace{\sum_{m \neq n} \frac{\left(\int \psi_{0m}^* \hat{H}' \psi_{0n} \, dV \right)}{E_{0n} - E_{0m}}}_{\text{1st order in } \hat{H}'} \psi_{0m}$$

Note: ψ_n carries some character of ψ_{0m}'s, in addition to ψ_{0n}.

Remarks:

Looking at Eq. (*), we have used this result in setting up the $\infty \times \infty$ matrix for band theory and the nearly free electron electron model.

In particular,

(a) the 1st order term $\int \psi_{on}^{*} \hat{H}' \psi_{on}\, dV$ is what gives the $\overline{V}$ term in the diagonal elements. In that case $\psi_0 \sim e^{i\vec{G}\cdot\vec{r}}$ and $\psi_0^* \sim e^{-i\vec{G}\cdot\vec{r}}$; $\hat{H}' = V(\vec{r})$.

(b) the second order term of the form

$$\frac{\left|\int \psi_{om}^{*} \hat{H}' \psi_{on}\, dV\right|^2}{E_{on} - E_{om}}$$

is what we obtained as an approximation to the eigenvalue of a 2×2 matrix of the form $\begin{pmatrix} \varepsilon_1 & \Delta \\ \Delta & \varepsilon_2 \end{pmatrix}$. The approximation gives a correction to ε_1 as $\tilde{\varepsilon}_1 \approx \varepsilon_1 + \underbrace{\frac{|\Delta|^2}{\varepsilon_1 - \varepsilon_2}}_{\text{same as 2nd order perturbation.}}$