Stationary State Problem in Quantum Mechanics

→ Solve following eigenvalue - eigenfunction problem:

$$\underset{\sim}{H} \psi_i = E_i \psi_i$$

where $\underset{\sim}{H}$ is the Hamiltonian operator for the system

ψ_i's are the eigenfunctions $(i = 1, 2, 3, \dots)$

E_i's are the eigenvalues or energies of the system

→ ψ_i's are orthonormal, i.e.,

$$\int \psi_i^* \psi_j = 0 \quad \text{if } i \neq j$$

$$\int \psi_i^* \psi_j = 1 \quad \text{if } i = j$$

So $\int \psi_i^* \underset{\sim}{H} \psi_i \, d\vec{r} = \int \psi_i^* E_i \psi_i \, d\vec{r} = E_i \int \psi_i^* \psi_i \, d\vec{r}$
$= E_i$

and $\int \psi_i^* H \psi_j \, d\vec{r} = \int \psi_i^* E_j \psi_j \, d\vec{r} = E_j \int \psi_i^* \psi_j \, d\vec{r} = 0$

→ Can summarize all these integrals in a matrix

$$\underset{\sim}{H} = \begin{pmatrix} \int \psi_1^* \underset{\sim}{H} \psi_1 d\vec{r} & \int \psi_1^* \underset{\sim}{H} \psi_2 d\vec{r} & \cdots & \\ \int \psi_2^* \underset{\sim}{H} \psi_1 d\vec{r} & \int \psi_2^* \underset{\sim}{H} \psi_2 d\vec{r} & \int \psi_2^* \underset{\sim}{H} \psi_3 d\vec{r} & \cdots \\ \cdots & \cdots & \int \psi_3^* \underset{\sim}{H} \psi_3 dr & \\ & & & \ddots \end{pmatrix}$$

$$= \begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \\ \vdots & \vdots & & \ddots \end{pmatrix}$$

$$= \begin{pmatrix} E_1 & 0 & 0 & 0 & \cdots \\ 0 & E_2 & 0 & 0 & \\ 0 & 0 & E_3 & 0 & \\ 0 & 0 & 0 & E_4 & \end{pmatrix}$$

$\underset{\sim}{H}$ Matrix is diagonal, with diagonal elements equal to the energies of the system.

→ Above for a problem that can be solved exactly. What happens when the Hamiltonian of the system can be written as

$$\underset{\sim}{\mathcal{H}} = \mathcal{H}^{\circ} + \mathcal{H}'$$

but you only know the solution for $\mathcal{H}^{\circ}$ exactly, i.e.,

$$\underset{\sim}{\mathcal{H}}^{\circ} \psi_i^{\circ} = E_i^{\circ} \psi_i^{\circ}, \qquad i = 1, 2, \cdots$$

→ Several ways to solve this problem

(1) Perturbation theory, if $\mathcal{H}' \ll \mathcal{H}^{\circ}$

(2) Variation theory

(3) Diagonalization of $\underset{\sim}{\mathcal{H}}$ matrix

→ Method (3)

Obtain $\underset{\sim}{H}$ matrix using ψ_i^0's, and diagonalize $\underset{\sim}{H}$

$$\underset{\sim}{H}^{(\psi^0)} = \begin{pmatrix} E_1^0 & 0 & 0 & 0 \\ 0 & E_2^0 & 0 & 0 \\ 0 & 0 & E_3^0 & 0 \\ & & & \ddots \end{pmatrix} + \begin{pmatrix} H_{11}' & H_{12}' & H_{13}' & \cdots \\ H_{21}' & H_{22}' & H_{23}' & \\ H_{31}' & H_{32}' & H_{33}' & H_{34}' \end{pmatrix}$$

$$= \begin{pmatrix} E_1^0 + H_{11}' & H_{12}' & H_{13}' & \cdots \\ H_{21}' & E_2^0 + H_{22}' & H_{23}' & \cdots \\ H_{31}' & H_{32}' & E_3^0 + H_{33}' & \\ \vdots & \vdots & & \end{pmatrix}$$

Numerically diagonalize $\underset{\sim}{H}^{\psi^0}$.

Wavefunctions $\longrightarrow$ $\sum_{i=1} c_i \psi_i^0$

Eigenvalues $\longrightarrow$ energies

→ If $H' << H^0$, appeal to perturbation theory in the case of "no degeneracies"

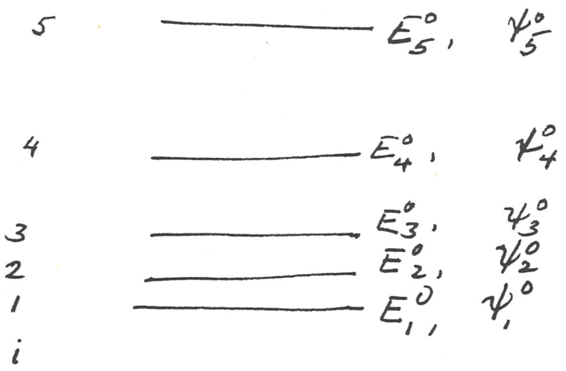
$$\psi_i^{\text{corrected}} = \psi_i^0 - \sum_j{}' \left(\frac{\int \psi_j^0 H' \psi_i^0 \, d\vec{r}}{E_j^0 - E_i^0} \right) \cdot \psi_j^0$$

and Energy $= E_i$ (to second order)

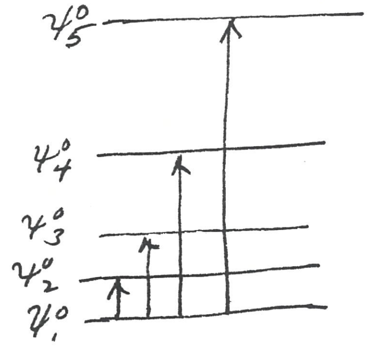
$$= \int \psi_i^{*\text{corrected}} (\underset{\sim}{H}^0 + \underset{\sim}{H}') \psi_i^{\text{corrected}} \, d\vec{r}$$

In the case that there are degeneracies, must diagonalize $\underset{\sim}{H}$ matrix.

<u>Non-degenerate case</u>



$\boxed{\underset{\sim}{H}^0}$



$$\psi_1^{\text{corrected}} \simeq \psi_1^0 + c_2\psi_2^0 + c_3\psi_3^0 + c_4\psi_4^0 + c_5\psi_5^0 + \ldots$$

$$\boxed{\underset{\sim}{H} = \underset{\sim}{H}^0 + \underset{\sim}{H}'}$$