NEARLY FREE ELECTRON MODEL

Free Electron Model

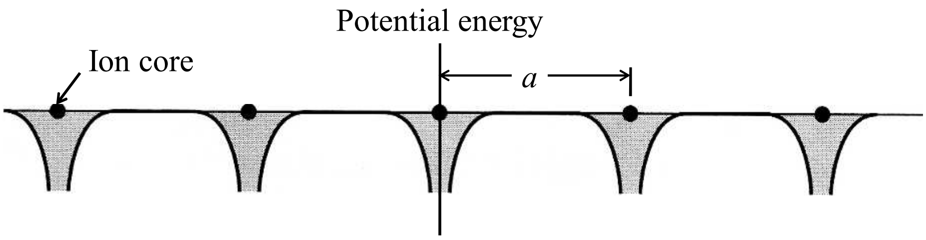
- Allowed energy values

$$\varepsilon_{\vec{k}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

- The free electron wavefunctions

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

Periodic Potential



- Free electrons are perturbed only weakly by the periodic potential of the ion cores.
- We will use time independent perturbation theory to calculate the energy values and the wavefunctions.

Perturbation Theory

- A set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system.
- Start with a simple system for which a mathematical solution is known, and add an additional perturbing Hamiltonian representing a weak disturbance to the system.
- The physical quantities of the perturbed system are expressed as the corrections to those of the simple system.
- Perturbation theory is applied to the complex systems where exact solutions of the Schrodinger equation are not possible.

Perturbation Theory

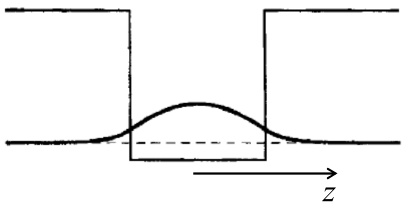
- Time independent perturbation theory
  - The perturbation Hamiltonian is static.
- Time dependent perturbation theory
  - The perturbation Hamiltonian is time-dependent.

5

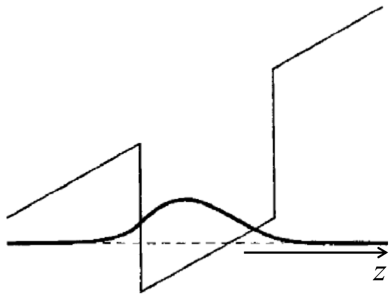
TIME-INDEPENDENT PERTURBATION THEORY

Theory

Rectangular potential well



Potential well with applied field



- A perturbed potential well may not be solved exactly.
- Usually, we need
    - First order correction in the wavefunctions
    - Second order correction in the energy values

7

Theory

- The unperturbed eigenstates are ϕ_n with energies ε_n

$$\hat{H}_0\phi_n = \varepsilon_n\phi_n$$

- The perturbed eigenstates are ψ_n with energies E_n

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

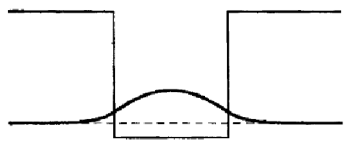
- Split the Hamiltonian into two parts:

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

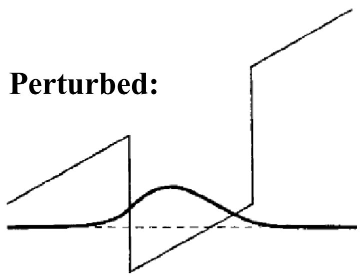
$\hat{H}_0$: Unperturbed system

$\hat{V}$: Perturbation

Unperturbed:



Perturbed:



8

Energy and Wavefunctions

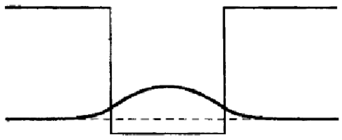
- We will expand the energy and wave function in powers of the perturbation. To aid the bookkeeping, we write

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

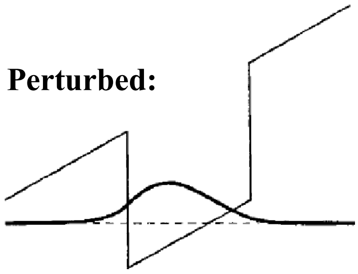
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots$$

Unperturbed:



Perturbed:



Energy and Wavefunctions

- Schrodinger equation

$$\left(\hat{H}_0 + \lambda \hat{V}\right)\left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right)\left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots\right)$$

- Equating the coefficients of powers of λ from both sides

$\lambda^0 \rightarrow$ $$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

$\lambda^1 \rightarrow$ $$\hat{V} \psi_n^{(0)} + \hat{H}_0 \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$\lambda^2 \rightarrow$ $$\hat{V} \psi_n^{(1)} + \hat{H}_0 \psi_n^{(2)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(0)} \psi_n^{(2)}$$

Zeroth Order Corrections

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

$$\psi_n^{(0)} = \phi_n$$

$$E_n^{(0)} = \varepsilon_n$$

Unperturbed solutions

First Order Corrections

$$\hat{V}\psi_n^{(0)} + \hat{H}_0 \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$$\left(\hat{H}_0 - \varepsilon_n\right)\psi_n^{(1)} = \left(E_n^{(1)} - \hat{V}\right)\phi_n$$

- Expand $\psi_n^{(1)}$ in terms of ϕ_n

$$\psi_n^{(1)} = \sum_k a_{nk}^{(1)} \phi_k$$

$E_n^{(1)}$

- After substitution:

$$\sum_k \left(\hat{H}_0 - \varepsilon_n\right) a_{nk}^{(1)} \phi_k = \left(E_n^{(1)} - \hat{V}\right) \phi_n$$

$$\hat{H}_0 \phi_k = \varepsilon_k \phi_k$$

$$\sum_k a_{nk}^{(1)} \left(\varepsilon_k - \varepsilon_n\right) \phi_k = E_n^{(1)} \phi_n - \hat{V} \phi_n$$

- Multiply both sides by ϕ_n* and integrate:

$$\sum_k a_{nk}^{(1)} \left(\varepsilon_k - \varepsilon_n\right) \int \phi_n^* \phi_k = E_n^{(1)} \int \phi_n^* \phi_n - \int \phi_n^* \hat{V} \phi_n$$

- Using orthogonality: $E_n^{(1)} = \int \phi_n^* \hat{V} \phi_n = V_{nn}$

13

$\psi_n^{(1)}$

$$\sum_k a_{nk}^{(1)} \left(\varepsilon_k - \varepsilon_n\right) \phi_k = E_n^{(1)} \phi_n - \hat{V} \phi_n$$

- Multiply both sides by ϕ_m* ($m \neq n$) and integrate:

$$\sum_k a_{nk}^{(1)} \left(\varepsilon_k - \varepsilon_n\right) \int \phi_m^* \phi_k = E_n^{(1)} \int \phi_m^* \phi_n - \int \phi_m^* \hat{V} \phi_n$$

- Using orthogonality:

$$a_{nm}^{(1)} \left(\varepsilon_m - \varepsilon_n\right) = -\int \phi_m^* \hat{V} \phi_n = -V_{mn}$$

$$a_{nm}^{(1)} = \frac{V_{mn}}{\varepsilon_n - \varepsilon_m}$$

- Change in wavefunction

$$\psi_n^{(1)} = a_{nn}^{(1)} \phi_n + \sum_{k, k \neq n} \frac{V_{kn}}{\varepsilon_n - \varepsilon_k} \phi_k$$

14

$a_{nn}^{(1)}$

- $a_{nn}^{(1)}$ can be calculated from the condition of normalization.

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)}$$

$$\int \psi_n^* \psi_n = 1$$

$$= \int \left(\phi_n + \lambda \psi_n^{(1)} \right)^* \left(\phi_n + \lambda \psi_n^{(1)} \right)$$

$$= \int \left(\phi_n + \lambda \sum_m a_{nm}^{(1)} \phi_m \right)^* \left(\phi_n + \lambda \sum_m a_{nm}^{(1)} \phi_m \right)$$

$$a_{nn}^{(1)} = 0$$

15

Second Order Correction

$$\hat{V}\psi_n^{(1)} + \hat{H}_0 \psi_n^{(2)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(0)} \psi_n^{(2)}$$

$$\left(\hat{H}_0 - \varepsilon_n \right) \psi_n^{(2)} = \left(V_{nn} - \hat{V} \right) \sum_k a_{nk}^{(1)} \phi_k + E_n^{(2)} \phi_n$$

- Expand the wavefunction

$$\psi_n^{(2)} = \sum_k a_{nk}^{(2)} \phi_k$$

$$\left(\hat{H}_0 - \varepsilon_n \right) \sum_k a_{nk}^{(2)} \phi_k = \left(V_{nn} - \hat{V} \right) \sum_k a_{nk}^{(1)} \phi_k + E_n^{(2)} \phi_n$$

$$\sum_k a_{nk}^{(2)} \left(\varepsilon_k - \varepsilon_n \right) \phi_k = \left(V_{nn} - \hat{V} \right) \sum_k a_{nk}^{(1)} \phi_k + E_n^{(2)} \phi_n$$

16

$E_n^{(2)}$

$$\sum_k a_{nk}^{(2)}\left(\varepsilon_k-\varepsilon_n\right)\phi_k=\left(V_{nn}-\hat{V}\right)\sum_k a_{nk}^{(1)}\phi_k+E_n^{(2)}\phi_n$$

- Multiply both sides by ϕ_n* and integrate:

$$\sum_k a_{nk}^{(2)}\left(\varepsilon_k-\varepsilon_n\right)\int\phi_n^*\phi_k=\sum_k a_{nk}^{(1)}\int\phi_n^*\left(V_{nn}-\hat{V}\right)\phi_k+E_n^{(2)}\int\phi_n^*\phi_n$$

$$E_n^{(2)}=\sum_k a_{nk}^{(1)}\int\phi_n^*\hat{V}\phi_k-V_{nn}a_{nn}^{(1)}=\sum_k a_{nk}^{(1)}V_{nk}-V_{nn}a_{nn}^{(1)}$$

$$E_n^{(2)}=\sum_{k,k\neq n}a_{nk}^{(1)}V_{nk}=\sum_{k,k\neq n}\frac{V_{nk}V_{kn}}{\varepsilon_n-\varepsilon_k}$$

- Since V is a Hermitian matrix

$$E_n^{(2)}=\sum_{k,k\neq n}\frac{\left|V_{kn}\right|^2}{\varepsilon_n-\varepsilon_k}$$

Corrections

$$E_n=\varepsilon_n+V_{nn}+\sum_{k,k\neq n}\frac{\left|V_{kn}\right|^2}{\varepsilon_n-\varepsilon_k}+\cdots$$

$$\psi_n=\phi_n+\sum_{k,k\neq n}\frac{V_{kn}}{\varepsilon_n-\varepsilon_k}\phi_k+\cdots$$

- To converge rapidly, the coupling between states induced by the perturbation must be smaller than the separation between the energy levels.
- This approach cannot be used if the states are degenerate.
- V_{kn} may be zero due to symmetry → *selection rules*.