

Applications of Quantum Mechanics.

Time-dependent Perturbation Theory.

(i) Decays of excited states of atoms.

(ii) Scattering cross-sections.

The Hamiltonian for the system of interest is $H = H_0 + V$, where H_0 is a well understood system and V is an interaction that is sufficiently weak that it can be treated perturbatively. The theory allows us to calculate transitions between eigenstates of H_0 .

Let $\{|n\rangle\}$, $n = 0, 1, 2, \dots$ be the eigenstates of H_0 , so that $H_0 |n\rangle = E_n |n\rangle$, $\langle n|m\rangle = \delta_{mn}$. Introduce a formal expansion parameter λ . Set $H = H_0 + \lambda V$, (set $\lambda = 1$ afterwards).

The Schrödinger equation governing the time evolution of the system is

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle = (H_0 + \lambda V) |\Psi(t)\rangle.$$

If $\lambda = 0$, $H = H_0$; $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H_0 |\Psi(t)\rangle$. $|\Psi(t)\rangle = e^{-iH_0 t/\hbar} |\Phi\rangle$, $|\Phi\rangle = |\Psi(0)\rangle$.

When $\lambda \neq 0$, this solution is no longer correct.

We accommodate the interaction by allowing $|\Phi\rangle$ to acquire a "weak" time dependence. We deal with the time-dependence of $|\Phi\rangle$ perturbatively.

Our assumption then is that the solution of the full Schrödinger equation is

$$|\Psi(t)\rangle = e^{-iH_0 t/\hbar} |\Phi(t)\rangle.$$

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H_0 e^{-iH_0 t/\hbar} |\Phi(t)\rangle + e^{-iH_0 t/\hbar} i\hbar \frac{\partial}{\partial t} |\Phi(t)\rangle = e^{-iH_0 t/\hbar} (H_0 + i\hbar \frac{\partial}{\partial t}) |\Phi(t)\rangle$$

The original Schrödinger equation implies:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H_0 + \lambda V) e^{-iH_0 t/\hbar} |\Phi(t)\rangle = e^{-iH_0 t/\hbar} (H_0 + \lambda \tilde{V}(t)) |\Phi(t)\rangle, \text{ where } \tilde{V}(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}.$$

By comparing both expressions for $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle$, we see that $i\hbar \frac{\partial}{\partial t} |\Phi(t)\rangle = \lambda \tilde{V}(t) |\Phi(t)\rangle$.

We call $|\Phi(t)\rangle = e^{iH_0 t/\hbar} |\Psi(t)\rangle$ the Interaction Picture ket corresponding to $|\Psi(t)\rangle$.

We can integrate the equation of motion for $|\Phi(t)\rangle$:

$$|\Phi(t)\rangle = |\Phi(0)\rangle + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t') |\Phi(t')\rangle.$$

This is an integral equation which implies the differential equation. It has the advantage that it incorporates the boundary conditions at $t=0$. We solve this integral equation by expanding $|\Phi(t)\rangle$ in powers of λ , Born Series:

$$|\Phi(t)\rangle = |\Phi_0\rangle + \lambda |\Phi_1(t)\rangle + \lambda^2 |\Phi_2(t)\rangle + \dots = |\Phi_0\rangle + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t') (|\Phi_0\rangle + \lambda |\Phi_1(t')\rangle + \dots)$$

By equating the coefficients of powers of λ , we have:

$$O(\lambda^1): |\Phi_1(t)\rangle = \frac{1}{i\hbar} \int_0^t dt' \tilde{V}(t') |\Phi_0\rangle,$$

$$O(\lambda^2): |\Phi_2(t)\rangle = \frac{1}{i\hbar} \int_0^t dt' \tilde{V}(t') |\Phi_1(t')\rangle, \text{ etc.}$$

$$\text{So, } |\Phi_2(t)\rangle = \frac{1}{(i\hbar)^2} \int_0^t dt' \tilde{V}(t') \int_0^{t'} dt'' \tilde{V}(t'') |\Phi_0\rangle, \text{ etc.}$$

$$\text{So } |\Phi(t)\rangle = \left(1 + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t') + \left(\frac{\lambda}{i\hbar} \right)^2 \int_0^t dt' \tilde{V}(t') \int_0^{t'} dt'' \tilde{V}(t'') + \dots \right) |\Phi_0\rangle = U(t) |\Phi_0\rangle,$$

$$\text{where } U(t) = 1 + \sum_{n=1}^{\infty} \left(\frac{\lambda}{i\hbar} \right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \tilde{V}(t_1) \dots \tilde{V}(t_n)$$

We can think of $U(t)$ as the evolution operator for the Interaction Picture. $U(t)$ satisfies the differential equation $i\hbar \frac{\partial}{\partial t} U(t) = \lambda \tilde{V}(t) U(t)$, $U(0) = 1$

$$\text{I.e. } U(t) = 1 + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t') U(t'). \text{ To lowest approximation, } U(t) = 1 + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t')$$

We will exploit this first order formula.

Transitions

The theory is set up to calculate transitions between eigenstates of H_0 . We assume that $|\phi_0\rangle = |m\rangle$, $H_0|m\rangle = E_m|m\rangle$, and we calculate the probability of a transition to a state $|n\rangle$ with $H_0|n\rangle = E_n|n\rangle$ at time t .

At time t , the state of the system is $|\Psi(t)\rangle = U(t)|m\rangle$

The overlap between $|\Psi(t)\rangle$ and $|n\rangle$ is $\langle n|\Psi(t)\rangle = \langle n|U(t)|m\rangle$

$P_{m \rightarrow n}(t) = |\langle n|\Psi(t)\rangle|^2 = |\langle n|U(t)|m\rangle|^2$. Set $T_{nm} = \langle n|U(t)|m\rangle$, so $P_{m \rightarrow n} = |T_{nm}|^2$.

Now, $T_{nm} = \langle n|U(t)|m\rangle = \langle n|(1 + \frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t') + \dots)|m\rangle$.

Assume $|n\rangle \neq |m\rangle$, so $\langle n|m\rangle = \langle n|1|m\rangle = 0$. So, in our approximation,
 $T_{nm} = \langle n|\frac{\lambda}{i\hbar} \int_0^t dt' \tilde{V}(t')|m\rangle = \frac{\lambda}{i\hbar} \int_0^t dt' \langle n|\tilde{V}(t')|m\rangle = \frac{\lambda}{i\hbar} \int_0^t dt' \langle n|e^{iH_0 t'/\hbar} V e^{-iH_0 t'/\hbar}|m\rangle$
 $= \frac{\lambda}{i\hbar} \int_0^t dt' e^{i(E_n - E_m)t'/\hbar} \langle n|V|m\rangle = \frac{\lambda}{i\hbar} \frac{e^{i(E_n - E_m)t/\hbar} - 1}{i(E_n - E_m)/\hbar} \cdot V_{nm}$, where $V_{nm} = \langle n|V|m\rangle$.

So, $T_{nm} = \frac{\lambda}{i\hbar} e^{i(E_n - E_m)t/2\hbar} \frac{(e^{i(E_n - E_m)t/2\hbar} - e^{-i(E_n - E_m)t/2\hbar})}{2i \left[\frac{E_n - E_m}{2\hbar} \right]} V_{nm} = \frac{\lambda}{i\hbar} e^{i(E_n - E_m)t/2\hbar} \frac{2\hbar \sin\left(\frac{(E_n - E_m)t}{2\hbar}\right)}{E_n - E_m} V_{nm}$

So, $P_{nm}(t) = \frac{\lambda^2}{\hbar^2} \left\{ \frac{2\hbar}{E_n - E_m} \sin\left[\frac{(E_n - E_m)t}{2\hbar}\right] \right\}^2 |V_{nm}|^2$. Take $\lambda = 1$.

The probability of transition from $|m\rangle$ to a range of final states $|n\rangle$, $n \in I$ is
 $P_{I,m}(t) = \sum_{n \in I} P_{nm}(t) = \frac{\lambda^2}{\hbar^2} \sum_{n \in I} \left[\frac{2\hbar}{E_n - E_m} \sin\left(\frac{(E_n - E_m)t}{2\hbar}\right) \right]^2 |V_{nm}|^2$.

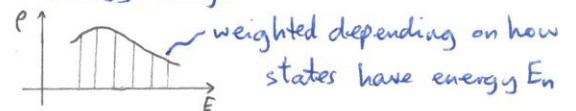
We are interested in situations where the final states are distributed continuously rather than discretely.

Important case: Scattering $H_0: \rightarrow$ free particle. The eigenstates are labelled by a momentum $|p\rangle$. p is continuously distributed.

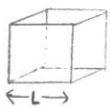
Density of States

This is the number of states per unit energy range. That is, if $\rho(E)$ is the density of states then $\rho(E)dE$ is the number of states in the energy range $E \rightarrow E+dE$.

Formally, we can write $\rho(E) = \sum_n \delta(E - E_n)$



Key step - sum over states.



Volume $V = L^3$. Free particles in this box are subject to boundary conditions. For any wavefunction $\Psi(\underline{r})$, $\Psi(\underline{r} + L\hat{e}_i) = \Psi(\underline{r})$, $i = 1, 2, 3$.

\hat{e}_i are the orthonormal cartesian basis vectors parallel to the sides of the box.

The hamiltonian for the free particle is its kinetic energy. $H_0 = \frac{1}{2M} P^2$, where $P = -i\hbar \nabla$ is the momentum operator.

We see that $\Psi_p(\underline{r}) = e^{i\mathbf{p} \cdot \underline{r}/\hbar}$ (up to normalisation). $E_p = P^2/2M$.

We require that the momenta are such that $\Psi(\underline{r} + L\hat{e}_i) = \Psi(\underline{r})$.

$e^{i\mathbf{p} \cdot (\underline{r} + L\hat{e}_i)/\hbar} = e^{i\mathbf{p} \cdot \underline{r}/\hbar} \Rightarrow e^{i\mathbf{p} \cdot (L\hat{e}_i)/\hbar} = 1$. So $\mathbf{p} \cdot \left(\frac{L\hat{e}_i}{\hbar}\right) = 2\pi n_i \pi$, $n_i = 0, \pm 1, \pm 2, \dots$. $\mathbf{p} \cdot \hat{e}_i = p_i$.

$p_i = 2\pi\hbar \left(\frac{n_i}{L}\right)$, $n_i \in \mathbb{Z}$.

Allowed momenta are $\mathbf{p} = 2\pi\hbar \left(\frac{n_1}{L}, \frac{n_2}{L}, \frac{n_3}{L}\right)$.

We have to deal with summations over these states of the form $\sum_{n_1, n_2, n_3} f(\mathbf{p})$, where $f(\mathbf{p})$ is a sufficiently smooth function.

$$\sum_{n_i=-\infty}^{\infty} f(p_i) = \frac{L}{2\pi\hbar} \sum_{n_i} \frac{2\pi\hbar}{L} f(p_i) = \frac{L}{2\pi\hbar} \sum_{n_i} \delta p_i f(p_i), \text{ when } L \text{ is large, } \frac{2\pi\hbar}{L} = \delta p_i \rightarrow dp_i$$

$$\text{So } \sum_{n_i} f(p_i) \approx \int_{-\infty}^{\infty} dp_i f(p_i) \cdot \frac{L}{2\pi\hbar}$$

$$\therefore \sum f(p) \rightarrow \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3 p f(p)$$

Density of states: $\rho(E) = \sum_n \delta(E - E_n)$, $E_n \rightarrow E(p) = \frac{p^2}{2m}$

$$= \frac{L^3}{(2\pi\hbar)^3} \int d^3 p \delta(E - E(p)) = \frac{V}{(2\pi\hbar)^3} \int d^3 p \delta(E - E(p))$$

$$d^3 p = p^2 dp d\Omega(p) = p^2 \frac{dp}{dE(p)} d\Omega dE(p)$$

$$\text{So } \rho(E) = \frac{V}{(2\pi\hbar)^3} \int p^2 dp d\Omega dE(p) \delta(E - E(p)) = \frac{V}{(2\pi\hbar)^3} \int d\Omega \frac{p^2}{dE(p)/dp} \quad [p \text{ chosen so that } E(p) = E]$$

$$\frac{dE(p)}{dp} = \frac{d}{dp} \frac{p^2}{2m} = \frac{p}{m}. \text{ So } \rho(E) = \frac{V}{(2\pi\hbar)^3} \int d\Omega M_p, \text{ where } \frac{p^2}{2m} = E.$$

The normalised eigenfunctions are $\Psi_p(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}}$, $\mathbf{p} = 2\pi\hbar \left(\frac{n_1}{L}, \frac{n_2}{L}, \frac{n_3}{L}\right)$

$$\langle \Psi_{p'} | \Psi_p \rangle = \int_{\text{box}} d^3 r \Psi_{p'}^*(\mathbf{r}) \Psi_p(\mathbf{r}) = \frac{1}{V} \int_{\text{box}} d^3 r e^{i(\mathbf{p}' - \mathbf{p})\cdot\mathbf{r}} = \delta_{\mathbf{p}\mathbf{p}'}$$

The sum over final states can be replaced by an integral over the density of states: $\sum_n \rightarrow \int dE(p) \rho(E_p)$

$$P_{\text{sum}} = \sum \frac{1}{\hbar^2} \left\{ \frac{2\hbar}{E_n - E_m} \cdot \sin\left(\frac{E_n - E_m}{2\hbar} t\right) \right\}^2 |V_{nm}|^2 = \frac{1}{\hbar^2} \int dE \rho(E) \left\{ \frac{2\hbar}{E - E_m} \cdot \sin\left(\frac{E - E_m}{2\hbar} t\right) \right\}^2 |V_{nm}|^2$$

We assume that (say) the large volume limit is taken so that E is continuously distributed.

$$\text{Set } E = E_m + \eta.$$

$$P = \frac{1}{\hbar^2} \int d\eta \rho(E_m + \eta) \left\{ \frac{2\hbar}{\eta} \cdot \sin\left(\frac{\eta t}{2\hbar}\right) \right\}^2 |V_{nm}|^2$$

$$\text{Set } y = \frac{\eta t}{2\hbar}$$

$$P = \frac{2\hbar}{\hbar^2} \int \frac{dy}{t} \rho\left(E_m + \frac{2\hbar y}{t}\right) \left(\frac{\sin y}{y/t}\right)^2 |V_{nm}|^2 = \frac{2\hbar t}{\hbar^2} \int dy \rho\left(E_m + \frac{2\hbar y}{t}\right) \left(\frac{\sin y}{y}\right)^2 |V_{nm}|^2$$

$$\text{(let } t \rightarrow \infty) \dots = \frac{2t}{\hbar} \int dy \left(\frac{\sin y}{y}\right)^2 \rho(E_m) |V_{nm}|^2. \quad n \text{ is chosen so that } E_n = E_m = E.$$

$$\text{Note that } \int dy \left(\frac{\sin y}{y}\right)^2 = \pi.$$

So, $P = t \cdot \frac{2\pi}{\hbar} \cdot \rho(E_n) |V_{nm}|^2$. This formula makes sense only in the large volume limit where $|V_{nm}|^2$ is very small. We interpret our result as predicting a transition probability per unit time.

The Golden Rule: $\Gamma = \frac{P}{t} = \frac{2\pi}{\hbar} \cdot \rho(E_n) |V_{nm}|^2$.

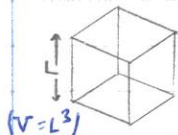
Scattering.

$V = V(\mathbf{r})$. $V(\mathbf{r})$ is substantial in some region near the origin.

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

Ultimately, $L \rightarrow \infty \Leftrightarrow V \rightarrow \infty$.

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2, \text{ free particle Hamiltonian.}$$



Far away from the origin $V(\mathbf{r}) \approx 0$ and the particle moves freely. It is sensible to think of a scattering process as a transition between eigenstates of H_0 , $\Psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}}$. $\hbar\mathbf{k} = \mathbf{p}$, momentum.

Consider a transition between \mathbf{k} and \mathbf{k}' induced by $V(\mathbf{r})$.

$$\langle n \rangle = \Psi_{\mathbf{k}'}(\mathbf{r}), \langle m \rangle = \Psi_{\mathbf{k}}(\mathbf{r}). \quad V_{nm} = \langle n | V | m \rangle = \int_{\text{box}} d^3 r \Psi_{\mathbf{k}'}^*(\mathbf{r}) V(\mathbf{r}) \Psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V} \int_{\text{box}} d^3 r e^{-i(\mathbf{k}' - \mathbf{k})\cdot\mathbf{r}} V(\mathbf{r})$$

$$\rightarrow \frac{1}{V} \tilde{V}(\mathbf{k}' - \mathbf{k}) \text{ - the Fourier Transform.}$$

Density of states associated with the elementary solid angle $d\Omega$ is $\rho(E) = \frac{V}{(2\pi\hbar)^3} d\Omega M_p$.

The initial and final energies are the same. $E(\mathbf{p}') = E(\mathbf{p}) \Rightarrow |\mathbf{p}'| = |\mathbf{p}| = p$. $E = \frac{p^2}{2m}$.

Transition rate is $\Gamma = \frac{2\pi}{\hbar} \frac{V}{(2\pi\hbar)^3} d\Omega M_p \cdot \frac{1}{V^2} |\tilde{V}(\mathbf{k}' - \mathbf{k})|^2$.

Transition rate \rightarrow cross-section \leftarrow characteristic of the scattering centre.

The transition rate is $F d\sigma$, where F is the incident flux, and $d\sigma$ is the elementary cross-section associated with scattering into the elementary solid angle $d\Omega$.

$F = (\text{density of the incident beam}) \times (\text{velocity})$.

The initial beam is represented by the initial wavefunction, $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$, density $= \frac{1}{V}$, flux $= \frac{1}{V} \times \frac{p}{M}$.

So, $\frac{1}{V} \cdot \frac{p}{M} \cdot d\sigma = \Gamma = \left(\frac{2\pi}{\hbar}\right) \frac{V}{(2\pi\hbar)^3} d\Omega M_p \cdot \frac{1}{V^2} |\tilde{V}(\mathbf{k}' - \mathbf{k})|^2$.

The volume factors cancel out of this equation: $d\sigma = \frac{2\pi}{\hbar} \cdot \frac{M^2}{(2\pi\hbar)^3} d\Omega |\tilde{V}(\mathbf{k}' - \mathbf{k})|^2$

The differential cross-section, $\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \cdot \frac{M^2}{(2\pi\hbar)^3} |\tilde{V}(\mathbf{k}' - \mathbf{k})|^2 = |T|^2$, where $T = -\frac{M}{2\pi\hbar^2} \tilde{V}(\mathbf{k}' - \mathbf{k})$, the scattering amplitude.

The total cross-section is $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int |T|^2 d\Omega = \int |T|^2 \sin\theta d\theta d\phi$, where θ, ϕ are the polar angles of \mathbf{p}' or \mathbf{k}' .

Momentum Transfer:

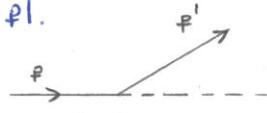
We define the momentum ^{transfer} to the scattering particle to be $\Delta = \mathbf{p}' - \mathbf{p} = \hbar(\mathbf{k}' - \mathbf{k})$.

Sometimes we mean the magnitude, $\Delta = |\Delta| = |\mathbf{p}' - \mathbf{p}|$.

Assume \mathbf{p} is aligned with the polar axis.

$\mathbf{p} \cdot \mathbf{p}' = p^2 \cos\theta$, θ the scattering angle.

$\Delta^2 = (\mathbf{p}' - \mathbf{p})^2 = 2p^2 - 2\mathbf{p} \cdot \mathbf{p}' = 2p^2(1 - \cos\theta)$



Example - shielded coulomb potential

$V = V(\mathbf{r}) = \frac{g}{4\pi} \frac{e^{-\alpha r}}{r}$

Want to calculate the scattering amplitude, $T = -\frac{M}{2\pi\hbar^2} \tilde{V}(\mathbf{k}' - \mathbf{k})$.

$\tilde{V}(\mathbf{k}' - \mathbf{k}) = \int d^3\mathbf{r} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V(\mathbf{r}) = \int d^3\mathbf{r} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} \frac{g}{4\pi} \frac{e^{-\alpha r}}{r}$

$\mathbf{r} \rightarrow (r, \theta, \phi)$ [Note: integration angles, not scattering angles]. $d^3\mathbf{r} \rightarrow r^2 dr \sin\theta d\theta d\phi$

$(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r} = \frac{1}{\hbar} \Delta \cdot \mathbf{r} = \frac{1}{\hbar} \Delta r \cos\theta$, choosing Δ to define the polar axis for \mathbf{r} .

$\tilde{V}(\frac{1}{\hbar} \Delta) = \frac{g}{4\pi} \int r^2 dr \sin\theta d\theta d\phi e^{-i\frac{\Delta}{\hbar} r \cos\theta} \cdot \frac{e^{-\alpha r}}{r}$

$\left(\int d\phi = 2\pi, \int \sin\theta d\theta \rightarrow d\cos\theta \right) = \frac{g}{4\pi} \cdot 2\pi \int r^2 dr \frac{e^{-\alpha r}}{r} \int_{-1}^1 d\cos\theta \cdot e^{-i\frac{\Delta}{\hbar} r \cos\theta}$

$\int_{-1}^1 d\cos\theta \cdot e^{-i\frac{\Delta}{\hbar} r \cos\theta} = \frac{1}{-i\frac{\Delta}{\hbar} r} \left(e^{-i\frac{\Delta}{\hbar} r} - e^{i\frac{\Delta}{\hbar} r} \right)$

$\tilde{V}(\frac{1}{\hbar} \Delta) = \frac{g}{4\pi} \cdot 2\pi \int_0^\infty \frac{dr}{-i\frac{\Delta}{\hbar}} \left(e^{-(\alpha + i\Delta/\hbar)r} - e^{-(\alpha - i\Delta/\hbar)r} \right) = \frac{1}{2} g \cdot \frac{1}{(-i\Delta/\hbar)} \left[\frac{1}{\alpha + i\Delta/\hbar} - \frac{1}{\alpha - i\Delta/\hbar} \right] = \frac{g}{\alpha^2 + (\Delta/\hbar)^2}$

The scattering amplitude is $T = -\frac{M}{2\pi\hbar^2} \cdot \frac{g}{\alpha^2 + (\Delta/\hbar)^2} = -\frac{M}{2\pi\hbar^2} \cdot \frac{g}{\alpha^2 + (\mathbf{k}' - \mathbf{k})^2}$, and

$\frac{d\sigma}{d\Omega} = |T|^2 = \frac{M^2 g^2}{4\pi^2 \hbar^4} \cdot [\alpha^2 + (\mathbf{k}' - \mathbf{k})^2]^{-2}$

At low energy, $\mathbf{p} \rightarrow 0, \mathbf{k} \rightarrow 0$, so $\frac{d\sigma}{d\Omega} \approx \frac{M^2 g^2}{4\pi^2 \hbar^4} \cdot \frac{1}{\alpha^4}$.

$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega \approx \int d\Omega \frac{M^2 g^2}{4\pi^2 \hbar^4} \cdot \frac{1}{\alpha^4} = \frac{M^2 g^2}{\pi \hbar^4 \alpha^4}$

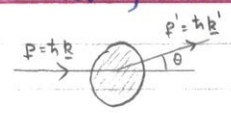
In general, $\sigma = \left(\frac{q^2 M^2}{4\pi^2 \hbar^4}\right) \int d\Omega [\alpha^2 + 2k^2(1-\cos\theta)]^{-2}$. θ is scattering angle.
 $\int d\Omega = \int d\phi \int d\cos\theta = \int 2\pi d\cos\theta$, so $\sigma = \left(\frac{q^2 M^2}{4\pi^2 \hbar^4}\right) \cdot 2\pi \int d\cos\theta [\alpha^2 + 2k^2(1-\cos\theta)]^{-2}$
 Claim the answer is $\sigma = \left(\frac{q^2 M^2}{4\pi^2 \hbar^4}\right) \cdot \frac{4\pi}{\alpha^2(\alpha^2 + 4k^2)}$. $E = \hbar^2 k^2 / 2M$.

The coulomb potential is the limit $\alpha \rightarrow 0$. $g = \frac{q_1 q_2}{\epsilon_0}$, q_1, q_2 are the charges on the particle and the scattering centre.

In taking the limit $\alpha \rightarrow 0$, $\frac{d\sigma}{d\Omega} = \left(\frac{q_1 q_2 M}{2\pi \hbar^2 \epsilon_0}\right)^2 \frac{1}{4k^4(1-\cos\theta)^2}$. Set $p = \hbar k$. Small $\theta \Rightarrow 1-\cos\theta \approx \frac{1}{2}\theta^2$.
 So $\frac{d\sigma}{d\Omega} \approx \left(\frac{q_1 q_2 M}{2\pi \epsilon_0}\right)^2 \frac{1}{2p \cdot \theta^4}$. So $\frac{d\sigma}{d\Omega} \sim \frac{1}{\theta^4}$ as $\theta \rightarrow 0$.

This is also referred to as Rutherford scattering. This formula is the same as that derived from the classical theory. This approximation to the scattering amplitude which we have used so far is lowest order perturbation theory and is referred to as the Born approximation. For coulomb scattering, the differential cross-section obtained from the Born approximation is also the exact result.

Scattering on a Charge Distribution.



$Q\rho(r)$, where Q is the total charge $\int d^3r \rho(r) = 1$

If the charge in the particle is q , $V(r) = q\phi(r) = \frac{qQ}{4\pi\epsilon_0} \int d^3r' \rho(r') \frac{1}{|r-r'|}$
 For the Born approximation we need $\tilde{V}(\frac{1}{\hbar}\Delta) = \tilde{V}(k'-k) = \int d^3r e^{-i(k'-k)\cdot r} V(r)$.
 $V(r) = \int d^3r' g(r-r') h(r')$, where $h(r') = \rho(r')$ and $g(r-r') = \frac{Qq}{\epsilon_0} \frac{1}{4\pi|r-r'|}$.
 I.e., we have a convolution structure: $\tilde{V}(k'-k) = \tilde{g}(k'-k) \tilde{h}(k'-k)$

$\tilde{V}(k'-k) = \frac{qQ}{\epsilon_0} \cdot \left(\frac{1}{4\pi r}\right) \tilde{\rho}(k'-k)$. What is the Fourier transform of $\frac{1}{4\pi r}$?
 FT $\left(\frac{e^{-kr}}{4\pi r}\right) = \frac{1}{\alpha^2 + (k'-k)^2}$, so FT $\left(\frac{1}{4\pi r}\right) = \frac{1}{(k'-k)^2}$. $[\nabla^2 \frac{1}{4\pi r} = -\delta(r)]$ so $\hbar^2 \left(\frac{1}{4\pi r}\right) = -1$, so $\left(\frac{1}{4\pi r}\right) = \frac{1}{\hbar^2}$.

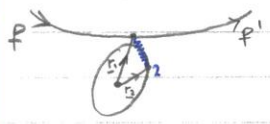
$\frac{d\sigma}{d\Omega} = \left(\frac{MqQ}{4\pi\epsilon_0}\right)^2 \frac{|\tilde{\rho}(k'-k)|^2}{p^4(1-\cos\theta)^2}$. - it is identical to scattering on a charge Q , but with the modification of the factor $|\tilde{\rho}(k'-k)|^2$.

For small angle scattering with $k' \approx k$, $\tilde{\rho}(k'-k) \rightarrow \tilde{\rho}(0)$.

$\tilde{\rho}(k'-k) = \int d^3r e^{-i(k'-k)\cdot r} \rho(r)$, $\tilde{\rho}(0) = \int d^3r \rho(r) = 1$.

For small angles, the scattering is identical to scattering on a point charge. To see the effect of the charge distribution we must measure scattering at large angles or momentum transfers. $\tilde{\rho}(k'-k)$ is called the form factor for the charge distribution. In the scattering process we can measure $|\tilde{\rho}(k'-k)|$. With some assumptions this will give us $\tilde{\rho}(k'-k) \Rightarrow$ structure of charge distribution. Scattering allows us to investigate the structure of the target.

Scattering on a Bound State - Simplified Model for Atomic Scattering.



Atomic Hamiltonian, $H_A = \frac{\hbar^2}{2m_2} \nabla_2^2 + V_A(r_2)$.

Particle 2 has a bound state, i.e. $\exists \phi_0(r_2)$ such that $H_A \phi_0(r_2) = -B\phi_0(r_2)$.

B is the binding energy of particle 2.

Particle 1 has a kinetic energy operator $-\frac{\hbar^2}{2M_1} \nabla_1^2$. We will define $H_0 = \frac{\hbar^2}{2M_1} \nabla_1^2 + H_A$.

Some relevant eigenstates of H_0 are: $\Psi_{k_1}(\underline{r}_1, \underline{r}_2) = \frac{e^{i \underline{k}_1 \cdot \underline{r}_1}}{\sqrt{V}} \Phi_0(\underline{r}_2)$.

$$H_0 \Psi_{k_1}(\underline{r}_1, \underline{r}_2) = \left(\frac{\hbar^2 k_1^2}{2M_1} - B \right) \Psi_{k_1}(\underline{r}_1, \underline{r}_2) \quad E_{k_1} = \frac{\hbar^2 k_1^2}{2M_1} - B$$

Density of states for the system with particle 2 in the state $\Phi_0(\underline{r}_2)$ is $\rho(E_{k_1}) = \frac{V}{(2\pi\hbar)^3} d\Omega M_1 p_1$.

The total hamiltonian is $H = H_0 + V(\underline{r}_1 - \underline{r}_2)$. $V(\underline{r}_1 - \underline{r}_2)$ induces the scattering of particle 1 on the bound state. $\frac{e^{i \underline{k}_1 \cdot \underline{r}_1}}{\sqrt{V}} \Phi_0(\underline{r}_2) \rightarrow \frac{e^{i \underline{k}'_1 \cdot \underline{r}_1}}{\sqrt{V}} \Phi_0(\underline{r}_2)$

Golden Rule Rate: $\Gamma = \frac{2\pi}{\hbar} \rho(E_{k_1}) |\langle \underline{k}'_1 \Phi_0 | V(\underline{r}_1 - \underline{r}_2) | \underline{k}_1 \Phi_0 \rangle|^2$

$$\text{Flux} \times d\sigma = \Gamma, \text{ so } \frac{1}{V} \frac{p_1}{M_1} d\sigma = \frac{2\pi}{\hbar} \cdot \frac{V M_1 p_1}{(2\pi\hbar)^3} d\Omega |\langle \underline{k}'_1 \Phi_0 | V(\underline{r}_1 - \underline{r}_2) | \underline{k}_1 \Phi_0 \rangle|^2$$

$$\langle \underline{k}'_1 \Phi_0 | V(\underline{r}_1 - \underline{r}_2) | \underline{k}_1 \Phi_0 \rangle = \frac{1}{V} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 e^{-i \underline{k}'_1 \cdot \underline{r}_1} \Phi_0^*(\underline{r}_2) V(\underline{r}_1 - \underline{r}_2) e^{i \underline{k}_1 \cdot \underline{r}_1} \Phi_0(\underline{r}_2)$$

$$= \frac{1}{V} \int d^3 \underline{r}_1 e^{-i (\underline{k}'_1 - \underline{k}_1) \cdot \underline{r}_1} \int d^3 \underline{r}_2 V(\underline{r}_1 - \underline{r}_2) |\Phi_0(\underline{r}_2)|^2 = \frac{1}{V} \tilde{V}(\underline{k}'_1 - \underline{k}_1) \tilde{F}(\underline{k}'_1 - \underline{k}_1), \text{ where } \tilde{F}$$

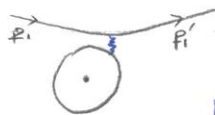
is the Fourier Transform for $F(\underline{r})$, and $F(\underline{r}) = |\Phi_0(\underline{r}_2)|^2$.

$F(\underline{r}_2)$ is the probability density distribution of particle 2

$$\frac{1}{V} \frac{p_1}{M_1} \frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \frac{V}{(2\pi\hbar)^3} M_1 p_1 \frac{|\tilde{V}(\underline{k}'_1 - \underline{k}_1)|^2 |\tilde{F}(\underline{k}'_1 - \underline{k}_1)|^2}{V^2}, \text{ so } \frac{d\sigma}{d\Omega} = \left(\frac{M_1}{2\pi\hbar^2} \right)^2 |\tilde{V}(\underline{k}'_1 - \underline{k}_1)|^2 |\tilde{F}(\underline{k}'_1 - \underline{k}_1)|^2$$

Again measuring the scattering tells us about the structure of the target.

Scattering on a Bound State



$$p_i + A \rightarrow p_i' + A, \quad p_i, \Phi_0 \rightarrow p_i', \Phi_0$$

$$\text{Energy conservation: } \frac{p_i^2}{2M_1} = \frac{p_i'^2}{2M_1}, \quad |p_i| = |p_i'|$$

Elastic scattering - scattering particle retains all of its kinetic energy.

Inelastic scattering - $p_i + A \rightarrow p_i' + A^*$

Assume that there is an excited state of the atom with wavefunction $\Phi_1(\underline{r}_2)$.

$$H_A \Phi_1(\underline{r}_2) = -B' \Phi_1(\underline{r}_2) \quad (\text{recall } H_A \Phi_0(\underline{r}_2) = -B \Phi_0(\underline{r}_2)) \quad B' < B$$

$$\text{Energy conservation tells us that } \frac{p_i^2}{2M_1} - B = \frac{p_i'^2}{2M_1} - B'. \text{ So } \frac{p_i'^2}{2M_1} = \frac{p_i^2}{2M_1} - (B - B') \Rightarrow p_i'^2 < p_i^2 \Rightarrow |p_i'| < |p_i|$$

Density of states for the final state is that appropriate to momentum p_i' : $\rho = \frac{V}{(2\pi\hbar)^3} d\Omega M_1 p_i'$.

$$\text{Incident flux} = \frac{1}{V} \frac{p_i}{M_1} \quad \Gamma = \text{flux} \times d\sigma = \frac{1}{V} \frac{p_i}{M_1} \cdot d\sigma \quad \text{Golden Rule: } \Gamma = \frac{2\pi}{\hbar} \rho \cdot |\langle \underline{k}'_1 | V | \underline{k}_1 \rangle|^2$$

$$\text{So } \Gamma = \frac{2\pi}{\hbar} \frac{V}{(2\pi\hbar)^3} \cdot d\Omega M_1 p_i' \cdot |\langle \underline{k}'_1 | V | \underline{k}_1 \rangle|^2$$

$$\langle \underline{k}'_1 | V | \underline{k}_1 \rangle = \langle p_i' \Phi_1 | V | p_i \Phi_0 \rangle = \frac{1}{V} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 e^{-i \underline{k}'_1 \cdot \underline{r}_1} \Phi_1^*(\underline{r}_2) V(\underline{r}_1 - \underline{r}_2) e^{i \underline{k}_1 \cdot \underline{r}_1} \Phi_0(\underline{r}_2)$$

$$= \frac{1}{V} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 e^{-i (\underline{k}'_1 - \underline{k}_1) \cdot \underline{r}_1} V(\underline{r}_1 - \underline{r}_2) \Phi_1^*(\underline{r}_2) \Phi_0(\underline{r}_2)$$

$$= \frac{1}{V} \tilde{V}(\underline{k}'_1 - \underline{k}_1) \tilde{F}_{10}(\underline{k}'_1 - \underline{k}_1) \text{ where } F_{10}(\underline{r}_2) = \Phi_1^*(\underline{r}_2) \Phi_0(\underline{r}_2)$$

$$\frac{1}{V} \frac{p_i}{M_1} d\sigma = \frac{2\pi}{\hbar} \frac{V}{(2\pi\hbar)^3} \cdot d\Omega M_1 p_i' \cdot \frac{1}{V^2} |\tilde{V}(\underline{k}'_1 - \underline{k}_1)|^2 |\tilde{F}_{10}(\underline{k}'_1 - \underline{k}_1)|^2$$

$$\text{So } \frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \frac{M_1^2}{(2\pi\hbar)^3} \cdot \frac{p_i'}{p_i} |\tilde{V}|^2 |\tilde{F}_{10}|^2 \quad (p_i = \hbar k_1, p_i' = \hbar k_1')$$

The differential cross-section will vanish when $p_i' = 0$.
 $\frac{p_i^2}{2m_i} - B = \frac{p_i'^2}{2m_i} - B'$ so when $p_i' = 0$, $\frac{p_i^2}{2m_i} = (B - B')$. This value of $\frac{p_i^2}{2m_i}$ is the threshold energy for the occurrence of the inelastic scattering process.

If $\frac{p_i^2}{2m_i} < B - B'$ then inelastic scattering cannot occur. Below this inelastic threshold only elastic scattering occurs.

Scattering Theory.

Simple model. Particle scattering on centre, at the origin, represented by a potential $V(r)$, spherically symmetric. Hamiltonian for the system is $H = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$.

Particle (or probability) current: let Ψ be the wavefunction. The Schrödinger equation is $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(r)\Psi$. Particle (or probability) density is $\rho = |\Psi|^2 = \Psi^* \Psi$, so

$$\frac{\partial \rho}{\partial t} = \Psi \frac{\partial \Psi^*}{\partial t} + \Psi^* \frac{\partial \Psi}{\partial t}$$

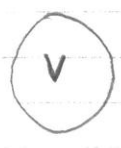
$$\text{Schrödinger Equation } \Rightarrow -i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V(r)\Psi^*$$

$$\text{So, } \frac{\partial \rho}{\partial t} = \frac{-1}{i\hbar} \Psi \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) + \frac{1}{i\hbar} \Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) = \frac{i\hbar}{2m} (\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*)$$

$$= \frac{i\hbar}{2m} \nabla \cdot (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) = -\nabla \cdot \underline{J}, \text{ if we set } \underline{J} = -\frac{i\hbar}{2m} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)$$

$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{J} = 0$. ρ is the particle density, \underline{J} is the particle current.

(number of particles is conserved).



$$N_v = \int_v d^3r \rho. \quad \frac{\partial N_v}{\partial t} = \int_v d^3r \frac{\partial \rho}{\partial t} = -\int_v d^3r \nabla \cdot \underline{J} = -\int_{\partial v} d\underline{S} \cdot \underline{J}$$

We see that the flux of particles through the boundary is the flux of \underline{J} across the boundary.

Example: Plane wave. $\Psi = A e^{i\mathbf{k} \cdot \mathbf{r}}$. $p = \hbar \mathbf{k}$. $\rho = |\Psi|^2 = |A|^2$.

$$\underline{J} = \frac{-i\hbar}{2m} (A^* e^{-i\mathbf{k} \cdot \mathbf{r}} \nabla A e^{i\mathbf{k} \cdot \mathbf{r}} - A e^{i\mathbf{k} \cdot \mathbf{r}} \nabla A^* e^{-i\mathbf{k} \cdot \mathbf{r}})$$

$$= \frac{-i\hbar}{2m} |A|^2 (e^{-i\mathbf{k} \cdot \mathbf{r}} (i\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} - e^{-i\mathbf{k} \cdot \mathbf{r}} (-i\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}}) = \frac{-i\hbar}{m} (i\mathbf{k}) |A|^2 = |A|^2 \frac{\mathbf{p}}{m} = \rho \times \text{velocity}.$$

Scattering Wavefunction.

Free particle, $H_0 = -\frac{\hbar^2}{2m} \nabla^2$. Eigenstates of energy can be identified as eigenstates of momentum.

$$\Psi_B^{(0)}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}. \quad H_0 \Psi_B^{(0)}(\mathbf{r}) = E_B \Psi_B^{(0)}(\mathbf{r}), \quad E_B = \frac{\hbar^2 k^2}{2m}. \quad p=1, \text{ current } \underline{J} = \frac{\hbar \mathbf{k}}{m} = \mathbf{v}.$$

Now introduce $V(r)$: $H = H_0 + V(r) = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$

(Note - we will always assume V is short range, $V(r) \approx 0$ for $r >$ some range a).

We seek a scattering solution with definite energy. Two properties:

i) contains an incident beam, $\Psi_B^{(0)}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}$.

ii) contains a scattered wave contribution, $\Psi_B(\mathbf{r}) = \Psi_B^{(0)}(\mathbf{r}) + \Psi_s(\mathbf{r})$.

$\Psi_s(\mathbf{r})$ represents outwardly moving particles. This is achieved by requiring, as $r \rightarrow \infty$, $\Psi_s \sim f(\theta) \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{r}$, $(r, \theta, \phi) \leftrightarrow \mathbf{r}$.

Because the potential is spherically symmetric the scattering problem is axially symmetric about the direction of the incident beam. No ϕ -dependence.

These solutions satisfy $H \Psi_B(\mathbf{r}) = E_B \Psi_B(\mathbf{r})$, $E_B = \frac{\hbar^2 k^2}{2m}$.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right) (e^{ik\cdot r} + \psi_s) = E_k (e^{ik\cdot r} + \psi_s). \quad \text{As } r \rightarrow \infty, V(r) \rightarrow 0, \psi_s \rightarrow 0, \Rightarrow E_k = \frac{\hbar^2 k^2}{2m}.$$

Flux associated with the scattered wave function: (note, $\underline{J}^{(\text{incident})} = \frac{\hbar k}{m}$)

$$\underline{J}^{(s)} = -\frac{i\hbar}{2m} (\psi_s^* \nabla \psi_s - \psi_s \nabla \psi_s^*). \quad \text{The leading term in } \underline{J}^{(s)} \text{ is the radial part:}$$

$$\begin{aligned} J^{(s)} &= -\frac{i\hbar}{2m} \left(\psi_s^* \frac{\partial}{\partial r} \psi_s - \psi_s \frac{\partial}{\partial r} \psi_s^* \right) = -\frac{i\hbar}{2m} |f(\theta)|^2 \left(\frac{e^{-ikr}}{r} \frac{\partial}{\partial r} e^{ikr} - e^{ikr} \frac{\partial}{\partial r} \frac{e^{-ikr}}{r} \right) \\ &\approx -\frac{i\hbar}{2m} |f(\theta)|^2 \cdot \frac{1}{r^2} (2ik) = \frac{\hbar k}{m} \frac{|f(\theta)|^2}{r^2} \end{aligned}$$

$$\underline{J}^{(s)} \approx \frac{\hbar k}{m} |f(\theta)|^2 \hat{r} \cdot \frac{1}{r^2}$$

The flux emerging in solid angle $d\Omega$ is $\underline{J}^{(s)} \cdot d\underline{S} = \frac{\hbar k}{m} |f(\theta)|^2 \hat{r} \cdot \frac{1}{r^2} \cdot r^2 d\Omega \hat{r} = \frac{\hbar k}{m} |f(\theta)|^2 d\Omega$.

(Note: $d\underline{S} = dS \hat{e}$, $dS = dr^2$).

This rate = $d\sigma \times (\text{incident flux}) = d\sigma \cdot \frac{\hbar k}{m}$, so $d\sigma = |f(\theta)|^2 d\Omega$, so $\frac{d\sigma}{d\Omega} = |f(\theta)|^2$.

Integral Equation for the Scattering Wavefunction

Time-independent Schrödinger Equation: $\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right) \psi_k(r) = \left(\frac{\hbar^2 k^2}{2m}\right) \psi_k(r)$.

Set $V(r) = \frac{\hbar^2}{2m} U(r)$, so $(-\nabla^2 + U(r)) \psi_k(r) = k^2 \psi_k(r)$, ie, $(\nabla^2 + k^2) \psi_k(r) = U(r) \psi_k(r)$

To convert to an integral equation we need a Green's function, with two appropriate boundary conditions. Introduce $G(r-r') = \int \frac{d^3q}{(2\pi)^3} e^{iq\cdot(r-r')} \hat{G}(q)$

So we get: $(\nabla^2 + k^2) G(r-r') = \delta(r-r')$. Fourier Transform: $(-q^2 + k^2) \hat{G}(q) = 1$

Ie, $\hat{G}(q) = \frac{-1}{q^2 - k^2}$, so $G(r-r') = -\int \frac{d^3q}{(2\pi)^3} \frac{e^{iq\cdot(r-r')}}{q^2 - k^2}$.

This integral is as yet ill-defined because of the singularity at $q^2 = k^2$. We modify the integrand by introducing a small imaginary term in the denominator.

We choose $G(r-r') = -\int \frac{d^3q}{(2\pi)^3} \frac{e^{iq\cdot(r-r')}}{q^2 - k^2 - i\epsilon}$, where it is inferred that $\epsilon \rightarrow 0^+$ after all calculations have been performed.

Demonstration of properties of $G(r)$:

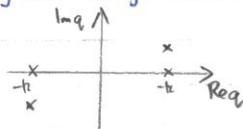
$$G(r) = -\int \frac{d^3q}{(2\pi)^3} \frac{e^{iq\cdot r}}{q^2 - k^2 - i\epsilon} \quad d^3q = q^2 dq d\phi \sin\theta d\theta = q^2 dq d\phi d\cos\theta$$

$$= -\int_0^\infty \frac{q^2 dq}{(2\pi)^3} \int_0^{2\pi} d\phi \int_{-1}^1 d\cos\theta \frac{e^{iqr \cos\theta}}{q^2 - k^2 - i\epsilon} = \frac{-2\pi}{(2\pi)^3} \int_0^\infty q^2 dq \frac{e^{iqr} - e^{-iqr}}{iqr} \cdot \frac{1}{q^2 - k^2 - i\epsilon}$$

$$= -\frac{1}{4\pi^2 i r} \int_0^\infty dq \cdot q \frac{e^{iqr} - e^{-iqr}}{q^2 - k^2 - i\epsilon} \quad \text{Extend the range for } q \text{ to } -\infty < q < \infty.$$

$$\text{So, } G(r) = \frac{-1}{4\pi^2 i r} \int_{-\infty}^\infty \frac{dq \cdot q e^{iqr}}{q^2 - k^2 - i\epsilon} \quad (\text{negative range covers second term}).$$

$$\frac{1}{q^2 - k^2 - i\epsilon} = \frac{1}{q - \sqrt{k^2 + i\epsilon}} \cdot \frac{1}{q + \sqrt{k^2 + i\epsilon}}$$



The integral dies away exponentially when $q \rightarrow \infty$ in the upper half complex plane. So we can choose the q -contour in the upper half plane, thus encircling the pole at $q = \sqrt{k^2 + i\epsilon}$.

We can evaluate the integral as $2\pi i \times (\text{residue})$ at this pole.

$$G(r) = \frac{-1}{4\pi^2} \cdot \frac{1}{r} \cdot \frac{1}{i} \cdot 2\pi i \cdot \frac{\sqrt{k^2 + i\epsilon}}{2\sqrt{k^2 + i\epsilon}} \cdot \frac{e^{i\sqrt{k^2 + i\epsilon} \cdot r}}{2\sqrt{k^2 + i\epsilon}} \quad \text{Let } \epsilon \rightarrow 0^+. \quad G(r) \equiv G(r) = -\frac{1}{4\pi} \cdot \frac{e^{ikr}}{r}$$

$$\text{So, } (\nabla^2 + k^2) \cdot \left(-\frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \right) = \delta(r).$$

$$G^*(r) = -\int \frac{d^3q}{(2\pi)^3} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2 - k^2 + i\epsilon} = -\frac{1}{4\pi} \frac{e^{-ikr}}{r}. \quad (\text{also satisfies equation})$$

Integral equation for scattering wavefunction: $\Psi_B(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \int d^3r' G(|\mathbf{r}-\mathbf{r}'|) U(\mathbf{r}') \Psi_B(\mathbf{r}')$

$$\text{Check: } (\nabla^2 + k^2)\Psi_B(\mathbf{r}) = (\nabla^2 + k^2)e^{i\mathbf{k}\cdot\mathbf{r}} + \int d^3r' (\nabla^2 + k^2)G(|\mathbf{r}-\mathbf{r}'|) U(\mathbf{r}') \Psi_B(\mathbf{r}') \\ = \int d^3r' \delta(\mathbf{r}-\mathbf{r}') U(\mathbf{r}') \Psi_B(\mathbf{r}') = U(\mathbf{r}) \Psi_B(\mathbf{r}).$$

Schrödinger equation is okay.

$$\text{Asymptotic boundary conditions: } \Psi_B(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} \int d^3r' \frac{e^{i\mathbf{k}'\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}') \Psi_B(\mathbf{r}') \\ \therefore \text{As } r \rightarrow \infty, \Psi_B(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} e^{ikr} f.$$

Choose $\hat{\mathbf{z}}$ as the polar axis for integration variable \mathbf{r}' . So $\mathbf{r}\cdot\mathbf{r}' = rr' \cos\theta$,
so $|\mathbf{r}-\mathbf{r}'| = \sqrt{r^2 + r'^2 - 2rr' \cos\theta} = r \left(1 - \frac{2r'}{r} \cos\theta + \frac{r'^2}{r^2}\right)^{1/2} \approx r \left(1 - \frac{r'}{r} \cos\theta + \dots\right) = r - r' \cos\theta = r - \hat{\mathbf{r}}\cdot\mathbf{r}'$.

$$\text{So, } G(|\mathbf{r}-\mathbf{r}'|) \approx -\frac{1}{4\pi} \frac{e^{i\mathbf{k}'\cdot(\mathbf{r}-\hat{\mathbf{r}}\cdot\mathbf{r}'+\dots)}}{r}, \quad \Psi_B(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} \frac{e^{ikr}}{r} \int d^3r' e^{-i\mathbf{k}'\cdot\mathbf{r}'} U(\mathbf{r}') \Psi_B(\mathbf{r}')$$

The scattering amplitude, which is a function of the direction in which $r \rightarrow \infty$, is

$$f = -\frac{1}{4\pi} \int d^3r' e^{-i\mathbf{k}'\cdot\mathbf{r}'} U(\mathbf{r}') \Psi_B(\mathbf{r}').$$

$\hat{\mathbf{r}}$ determines the direction of the observed scattered beam. $k\hat{\mathbf{r}}$ is the final state momentum that we are observing. Set $\mathbf{k}' = k\hat{\mathbf{r}}$.

$$f(\mathbf{k}, \mathbf{k}') = -\frac{1}{4\pi} \int d^3r' e^{-i\mathbf{k}'\cdot\mathbf{r}'} U(\mathbf{r}') \Psi_B(\mathbf{r}')$$

- expression for the scattering amplitude is in terms of the scattering wavefunction

Scattering in a central potential. $H = -\frac{\hbar^2}{2M} \nabla^2 + V(r)$

Scattering eigenfunction of H : $[-\frac{\hbar^2}{2M} \nabla^2 + V(r)] \Psi(\mathbf{r}) = E \Psi(\mathbf{r}), \quad E = \frac{\hbar^2 k^2}{2M}$.

Set $V(r) = \frac{\hbar^2}{2M} U(r)$, get $(\nabla^2 + k^2)\Psi(\mathbf{r}) = U(r)\Psi(\mathbf{r})$.

Solutions $\Psi(\mathbf{r}) \approx e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{e^{ikr}}{r} f(\theta)$. Want $f(\theta)$, $\frac{d\sigma}{d\Omega} = |f(\theta)|^2$

Partial Wave Phase Shifts.

Each partial wave is associated with an angular momentum quantum number $l = 0, 1, 2, \dots$

Because we have an axisymmetric situation where we can choose the z -axis to be the symmetry axis (ie the direction of \mathbf{k}), only wavefunctions with axisymmetrical quantum number $m=0$ are involved.

$Y_{l0}(\theta, \phi) \propto P_l(\cos\theta)$, Legendre polynomial.

The incident beam is $e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikz} = e^{ikr \cos\theta}$.

Partial wave expansion: $e^{ikr \cos\theta} = \sum_{l=0}^{\infty} (2l+1) \phi_l(kr) P_l(\cos\theta)$

[Recall, $\int_{-1}^1 dz P_l(z) P_m(z) = \frac{2\delta_{lm}}{2l+1}$]. $\phi_l(kr)$ is proportional to the spherical Bessel function of $O(l)$.

$$\phi_l(kr) = \frac{1}{2} \int_{-1}^1 d\cos\theta P_l(\cos\theta) e^{ikr \cos\theta}$$

We want to look at the large r behaviour of the partial waves of $e^{ikr \cos\theta}$. We ~~expose~~ expose the large r behaviour performing an integration by parts.

$$\phi_l(kr) = \frac{1}{2} \left\{ P_l(\cos\theta) \frac{e^{ikr \cos\theta}}{ikr} \Big|_{\cos\theta=-1}^{\cos\theta=+1} - \frac{1}{ikr} \int_{-1}^1 d\cos\theta P_l'(\cos\theta) e^{ikr \cos\theta} \right\}$$

A second integration by parts shows that $\int_{-1}^1 d\cos\theta P_l'(\cos\theta) e^{ikr \cos\theta} = O\left(\frac{1}{kr}\right)$ as $kr \rightarrow \infty$.

$$\phi_l(kr) \underset{r \rightarrow \infty}{\approx} \frac{1}{2ikr} [e^{ikr} P_l(1) - e^{-ikr} P_l(-1)] + O\left(\frac{1}{(kr)^2}\right) = \frac{e^{ikr} - (-1)^l e^{-ikr}}{2ikr} + O\left(\frac{1}{(kr)^2}\right)$$

The interpretation is: for the l th partial wave there is an incoming spherical wave $\frac{-(-1)^l e^{-ikr}}{2ikr}$ and an outgoing spherical wave $\frac{e^{ikr}}{2ikr}$.

Incoming and outgoing waves have the same intensity. Associated with the idea that angular momentum is conserved. So, # incoming particles with a given l -value = # outgoing particles with that l -value.

This is also true for the spherically symmetric potential. What the potential does is to shift the phase of the outgoing wave.

Plane Wave - No Scattering: $e^{ikr \cos \theta} \sim \sum_{l=0}^{\infty} (2l+1) \left(\frac{e^{ikr} - (-1)^l e^{-ikr}}{2ikr} \right) P_l(\cos \theta)$

Scattering wavefunction is $\Psi \sim \sum_{l=0}^{\infty} (2l+1) \left(\frac{e^{ikr} + e^{i\delta_l}}{r} f(\theta) \right)$ ← only the outgoing spherical waves are modified.

So, we expect that $\Psi \sim \sum_{l=0}^{\infty} (2l+1) \frac{S_l e^{ikr} - (-1)^l e^{-ikr}}{2ikr} P_l(\cos \theta)$

Because angular momentum is conserved in the scattering (spherically symmetric potential), the number of outgoing particles of angular momentum l = # incoming with angular momentum l .

∴ $|S_l| = 1$, so $S_l = e^{i(\text{phase})}$, phase = real.

Conventionally, we write, $S_l = e^{2i\delta_l}$, δ_l real. δ_l is called the l th partial wave phase shift.

Plane Wave - no scattering.

$$e^{ikr \cos \theta} \sim \sum_{l=0}^{\infty} (2l+1) \left(\frac{e^{ikr} - (-1)^l e^{-ikr}}{2ikr} \right) P_l(\cos \theta).$$

$$\text{The scattering wave is } \Psi \sim \sum_{l=0}^{\infty} (2l+1) \left(\frac{e^{2i\delta_l} e^{ikr} - (-1)^l e^{-ikr}}{2ikr} \right) P_l(\cos \theta)$$

$$\Psi - e^{ikr \cos \theta} \sim \frac{e^{ikr}}{r} f(\theta)$$

$$\text{But } \Psi - e^{ikr \cos \theta} \approx \sum_{l=0}^{\infty} (2l+1) \frac{e^{2i\delta_l} - 1}{2ikr} \cdot \frac{e^{ikr}}{r} P_l(\cos \theta)$$

We can deduce a structure for $f(\theta)$ in terms of the partial wave phase shifts.

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) \frac{e^{2i\delta_l} - 1}{2ikr} P_l(\cos \theta)$$

Partial wave expansion of the scattering amplitude.

$f(\theta) = \sum_{l=0}^{\infty} (2l+1) t_l(k) P_l(\cos \theta)$. $t_l(k)$ is the l th partial wave scattering amplitude

$$t_l(k) = \frac{1}{2} \int_{-1}^1 d\cos \theta P_l(\cos \theta) f(\theta). \text{ Our partial wave analysis } \Rightarrow t_l(k) = \frac{e^{2i\delta_l} - 1}{2ikr}$$

$$\text{I.e., } t_l(k) = \frac{1}{k} e^{i\delta_l} \sin \delta_l, \quad \delta_l = \delta_l(k)$$

Cross-section in terms of partial waves.

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2. \quad \sigma_{\text{TOT}} = \int d\Omega |f(\theta)|^2 = \int_0^{2\pi} d\varphi \int_{-1}^1 d\cos \theta |f(\theta)|^2$$

$$= 2\pi \int_{-1}^1 d\cos \theta \sum_{l=0}^{\infty} (2l+1) t_l^*(k) P_l(\cos \theta) \cdot \sum_{l'=0}^{\infty} (2l'+1) t_{l'}(k) P_{l'}(\cos \theta).$$

$$\int_{-1}^1 d\cos \theta P_l(\cos \theta) P_{l'}(\cos \theta) = \frac{2\delta_{ll'}}{2l+1}$$

$$\text{So } \sigma_{\text{TOT}} = \sum_{l,l'} (2l+1)(2l'+1) t_l^*(k) t_{l'}(k) \cdot \frac{2\delta_{ll'}}{2l+1} = 4\pi \sum_{l=0}^{\infty} (2l+1) |t_l(k)|^2 = \sum_{l=0}^{\infty} \sigma_l, \quad \sigma_l = 4\pi (2l+1) |t_l(k)|^2$$

Sometimes, a given partial wave can dominate the cross-section experiment → tells us about that partial wave.

Optical Theorem

$$t_l(k) = \frac{1}{k} e^{i\delta_l} \sin \delta_l. \text{ So } |t_l(k)|^2 = \frac{\sin^2 \delta_l}{k^2}. \quad \text{Im } t_l(k) = \frac{\sin 2\delta_l}{k}, \text{ so } |t_l(k)|^2 = \frac{1}{k} \text{Im } t_l(k).$$

$$\therefore \sigma_{\text{TOT}} = 4\pi \sum_{l=0}^{\infty} (2l+1) |t_l(k)|^2 = \frac{4\pi}{k} \sum_{l=0}^{\infty} (2l+1) \text{Im } t_l(k) = \frac{4\pi}{k} \text{Im} \sum_{l=0}^{\infty} (2l+1) t_l(k)$$

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) t_l(k) P_l(\cos \theta) \quad \therefore f(\theta=0) = \sum_{l=0}^{\infty} (2l+1) t_l(k) P_l(1) = \sum_{l=0}^{\infty} (2l+1) t_l(k).$$

$$\therefore \sigma_{\text{TOT}} = \frac{4\pi}{k} \text{Im } f(\theta=0) - \text{optical theorem. } f(\theta=0) \text{ is called the forward scattering amplitude.}$$

Partial Wave Scattering

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi = E \Psi = \frac{\hbar^2 k^2}{2m} \Psi \quad \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} L^2$$

L^2 is the angular momentum operator that has eigenvalue $l(l+1)$.

l^{th} partial wave: $\Psi = \Psi_l(r) P_l(\cos\theta)$, Ψ_l a partial wavefunction.

Substitute this above: $\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) + V(r) \right] \Psi_l(r) P_l(\cos\theta) = E \Psi_l(r) P_l(\cos\theta)$.

$$L^2 P_l(\cos\theta) = l(l+1) P_l(\cos\theta), \text{ so we have: } -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) \Psi_l(r) + V(r) \Psi_l(r) = E \Psi_l(r)$$

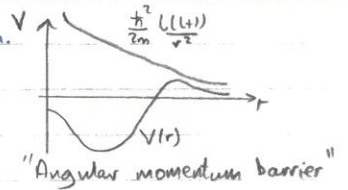
$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \Psi_l = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r \Psi_l)$$

If we define a modified wavefunction $\Phi_l(r) = r \Psi_l(r)$, then:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \Phi_l(r) + \left[\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + V(r) \right] \Phi_l(r) = E \Phi_l(r) \text{ - an equivalent version of the radial equation.}$$

Very similar to the Schrödinger equation for a particle moving in 1d, but with a modified potential: $\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + V(r)$ - effective potential for radial motion. We confine ourselves to the range $r > 0$, and since $\Phi_l(r) = r \Psi_l(r)$, we make $\Phi_l(0) = 0$ as boundary condition.

On the assumption that $V(r) \rightarrow 0$ as $r \rightarrow \infty$, we see that for larger, $\Phi_l(r)$ satisfies $-\frac{\hbar^2}{2m} \frac{\partial^2 \Phi_l}{\partial r^2} = E \Phi_l$.



i.e. $E = \frac{\hbar^2 k^2}{2m} \Rightarrow \Phi_l''(r) + k^2 \Phi_l(r) = 0$ for large r . $\therefore \Phi_l(r) \sim e^{\pm ikr}$ as $r \rightarrow \infty$.

We can choose real basis solutions: $\Phi_l^{(1)}(r) \sim \sin(kr - \frac{l\pi}{2})$, $\Phi_l^{(2)}(r) \sim \cos(kr - \frac{l\pi}{2})$

The general solution is a superposition of the two. The precise linear combination is fixed by requiring the physical boundary condition $\Phi_l(0) = 0$. When $r \rightarrow 0$, assume that $V(r) \sim$ finite; then the angular momentum barrier dominates and we have $\Phi_l'' - \frac{l(l+1)}{r^2} \Phi_l = 0$.

If we set $\Phi_l = r^p \Rightarrow p(p-1)r^{p-2} - l(l+1)r^{p-2} = 0 \Rightarrow p = l+1$ or $p = -l$.

The physical solution has $p = l+1 \therefore \Phi_l(r) \sim r^{l+1}$, $r \rightarrow 0$.

$$\Phi_l(r) = A \Phi_l^{(1)}(r) + B \Phi_l^{(2)}(r) \underset{r \rightarrow 0}{\approx} A \sin(kr - \frac{l\pi}{2}) + B \cos(kr - \frac{l\pi}{2})$$

$$\therefore \Psi_l^p \approx r^l (r \rightarrow 0), \approx \frac{1}{r} \left[A \sin(kr - \frac{l\pi}{2}) + B \cos(kr - \frac{l\pi}{2}) \right] (r \rightarrow \infty)$$

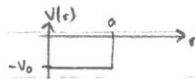
$$\text{Actually, } \Psi_l^p \approx \frac{e^{2i\delta_l}}{(2i)kr} e^{ikr} - \frac{(-1)^l}{k} e^{-ikr} = \frac{e^{i\delta_l}}{k} e^{i\frac{l\pi}{2}} \left[\frac{e^{i(kr - \frac{l\pi}{2} + \delta_l)}}{2i} - e^{-i(kr - \frac{l\pi}{2} + \delta_l)} \right] \approx \frac{1}{r} \sin(kr - \frac{l\pi}{2} + \delta_l)$$

We know, from the equation, that: $\Psi_l(r) \sim \frac{1}{r} \left(A \sin(kr - \frac{l\pi}{2}) + B \cos(kr - \frac{l\pi}{2}) \right)$

From scattering theory, $\Psi_l(r) \sim \frac{1}{r} \left[\sin(kr - \frac{l\pi}{2} + \delta_l) \right] = \frac{1}{r} \left[\cos \delta_l \sin(kr - \frac{l\pi}{2}) + \sin \delta_l \cos(kr - \frac{l\pi}{2}) \right]$

$$\text{So, } \frac{B}{A} = \frac{\sin \delta_l}{\cos \delta_l} = \tan \delta_l$$

Example: $V(r) = \begin{cases} 0, & r > a \\ -V_0, & r < a \end{cases}, V_0 = \frac{\hbar^2 \gamma^2}{2m}$



Consider S -wave ($l=0$) scattering. It is very useful to use the modified wavefunction $\Phi_0(r) = r \Psi_0(r)$. $\therefore \Phi_0'' + k^2 \Phi_0 = \left(\frac{2m}{\hbar^2} \right) V(r) \Phi_0(r) = U(r) \Phi_0(r)$.

$$r > a: U = V = 0 \therefore \Phi_0'' + k^2 \Phi_0 = 0$$

$$r < a: U = -\gamma^2 \therefore \Phi_0'' + K^2 \Phi_0 = 0 \quad (K^2 = k^2 + \gamma^2)$$

$\frac{\hbar^2 K^2}{2m}$ is the kinetic energy inside the potential range.

$$r < a: \Phi_0(r) = \alpha \sin Kr + \beta \cos Kr. \text{ Physical boundary condition: } \Phi_0(0) = 0 \Rightarrow \beta = 0.$$

If we (arbitrarily) set $\alpha = 1$, get $\Phi_0 = \sin Kr$.

$r > a: \Phi_0(r) = A \sin kr + B \cos kr$. Complete the calculation by matching at $r = a$.

i.e. we insist that Φ_0 and Φ_0' are continuous at $r = a$.

$$\begin{aligned} \therefore \sin Ka &= A \sin ka + B \cos ka, \quad K \cos Ka = k A \cos ka - k B \sin ka. \\ \therefore K \cot Ka &= k \frac{A \cos ka - B \sin ka}{A \sin ka + B \cos ka} = k \frac{\cos ka - \frac{B}{A} \sin ka}{\sin ka + \frac{B}{A} \cos ka} = k \frac{\cos ka - \tan \delta_0 \sin ka}{\sin ka + \tan \delta_0 \cos ka} \\ \therefore \tan \delta_0 &= \frac{K \cot ka - K \cot Ka}{K + K \cot ka \cot Ka} \end{aligned}$$

For a general partial wave it is just as convenient to use $\Psi_l(r)$ (as opposed to $\Phi_l(r)$). Free particle radial equations: $\Psi_l'' + \frac{2}{r} \Psi_l' - \frac{l(l+1)}{r^2} \Psi_l + k^2 \Psi_l = 0$. Two standard solutions: radial Bessel functions: $j_l(kr), n_l(kr)$. These are specified by their asymptotic behaviour.

$$\begin{aligned} r \rightarrow \infty, \quad j_l(kr) &\sim \frac{1}{r} \sin(kr - \frac{l\pi}{2}), \quad n_l(kr) \sim -\frac{1}{r} \cos(kr - \frac{l\pi}{2}). \\ r \rightarrow 0, \quad j_l(kr) &\approx \frac{(kr)^l}{1 \cdot 3 \cdot 5 \dots (2l+1)}, \quad n_l(kr) \approx -\frac{1 \cdot 3 \cdot 5 \dots (2l-1)}{(kr)^{l+1}}. \end{aligned}$$

For the square well, $r < a$, $\Psi_l = j_l(Kr)$ (since $j_l(Kr)$ is finite as $r \rightarrow 0$)
 $r > a$, $\Psi_l = A_l j_l(kr) - B_l n_l(kr) \approx \frac{1}{r} [A_l \sin(kr - \frac{l\pi}{2}) + B_l \cos(kr - \frac{l\pi}{2})]$

From scattering theory, $\Psi_l \approx \frac{1}{r} \sin(kr - \frac{l\pi}{2} + \delta_l)$

By the previous argument, $\tan \delta_l = \frac{B_l}{A_l}$.

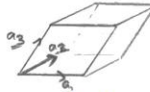
We require Ψ_l and Ψ_l' to be continuous at $r=a$ [$\frac{d}{dr} j_l(kr) = k j_l'(kr)$, etc].

$$j_l(Ka) = A_l j_l(ka) - B_l n_l(ka)$$

$$K j_l'(Ka) = k [A_l j_l'(ka) - B_l n_l'(ka)] \quad - \text{again we can solve for } \tan \delta_l = \frac{B_l}{A_l}.$$

Crystals

Discrete translation invariance. Basic cell, and space is translated with this cell. Let the cell - parallelepiped - have basis vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$.



The environment in the crystal is invariant under translations that are multiples of the basis vectors. The points \underline{r} and $\underline{r} + \underline{L}$, where $\underline{L} = L_1 \underline{a}_1 + L_2 \underline{a}_2 + L_3 \underline{a}_3$ with $L_1, L_2, L_3 \in \mathbb{Z}$ are equivalent. The set of steps \underline{L} under which the crystal is invariant is called the Bravais lattice, the crystal lattice, a discrete translation group. Note that the basis vectors are not unique.

Eg:



Volume of the basic cell is $V_c = \underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3$, invariant under ~~under~~ choice of basis vectors.

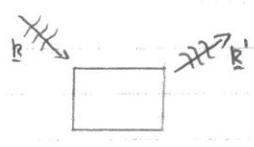
Reciprocal Lattice

Associated with the basis vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$, we define a reciprocal basis: $\underline{b}_1 = \frac{1}{V_c} \underline{a}_2 \times \underline{a}_3$, $\underline{b}_2 = \frac{1}{V_c} \underline{a}_3 \times \underline{a}_1$, $\underline{b}_3 = \frac{1}{V_c} \underline{a}_1 \times \underline{a}_2$.
 $\underline{b}_i \cdot \underline{a}_j = \delta_{ij}$. $\underline{r} = x_1 \underline{a}_1 + x_2 \underline{a}_2 + x_3 \underline{a}_3$, $\underline{k} = k_1 \underline{b}_1 + k_2 \underline{b}_2 + k_3 \underline{b}_3 \Rightarrow \underline{k} \cdot \underline{r} = k_1 x_1 + k_2 x_2 + k_3 x_3$.

The reciprocal lattice is the set $\{\underline{g} : \underline{g} = 2\pi(n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3), n_i \in \mathbb{Z}\}$

Scattering on a Crystal

The scattering of a neutral particle on a crystal, mass m . Interacts with the atoms in the crystal through a potential $V_A(\underline{r})$. Assume that the crystal has one atom per unit cell. The atoms in the crystal are at the points $\underline{L} \in$ Bravais lattice. The complete potential seen by the incident particle is: $V(\underline{r}) = \sum_{\underline{L} \in \mathbb{C}} V_A(\underline{r} - \underline{L})$. Assume that the crystal is a parallelepiped which is a large version of the basic cell. The vertices of the crystal are $0, L_1 \underline{a}_1, L_2 \underline{a}_2, L_3 \underline{a}_3$ (L_i large).



Incident wave: $\frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$
 Scattered wave: $\frac{1}{\sqrt{V}} e^{i\mathbf{k}'\cdot\mathbf{r}}$

Work in Born approximation - Golden Rule.

Rate of scattering $\Gamma = \frac{2\pi}{\hbar} \rho(E) |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2$. Incident flux: $\frac{v}{V} \frac{P}{m}$.

The rate per incident particle = $\frac{\Gamma}{\text{flux}} = \tilde{\Gamma} = \frac{2\pi}{\hbar} \cdot \frac{m}{P} V \rho(E) |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 = \frac{2\pi}{\hbar} \cdot \frac{m}{P} \cdot \frac{v^2}{(2\pi\hbar)^3} d\Omega |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2$.

$$\begin{aligned} \langle \mathbf{k}' | V | \mathbf{k} \rangle &= \frac{1}{\sqrt{V}} \int d^3\mathbf{r} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} V(\mathbf{r}) = \frac{1}{\sqrt{V}} \int d^3\mathbf{r} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} \sum_{\mathbf{l} \in \text{CC}} V_A(\mathbf{r}-\mathbf{l}) \\ &= \frac{1}{\sqrt{V}} \sum_{\mathbf{l} \in \text{CC}} \int d^3\mathbf{r} e^{-i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}-\mathbf{l})} V_A(\mathbf{r}-\mathbf{l}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \quad [\text{Shift integration, } \mathbf{r} \rightarrow \mathbf{r}+\mathbf{l}] \\ &= \frac{1}{\sqrt{V}} \sum_{\mathbf{l} \in \text{CC}} \int d^3\mathbf{r} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} V_A(\mathbf{r}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} = \frac{1}{\sqrt{V}} \tilde{V}_A(\mathbf{k}'-\mathbf{k}) \sum_{\mathbf{l} \in \text{CC}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \end{aligned}$$

$$\therefore \text{Rate per particle} = \tilde{\Gamma} = \frac{2\pi}{\hbar} \cdot \frac{m}{P} \cdot \frac{1}{(2\pi\hbar)^3} \cdot d\Omega \underbrace{|\tilde{V}_A(\mathbf{k}'-\mathbf{k})|^2}_{\text{atomic factor}} \underbrace{\left| \sum_{\mathbf{l}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \right|^2}_{\text{crystal factor}}$$

Consider $I_c = \sum_{\mathbf{l} \in \text{CC}} e^{-i\Delta\mathbf{k}\cdot\mathbf{l}}$, $\Delta\mathbf{k} = \mathbf{k}'-\mathbf{k}$.

$$\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad \Delta\mathbf{k} = \Delta k_1 \mathbf{b}_1 + \Delta k_2 \mathbf{b}_2 + \Delta k_3 \mathbf{b}_3 \quad (0 \leq l_i \leq L_i - 1, i=1,2,3)$$

$$I_c = \sum_{l_1, l_2, l_3} e^{-i(l_1 \Delta k_1 + l_2 \Delta k_2 + l_3 \Delta k_3)} = \sum_{l_1=0}^{L_1-1} e^{-il_1 \Delta k_1} \cdot \sum_{l_2=0}^{L_2-1} e^{-il_2 \Delta k_2} \cdot \sum_{l_3=0}^{L_3-1} e^{-il_3 \Delta k_3}$$

Clearly, $\sum_{l=0}^{L-1} e^{-il \Delta k} = \frac{1 - e^{-iL \Delta k}}{1 - e^{-i \Delta k}} = e^{-i(\frac{L-1}{2} \Delta k)} \cdot \frac{\sin(L \Delta k / 2)}{\sin(\Delta k / 2)}$

$$\tilde{\Gamma} \propto |I_c|^2 = \left(\frac{\sin(L_1 \Delta k_1 / 2)}{\sin(\Delta k_1 / 2)} \right)^2 \left(\frac{\sin(L_2 \Delta k_2 / 2)}{\sin(\Delta k_2 / 2)} \right)^2 \left(\frac{\sin(L_3 \Delta k_3 / 2)}{\sin(\Delta k_3 / 2)} \right)^2$$

The crystal factor is large where all three factors $(\frac{\sin}{\sin})^2$ are large.

Consider $\left(\frac{\sin(L_1 \Delta k_1 / 2)}{\sin(\Delta k_1 / 2)} \right)^2$. The peaks here occur when $\sin \frac{\Delta k_1}{2} = 0$, i.e., $\frac{\Delta k_1}{2} = n_1 \pi, \Delta k_1 = 2n_1 \pi$.

If $\Delta k_1 = 2\pi n_1 + \epsilon$, (ϵ small), $\sin \frac{\Delta k_1}{2} = \sin(\pi n_1 + \frac{\epsilon}{2}) = (-1)^{n_1} \sin \frac{\epsilon}{2} \approx (-1)^{n_1} \cdot \epsilon / 2$,

and $\sin(L_1 \Delta k_1 / 2) = \sin(\pi L_1 n_1 + \frac{L_1 \epsilon}{2}) = (-1)^{L_1 n_1} \sin \frac{L_1 \epsilon}{2} \approx (-1)^{L_1 n_1} \cdot \frac{L_1 \epsilon}{2}$.

The value of the peak is $[(-1)^{(L_1+n_1)} L_1]^2 = L_1^2$. Similarly for the others.

So, at its peak, the crystal factor $\propto L_1^2 L_2^2 L_3^2 = N^2$, where N is the number of atoms in the crystal.

At the peak, the intensity of scattering $\propto N^2$, i.e. the amplitude $\propto N \Leftrightarrow$ at the peak all atoms in the crystal are scattering coherently.

The coherent scattering of a wave on the crystal is called Bragg scattering.

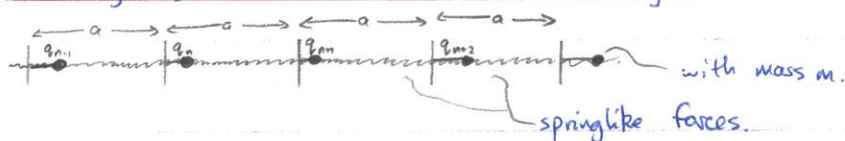
Peaks occur when $\Delta k_i = n_i \pi$ ($i=1,2,3$), $\therefore \mathbf{k}'-\mathbf{k} = 2\pi(n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3)$, i.e. $\mathbf{k}'-\mathbf{k} = \mathbf{g}$, where \mathbf{g} is an element of the reciprocal lattice.

Crystal factor, $\left| \sum_{\mathbf{l}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \right|^2$. When $\mathbf{k}'-\mathbf{k} = \mathbf{g} \in$ reciprocal lattice, $\sum_{\mathbf{l}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} = \sum_{\mathbf{l}} e^{-i\mathbf{g}\cdot\mathbf{l}}$, where $\mathbf{g} = 2\pi(n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3)$, $\therefore \mathbf{g}\cdot\mathbf{l} = 2\pi(n_1 l_1 + n_2 l_2 + n_3 l_3) = 2\pi(\text{integer})$.

$$\therefore e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} = e^{-2\pi i(\text{integer})} = 1$$

$$\therefore \left| \sum_{\mathbf{l}} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \right|^2 = \left| \sum_{\mathbf{l}} 1 \right|^2 = N^2$$

Vibrating Crystals. 1d models - classical analysis.



For convenience, we impose a periodicity that $q_{n+L} = q_n$. We only need to consider $-\frac{1}{2} < n \leq \frac{1}{2}$.

Kinetic energy, $T = \sum_n \frac{1}{2} m \dot{q}_n^2$, $V = \sum_n \frac{\lambda}{2} (q_{n+1} - q_n)^2$. $\mathcal{L} = T - V$.

Classical equations of motion: $\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_n} = \frac{\partial \mathcal{L}}{\partial q_n} \therefore m \ddot{q}_n = \frac{\partial V}{\partial q_n} = -\lambda (2q_n - q_{n+1} - q_{n-1})$

We are interested in ~~solutions of the form~~ coherent periodic vibrations (Normal modes). Look for a solution of the form $q_n = \alpha_n e^{-i\omega t}$. $q_n'' = -\omega^2 \alpha_n e^{-i\omega t}$

$\therefore -m\omega^2 \alpha_n = -\lambda (2\alpha_n - \alpha_{n+1} - \alpha_{n-1})$

This is a recursion relation. Try $\alpha_n = \alpha (e^{i\theta})^n = \alpha e^{in\theta}$ - which remains bounded as $n \rightarrow \pm\infty$. (We can also impose periodicity on it).

\therefore we have: $-m\omega^2 \alpha e^{in\theta} = -\lambda (2\alpha e^{in\theta} - \alpha e^{i(n+1)\theta} - \alpha e^{i(n-1)\theta})$

$\alpha \neq 0$, so: $-m\omega^2 = -\lambda (2 - 2\cos\theta)$, $\omega^2 = \frac{2\lambda}{m} (1 - \cos\theta)$

Periodicity: $q_{n+L} = q_n \Rightarrow e^{i(n+L)\theta} = e^{in\theta} \Rightarrow e^{iL\theta} = 1 \Rightarrow L\theta = 2l\pi$ ($l \in \mathbb{Z}$) $\Rightarrow \theta = \frac{2\pi}{L} l$

There are only L independent solutions - choose $-\frac{1}{2} < l \leq \frac{1}{2}$.

Solutions are of the form: $q_n = \alpha e^{-i\omega t + in\theta}$ (travelling wave).

Set $x = na$. Introduce k such that $kx = n\theta$. $\therefore kna = n\theta \Rightarrow \therefore k = \frac{\theta}{a}$. $\therefore k = (\frac{2\pi}{La}) l$. $-\frac{1}{2} < l \leq \frac{1}{2} \Rightarrow -\frac{\pi}{a} < k \leq \frac{\pi}{a}$.

Interpret x as position in the crystal, and k as the wave vector of the wave in the crystal.

$q_n = q(x) = \alpha e^{-i\omega t + ikx}$. Collective motion, normal modes, waves of oscillation. (Quantised \leftrightarrow Phonons)

The dispersion relation between ω and k is then: $\omega^2 = \frac{2\lambda}{m} (1 - \cos ka)$

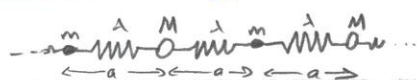
Large wavelength \leftrightarrow small wavenumber k . $\therefore \cos ka \approx 1 - \frac{1}{2}(ka)^2$

$\therefore \omega^2 = \frac{2\lambda}{m} (1 - \frac{1}{2}(ka)^2) = \frac{\lambda a^2}{m} k^2$. $\therefore \omega = (\sqrt{\frac{\lambda}{m}} a) k$

For long wavelength modes, the waves are non-dispersive, i.e., $\omega \propto k$.

$\therefore \omega = ck$, where $c = \sqrt{\frac{\lambda}{m}} a =$ velocity of sound in the crystal.

1-d model - two types of atom.



Unit cell contains 2 degrees of freedom.

Impose periodic boundary conditions: $\begin{pmatrix} q_{n+L} \\ r_{n+L} \end{pmatrix} = \begin{pmatrix} q_n \\ r_n \end{pmatrix}$

Newton's equations of motion: $M \ddot{r}_n = -\lambda (2r_n - q_n - q_{n-1})$

$m \ddot{q}_n = -\lambda (2q_n - r_{n+1} - r_n)$

Look for normal modes - seek a solution of the form $\begin{pmatrix} q_n \\ r_n \end{pmatrix} = \begin{pmatrix} \alpha_n \\ \beta_n \end{pmatrix} e^{-i\omega t}$

So, get $-\omega^2 M \alpha_n = -\lambda (2\alpha_n - \beta_{n-1} - \beta_n)$

$-\omega^2 m \beta_n = -\lambda (2\beta_n - \alpha_{n+1} - \alpha_n)$

Then we seek a solution of the form $\begin{pmatrix} \alpha_n \\ \beta_n \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} e^{in\theta}$.

When we insert hypothesis into the above recursion relation: $-\omega^2 M \alpha = \lambda (\beta e^{-i\theta} + \beta - 2\alpha)$
 $-\omega^2 m \beta = \lambda (\alpha e^{i\theta} + \alpha - 2\beta)$

$$\Rightarrow (2\lambda - \omega^2 M) \alpha - \lambda (1 + e^{-i\theta}) \beta = 0$$

$$-\lambda (1 + e^{i\theta}) \alpha + (2\lambda - \omega^2 m) \beta = 0.$$

For a non-trivial solution, $\det \begin{pmatrix} 2\lambda - \omega^2 M & -\lambda(1+e^{i\theta}) \\ -\lambda(1+e^{-i\theta}) & 2\lambda - \omega^2 m \end{pmatrix} = 0$

$$\text{I.e., } (\omega^2)^2 M m - \omega^2 \cdot 2\lambda(m+M) + 4\lambda^2 - 2\lambda^2(1+\cos\theta) = 0.$$

$$\text{So, } \omega_{\pm}^2 = \frac{1}{mM} \left\{ \lambda(m+M) \pm \sqrt{\lambda^2(m+M)^2 - 2mM\lambda^2(1-\cos\theta)} \right\}$$

Set $x = 2a\pi$ (as basic cell has size $2a$), $n\theta = kx = \frac{\theta}{2a} x \therefore k = \frac{\theta}{2a}$.

$$r_{n+1} = r_n, q_{n+1} = q_n \Rightarrow e^{i(n+1)\theta} = e^{in\theta} \therefore L\theta = 2\pi L \therefore -\frac{L}{2} < L \leq \frac{L}{2}.$$

$$\therefore k = \frac{1}{2a} \cdot \frac{2\pi L}{L} = \frac{\pi L}{La}, \quad -\frac{\pi}{2a} < k \leq \frac{\pi}{2a}.$$

The dispersion relation is double-branched \therefore 2 kinds of phonons.

$$\omega_{-}^2 = \frac{1}{mM} \left\{ \lambda(m+M) - \sqrt{\lambda^2(m+M)^2 - 2mM\lambda^2(1-\cos 2ak)} \right\}$$

For small k , (ie, long wavelength), $\omega_{-} \rightarrow 0$, $\cos 2ak \approx 1 - \frac{1}{2}(2ak)^2 = 1 - 2(ak)^2$.

$$\text{So, } \sqrt{\omega_{-}^2} = \lambda(m+M) \left\{ 1 - \frac{2\lambda^2 m M (2ak)^2}{\lambda^2(m+M)^2} \right\}^{1/2} \approx \lambda(m+M) \left\{ 1 - \frac{2mM(ak)^2}{(m+M)^2} \right\}$$

$$\text{So, } \omega_{-}^2 \approx \frac{1}{mM} \cdot \frac{2\lambda m M}{m+M} (ak)^2 = \frac{2\lambda}{m+M} (ak)^2 \therefore \omega_{-} \approx ak \cdot \sqrt{\frac{2\lambda}{m+M}}.$$

At low k , these modes are non-dispersive. Velocity of sound is $v_s = \frac{\omega}{k} = \sqrt{\frac{2\lambda}{m+M}} \cdot a$.
 ω_{-} is the frequency for the acoustic phonons (sound)

$$\text{The other branch at low } k: \omega_{+}^2 = \frac{1}{mM} \left\{ \lambda(m+M) + \sqrt{\lambda^2(m+M)^2 - 2mM\lambda^2(1-\cos 2ak)} \right\}$$

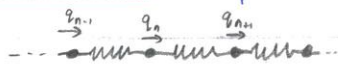
$$(\text{as } k \rightarrow 0) \approx \frac{1}{mM} \cdot 2\lambda(m+M) = \frac{2\lambda(m+M)}{mM}$$

This is a high-frequency phonon mode (relative to the acoustic mode) - the optical phonon frequency.

For acoustic phonons at low k , $\alpha \approx \beta$ (same sign).

For optical phonons at low k , $|\alpha| \approx |\beta|$ (opposite sign).

Quantisation (simple model again)



$$\mathcal{L} = \sum_n \left(\frac{1}{2} m \dot{q}_n^2 - \frac{1}{2} \lambda (q_{n+1} - q_n)^2 \right), \quad P_n = \frac{\partial \mathcal{L}}{\partial \dot{q}_n} = m \dot{q}_n$$

$$\therefore H = \sum_n \left(\frac{P_n^2}{2m} + \frac{1}{2} \lambda (q_{n+1} - q_n)^2 \right)$$

Quantise: P_n and q_n hermitian operators.

Impose canonical commutation relations: $[q_n, q_{n'}] = [P_n, P_{n'}] = 0$, $[q_n, P_{n'}] = i\hbar \delta_{nn'}$.

This, so far, is the Schrödinger picture - state vector develops in time according to $i\hbar \frac{d}{dt} |\Psi\rangle = H |\Psi\rangle$.

Change to the Heisenberg picture. Operators move, but states are fixed.

$$\left. \begin{aligned} q_n(t) &= e^{iHt/\hbar} q_n e^{-iHt/\hbar} \\ P_n(t) &= e^{iHt/\hbar} P_n e^{-iHt/\hbar} \end{aligned} \right\} \Rightarrow \begin{aligned} \dot{q}_n(t) &= \frac{i}{\hbar} [H, q_n(t)] \\ \dot{P}_n(t) &= \frac{i}{\hbar} [H, P_n(t)] \end{aligned} \quad ([q_n(t), P_{n'}(t)] = i\hbar \delta_{nn'})$$

$$H(t) = e^{i\frac{H}{\hbar}t} H e^{-i\frac{H}{\hbar}t} = H, \text{ independent of time. } H = H(t) = \sum_n \left\{ \frac{p_n(t)^2}{2m} + \frac{1}{2} \lambda (q_{n+1}(t) - q_n(t))^2 \right\}.$$

$$q_n''(t) = \frac{i}{\hbar} [H, q_n(t)] = \frac{i}{\hbar} \left[\frac{p_n(t)^2}{2m}, q_n(t) \right] \quad (\text{commutes with everything else}).$$

$$= \frac{i}{\hbar} \cdot \frac{1}{2m} \cdot 2 p_n(t) [p_n(t), q_n(t)] = \frac{i}{\hbar} \cdot \frac{1}{m} \cdot (-i\hbar) p_n(t) = \frac{1}{m} p_n(t).$$

$$p_n''(t) = \frac{i}{\hbar} [H, p_n(t)] = \frac{i}{\hbar} \left[\frac{1}{2} \lambda (q_{n+1}(t) - q_n(t))^2 + \frac{1}{2} \lambda (q_n(t) - q_{n-1}(t))^2, p_n(t) \right]$$

$$= \frac{i}{\hbar} \lambda \left\{ (q_{n+1}(t) - q_n(t)) [q_{n+1}(t) - q_n(t), p_n(t)] + (q_n(t) - q_{n-1}(t)) [q_n(t) - q_{n-1}(t), p_n(t)] \right\}.$$

$$= \frac{i}{\hbar} \lambda \left\{ -i\hbar (q_{n+1}(t) - q_n(t)) - i\hbar (q_n(t) - q_{n-1}(t)) \right\} = \lambda (q_{n+1}(t) + q_{n-1}(t) - 2q_n(t))$$

These are identical to the classical Hamiltonian equations of motion.

$$\therefore q_n''(t) = \frac{1}{m} p_n'(t) = \frac{\lambda}{m} (q_{n+1}(t) + q_{n-1}(t) - 2q_n(t)) \text{ - identical to the classical equation we considered before.}$$

We can solve this linear operator equation in the same way as for the classical model.

Phonons - Quantising Lattice Vibrations.

Hamilton's Equations: $p_n'(t) = \lambda (q_{n+1}(t) + q_{n-1}(t) - 2q_n(t))$
 $q_n'(t) = \frac{1}{m} p_n(t).$

Equation of motion: $q_n''(t) = \frac{\lambda}{m} (q_{n+1}(t) + q_{n-1}(t) - 2q_n(t))$

We seek solutions of the form: $q_n = \alpha \cdot e^{-i\omega t + i n \theta}$ (α an operator).

Perform the standard algebra (cf. classical calculations). $\therefore -\omega^2 \alpha = \frac{2\lambda}{m} (\cos \theta - 1) \alpha.$

Must have $\omega^2 = \frac{2\lambda}{m} (1 - \cos \theta).$

Periodicity $\Rightarrow e^{i\theta} = 1 \therefore \theta = \frac{2\pi l}{L} \quad \therefore -\frac{1}{2} < l \leq \frac{1}{2}.$

We set $x = na$, $kx = n\theta \therefore k = \theta/a = \frac{2\pi l}{La} \quad \therefore -\frac{\pi}{a} < k \leq \frac{\pi}{a}$

$q_n = q(na) = q(x).$

We have obtained a solution: $q(x) = \alpha e^{-i\omega_k t + i k x} \quad ; \quad \omega_k = + \sqrt{\frac{2\lambda}{m} (1 - \cos ka)}$

Another solution is the hermitian conjugate. General solution is a superposition of these basic solutions: $q_n \equiv q(x) = \sum_k (\alpha_k e^{-i\omega_k t + i k x} + \alpha_k^\dagger e^{i\omega_k t - i k x}).$

This form ensures that $q^\dagger(x) = q(x)$

We have to fix the α_k 's. We do this by requiring that the q 's and p 's obey the canonical commutation relations.

$p_n \equiv p(x) = m \dot{q}_n \equiv m \dot{q}(x) = m \sum_k (-i\omega_k) \{ \alpha_k e^{-i\omega_k t + i k x} - \alpha_k^\dagger e^{i\omega_k t - i k x} \}.$

What we want is $[q_n, p_{n'}] = i\hbar \delta_{nn'}$, ie, $[q(x), p(x')] = i\hbar \delta_{xx'}$

We can achieve this by requiring $[\alpha_k, \alpha_{k'}] = [\alpha_k^\dagger, \alpha_{k'}^\dagger] = 0, [\alpha_k, \alpha_{k'}^\dagger] = C(k) \delta_{kk'}$

Evaluate $[q(x), p(x')] = m \sum_{k, k'} (-i\omega_k) \left[(\alpha_k e^{-i\omega_k t + i k x} + \alpha_k^\dagger e^{i\omega_k t - i k x}), (\alpha_{k'} e^{-i\omega_{k'} t + i k' x'} - \alpha_{k'}^\dagger e^{i\omega_{k'} t - i k' x'}) \right]$

$$= m \sum_{k, k'} (-i\omega_{k'}) \left\{ -[\alpha_k, \alpha_{k'}^\dagger] e^{-i(\omega_k - \omega_{k'}) t + i k x - i k' x'} + [\alpha_k^\dagger, \alpha_{k'}] e^{i(\omega_k - \omega_{k'}) t - i k x + i k' x'} \right\}$$

$$= m \sum_{k, k'} (-i\omega_{k'}) \left\{ -C(k) \delta_{kk'} e^{-i(\omega_k - \omega_{k'}) t + i k x - i k' x'} - C(k) \delta_{kk'} e^{i(\omega_k - \omega_{k'}) t - i k x + i k' x'} \right\}$$

$$= m \sum_k i\omega_k C(k) \left[e^{i k (x-x')} + e^{-i k (x-x')} \right]$$

Now, $\sum_k e^{\pm i k (x-x')} = 0$ unless $x=x'$. So $\sum_k e^{\pm i k (x-x')} = L \delta_{xx'}$

If we choose $C(k) = \frac{\hbar}{2m\omega_k L}$ then $[q(x), p(x')] = i\hbar \delta_{xx'}$.

If now we set $\alpha_k = \sqrt{C(k)} a_k = \sqrt{\frac{\hbar}{2m\omega_k L}} a_k$, we can reproduce the commutation relations if we set $[a_k, a_{k'}^\dagger] = \delta_{kk'}$.

We have: $q_n \equiv q(x) = \sum_k \sqrt{\frac{\hbar}{2m\omega_k L}} (a_k e^{-i\omega_k t + i k x} + a_k^\dagger e^{i\omega_k t - i k x})$

What is H? H is: $H = \sum_k (a_k^\dagger a_k + \frac{1}{2}) \hbar \omega_k$. (checked later)

General: $B = A^\dagger A$, $\langle B \rangle_\psi \geq 0$. $\langle \psi | B | \psi \rangle = \langle \psi | A^\dagger A | \psi \rangle$.

Set $|\varphi\rangle = A|\psi\rangle$ $\therefore \langle \psi | B | \psi \rangle = \langle \varphi | \varphi \rangle \geq 0$.

$\langle H \rangle \geq \sum_k \frac{1}{2} \hbar \omega_k$ This means that the eigenvalues of H are $\geq \sum_k \frac{1}{2} \hbar \omega_k$.

So the eigenstates of H are bounded below.

Suppose $|\psi\rangle$ is an eigenstate of H , $H|\psi\rangle = E|\psi\rangle$.

In our case: Consider $|\varphi\rangle = a_k |\psi\rangle$. $H|\varphi\rangle = H a_k |\psi\rangle = a_k H |\psi\rangle + [H, a_k] |\psi\rangle$
 $= a_k E |\psi\rangle + [H, a_k] |\psi\rangle$.

$$[H, a_k] = \left[\sum_{k'} (a_{k'}^\dagger a_{k'} + \frac{1}{2}) \hbar \omega_{k'}, a_k \right] = \sum_{k'} [a_{k'}^\dagger a_{k'}, a_k] \hbar \omega_{k'} = \sum_{k'} [a_{k'}^\dagger, a_k] a_{k'} \hbar \omega_{k'}$$

$$= - \sum_{k'} \delta_{kk'} a_{k'} \hbar \omega_{k'} = -\hbar \omega_k a_k$$

So, $H|\varphi\rangle = E a_k |\psi\rangle - \hbar \omega_k a_k |\psi\rangle = (E - \hbar \omega_k) |\varphi\rangle$, so either $|\varphi\rangle$ is an eigenstate with energy $E - \hbar \omega_k$, or it is the null state.

Because a_k^\dagger lowers the energy by $\hbar \omega_k$, we must reach a state $|\psi_0\rangle$ such that $a_k |\psi_0\rangle = 0$.

By extending the argument, we see that because $\langle H \rangle \geq \sum_k \frac{1}{2} \hbar \omega_k$, \exists a state $|0\rangle$ such that $a_k |0\rangle = 0 \forall k$. This state is called the ground state of the lattice.

$$H|0\rangle = E_0 |0\rangle \quad \text{:- } E_0, \text{ the ground state energy}$$

$$= \sum_k (a_k^\dagger a_k + \frac{1}{2}) \hbar \omega_k |0\rangle = \sum_k \frac{1}{2} \hbar \omega_k |0\rangle \quad \text{So } E_0 = \sum_k \frac{1}{2} \hbar \omega_k$$

We showed that $[H, a_k] = -\hbar \omega_k a_k$, therefore $H a_k = a_k (H - \hbar \omega_k)$.

Hermitian conjugate relation: $H a_k^\dagger = a_k^\dagger (H + \hbar \omega_k)$.

If $H|\psi\rangle = E|\psi\rangle$, set $|X\rangle = a_k^\dagger |\psi\rangle$.

$$H|X\rangle = H a_k^\dagger |\psi\rangle = a_k^\dagger (H + \hbar \omega_k) |\psi\rangle = a_k^\dagger (E + \hbar \omega_k) |\psi\rangle = (E + \hbar \omega_k) |X\rangle$$

a_k - lowering operator: $-\hbar \omega_k$.

a_k^\dagger - raising operator: $+\hbar \omega_k$.

$$|k\rangle = a_k^\dagger |0\rangle \quad \text{: } E = E_0 + \hbar \omega_k$$

$$|k, r\rangle = (a_k^\dagger)^r |0\rangle \quad \text{: } E = E_0 + r \hbar \omega_k$$

$$|k_1, r_1; k_2, r_2; \dots\rangle = (a_{k_1}^\dagger)^{r_1} (a_{k_2}^\dagger)^{r_2} \dots |0\rangle$$

$$E(k_1, r_1; k_2, r_2; \dots) = E_0 + \sum_i r_i \hbar \omega_i$$

$|k_1, r_1; k_2, r_2; \dots\rangle$ - eigenstates of the Hamiltonian.

Quantisation of Vibrations - Phonons

$$q(x) = \sum_R \sqrt{\frac{\hbar}{2mL\omega(k)}} (a_R e^{-i\omega(k)t + ikx} + a_R^\dagger e^{i\omega(k)t - ikx}) \quad , \quad p(x) = m\dot{q}(x) = m \sum_{k'} \sqrt{\frac{\hbar}{2mL\omega(k')}} [-i\omega(k')] \{ a_{k'} e^{-i\omega(k')t + ik'x} - a_{k'}^\dagger e^{i\omega(k')t - ik'x} \}$$

$$K.E. = \sum_x \frac{p(x)^2}{2m} = \frac{m}{2} \sum_{R,R'} \sqrt{\frac{\hbar^2}{2^2 m^2 L^2 \omega(k)\omega(k')}} \cdot (-i\omega(k))(-i\omega(k')) \cdot \sum_x \{ -a_R^\dagger a_{R'} e^{i(\omega(k)-\omega(k'))t} e^{-i(k-k')x} - a_R a_{R'}^\dagger e^{-i(\omega(k)-\omega(k'))t} e^{i(k-k')x} + \dots \}$$

$$\sum_x e^{\pm i(k-k')x} = \begin{cases} L & \text{if } k=k' \\ 0 & \text{if } k \neq k' \end{cases} = L \delta_{kk'}$$

$$\therefore K.E. = \frac{m}{2} \sum_{R,R'} \sqrt{\frac{\hbar^2}{2^2 m^2 L^2 \omega(k)\omega(k')}} \cdot (-i\omega(k))(-i\omega(k')) (-1) L \delta_{kk'} (a_R^\dagger a_{R'} + a_R a_{R'}^\dagger) + \dots$$

$$= \frac{m}{2} \sum_R \frac{\hbar}{2mL\omega(k)} \cdot \omega(k)^2 \cdot L \cdot (a_R^\dagger a_R + a_R a_R^\dagger) + \dots$$

$$= \frac{1}{4} \sum_R (a_R^\dagger a_R + a_R a_R^\dagger) \hbar \omega(k) + \dots$$

Note - ignoring time-dependent terms. These will drop out as H is time-independent.

$$V = \frac{\lambda}{2} \sum_x (q(x+a) - q(x))^2 \quad [q(x+La) = q(x)]$$

$$q(x+a) - q(x) = \sum_R \sqrt{\frac{\hbar}{2mL\omega(k)}} \cdot \{ a_R e^{-i\omega(k)t} (e^{ik(x+a)} - e^{ikx}) + a_R^\dagger e^{i\omega(k)t - ikx} (e^{-ika} - 1) \}$$

$$\therefore V = \frac{\lambda}{2} \sum_{R,R'} \sqrt{\frac{\hbar^2}{2^2 m^2 L^2 \omega(k)\omega(k')}} \{ a_R a_{R'}^\dagger e^{-i(\omega(k)-\omega(k'))t} e^{i(k-k')x} + a_R^\dagger a_{R'} e^{i(\omega(k)-\omega(k'))t} e^{-i(k-k')x} \} + \dots$$

$$\sum_x e^{\pm i(k-k')x} = L \delta_{kk'}, \text{ so:}$$

$$V = \frac{\lambda}{2} \sum_R \frac{\hbar L}{2m\omega(k)L} \cdot \{ a_R a_R^\dagger (e^{ika} - 1)(e^{-ika} - 1) + a_R^\dagger a_R (e^{-ika} - 1)(e^{ika} - 1) \} + \dots$$

$$(e^{ika} - 1)(e^{-ika} - 1) = 2(1 - \cos ka), \quad \omega^2(k) = \frac{2\lambda}{m} (1 - \cos ka).$$

$$\therefore V = \frac{\lambda}{2} \sum_R \frac{\hbar}{2m\omega(k)} \cdot 2(1 - \cos ka) (a_R a_R^\dagger + a_R^\dagger a_R) + \dots = \frac{1}{4} \sum_R (a_R a_R^\dagger + a_R^\dagger a_R) \hbar \omega(k) + \dots$$

$$\therefore H = K.E. + V = \frac{1}{2} \sum_R (a_R a_R^\dagger + a_R^\dagger a_R) \hbar \omega(k)$$

$$[a_R, a_{R'}^\dagger] = \delta_{RR'}, \text{ so } a_R a_R^\dagger = a_R^\dagger a_R + 1 \quad \therefore H = \sum_R (a_R^\dagger a_R + \frac{1}{2}) \hbar \omega(k)$$

In the two atom crystal: ~~—O—m—m—O—m—~~

There are two branches to the dispersion relation: $\omega_-(k)$, acoustic: $a(k), a^\dagger(k)$
 $\omega_+(k)$, optical: $b(k), b^\dagger(k)$

In this case, the Hamiltonian acquires the form: $H = \sum_R (a_R^\dagger a_R + \frac{1}{2}) \hbar \omega_-(k) + \sum_R (b_R^\dagger b_R + \frac{1}{2}) \hbar \omega_+(k)$

$$[a, b] = 0 = [a, a] = [b, b], \text{ etc. } [a_R, a_{R'}^\dagger] = [b_R, b_{R'}^\dagger] = \delta_{RR'}$$

$$\text{Ground state, } \rightarrow |0\rangle. \quad a_R |0\rangle = b_R |0\rangle = 0.$$

Get eigenstates of the Hamiltonian by applying a^\dagger, b^\dagger to $|0\rangle$.

Electrons in a Periodic Potential.

$V(\underline{r}) = V(\underline{r} + \underline{L})$, $\underline{L} \in$ Bravais Lattice.

$$H = \frac{\underline{p}^2}{2m} + V(\underline{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r})$$

Let Ψ be an eigenstate of the Hamiltonian, $H\Psi(\underline{r}) = E\Psi(\underline{r})$: $-\frac{\hbar^2}{2m} \nabla^2 \Psi(\underline{r}) + V(\underline{r})\Psi(\underline{r}) = E\Psi(\underline{r})$ (*)

We translate the state by the map $\Psi(\underline{r}) \rightarrow \Psi_{\underline{L}}(\underline{r}) \equiv \Psi(\underline{r} - \underline{L})$.

From (*) we have: $-\frac{\hbar^2}{2m} \nabla^2 \Psi(\underline{r} - \underline{L}) + V(\underline{r} - \underline{L})\Psi(\underline{r} - \underline{L}) = E\Psi(\underline{r} - \underline{L})$

$\underline{L} \in$ Bravais lattice $\Rightarrow V(\underline{r} - \underline{L}) = V(\underline{r}) \Rightarrow -\frac{\hbar^2}{2m} \nabla^2 \Psi(\underline{r} - \underline{L}) + V(\underline{r})\Psi(\underline{r} - \underline{L}) = E\Psi(\underline{r} - \underline{L}) \Rightarrow H\Psi(\underline{r} - \underline{L}) = E\Psi(\underline{r} - \underline{L})$

$\therefore \Psi(\underline{r})$ and $\Psi_{\underline{L}}(\underline{r})$ are both eigenstates, with the same energy.

The effect of a translation by an element of the Bravais lattice is to map the eigen-subspace corresponding to a given energy into itself. If the eigen-subspace were one-dimensional, this would imply that $\Psi_{\underline{L}}(\underline{r}) = e^{i\phi(\underline{L})} \Psi(\underline{r})$. The effect of translation is clearly a unitary map. Hence the phase factor.

Even when the subspace is degenerate - i.e. of dimension 2 or greater - the effect of the translation map is still unitary. Therefore we can choose a basis for the subspace that diagonalises the unitary map. That is, we can choose a basis of energy eigenfunctions $\{\Psi(\underline{r})\}$ such that $\Psi(\underline{r} - \underline{L}) = e^{i\phi(\underline{L})} \Psi(\underline{r})$

$\underline{L} = L_1 \underline{a}_1 + L_2 \underline{a}_2 + L_3 \underline{a}_3$ (\underline{a}_i - basis vectors for the Bravais lattice), $L_i \in \mathbb{Z}$.

Let $\Psi(\underline{r} - \underline{a}_i) = e^{i\phi_i} \Psi(\underline{r})$, ($i=1,2,3$)

$\therefore \Psi(\underline{r} - L_i \underline{a}_i) = e^{iL_i \phi_i} \Psi(\underline{r})$, ($i=1,2,3$)

$\therefore \Psi(\underline{r} - \underline{L}) = \Psi(\underline{r} - L_1 \underline{a}_1 - L_2 \underline{a}_2 - L_3 \underline{a}_3) = e^{i(L_1 \phi_1 + L_2 \phi_2 + L_3 \phi_3)} \Psi(\underline{r})$

If we set $\underline{k} = \phi_1 \underline{b}_1 + \phi_2 \underline{b}_2 + \phi_3 \underline{b}_3$ then $L_1 \phi_1 + L_2 \phi_2 + L_3 \phi_3 = \underline{L} \cdot \underline{k} = \underline{k} \cdot \underline{L}$.

The eigenfunctions of the Hamiltonian with invariance under a discrete translation group can be chosen such that $\Psi(\underline{r} - \underline{L}) = e^{i\underline{k} \cdot \underline{L}} \Psi(\underline{r})$ (dodgy signs here...)

Bloch's Theorem.

The eigenfunctions of a Hamiltonian with a discrete translation symmetry can be expressed in the form: $\Psi(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} u(\underline{k}, \underline{r})$, for some \underline{k} , where $u(\underline{k}, \underline{r} - \underline{L}) = u(\underline{k}, \underline{r})$, i.e. $u(\underline{k}, \underline{r})$ is periodic on the crystal lattice.

Proof: We know that $\exists \underline{k}$ such that $\Psi(\underline{r} - \underline{L}) = e^{-i\underline{k} \cdot \underline{L}} \Psi(\underline{r})$.

If we set $\Psi(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} u(\underline{k}, \underline{r})$ then $e^{i\underline{k} \cdot (\underline{r} - \underline{L})} u(\underline{k}, \underline{r} - \underline{L}) = e^{-i\underline{k} \cdot \underline{L}} e^{i\underline{k} \cdot \underline{r}} u(\underline{k}, \underline{r})$

$\Rightarrow u(\underline{k}, \underline{r} - \underline{L}) = u(\underline{k}, \underline{r})$.

We can label the eigenstates with the crystal wave vector, or Bloch wavevector, \underline{k} .

\underline{k} is not uniquely identified. Suppose $\underline{k}' = \underline{k} + \underline{g}$, $\underline{g} = 2\pi(n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3) \in$ reciprocal lattice.

Then $H\Psi(\underline{k}, \underline{r}) = E\Psi(\underline{k}, \underline{r})$; $H\Psi(\underline{k}', \underline{r}) = E\Psi(\underline{k}', \underline{r})$

... and, $\Psi(\underline{k}', \underline{r} - \underline{L}) = e^{-i\underline{k}' \cdot \underline{L}} \Psi(\underline{k}', \underline{r}) = e^{-i(\underline{k} + \underline{g}) \cdot \underline{L}} \Psi(\underline{k}', \underline{r}) = e^{-i\underline{g} \cdot \underline{L}} e^{i\underline{k} \cdot \underline{L}} \Psi(\underline{k}', \underline{r})$

$\underline{g} \cdot \underline{L} = 2\pi(n_1 L_1 + n_2 L_2 + n_3 L_3) \therefore -i\underline{g} \cdot \underline{L} = 2\pi i \times \text{integer} \therefore e^{-i\underline{g} \cdot \underline{L}} = 1$.

So $\Psi(\underline{k}, \underline{r} - \underline{L}) = e^{-i\underline{k} \cdot \underline{L}} \Psi(\underline{k}', \underline{r})$. We see that $\Psi(\underline{k}', \underline{r}) = \Psi(\underline{k}, \underline{r})$.

So the Bloch wavevectors are defined only up to elements of the reciprocal lattice.

We can use this equivalence to identify a basic set of Bloch wavevectors in \mathbf{k} -space that tessellates \mathbf{k} -space under displacements by elements of the reciprocal lattice. We normally classify the ~~Bloch~~ eigenfunctions using the Bloch wavevector. The energy of the eigenfunction is then a function of \mathbf{k} .

As $\mathbf{k}' = \mathbf{k} + \mathbf{g}$ and \mathbf{k} are equivalent, $E(\mathbf{k} + \mathbf{g}) = E(\mathbf{k})$. $E(\mathbf{k})$ and $\Psi(\mathbf{k}, \mathbf{r})$ are periodic in \mathbf{k} -space, with the periodicity of the reciprocal lattice.

Bloch momentum of the state is crystal momentum $\mathbf{p} = \hbar \mathbf{k}$

The basic region used for tessellating reciprocal space is referred to as the Brillouin zone. It can be chosen in many different ways.

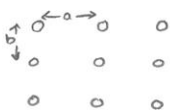
1 dimension: $\Psi(\mathbf{k}, x)$, $V(x+a) = V(x)$

Then $g = \frac{2\pi}{a}$ $\therefore k' = k + \frac{2\pi n}{a}$ ($n \in \mathbb{Z}$), equivalent to k .

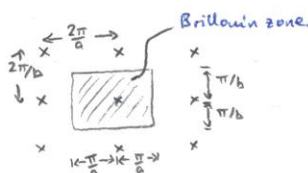


2 dimensions:

lattice:



Reciprocal lattice:



or,



etc...

Structure of Eigenfunctions of $H \leftrightarrow$ Allowed Energy Bands.

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad V(\mathbf{r} + \mathbf{L}) = V(\mathbf{r})$$

Bloch \Leftrightarrow Eigenfunctions have the form: $\Psi(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r})$, where $u(\mathbf{k}, \mathbf{r} - \mathbf{L}) = u(\mathbf{k}, \mathbf{r})$
 $u(\mathbf{k}, \mathbf{r})$ is determined by its values in a basic cell in the Bravais lattice.

Therefore, the problem reduces to that of a wavefunction $u(\mathbf{k}, \mathbf{r})$ in the basic cell of the Bravais lattice that obeys periodic boundary conditions.

$$H \Psi(\mathbf{k}, \mathbf{r}) = E \Psi(\mathbf{k}, \mathbf{r})$$

$$\hbar e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) = E e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}), \text{ so } e^{-i\mathbf{k} \cdot \mathbf{r}} H e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) = u(\mathbf{k}, \mathbf{r})$$

$$\text{Define } H(\mathbf{k}) = e^{-i\mathbf{k} \cdot \mathbf{r}} H e^{i\mathbf{k} \cdot \mathbf{r}}$$

$$H(\mathbf{k}) \text{ is a hermitian operator: } H(\mathbf{k})^\dagger = [e^{-i\mathbf{k} \cdot \mathbf{r}} H e^{i\mathbf{k} \cdot \mathbf{r}}]^\dagger = (e^{i\mathbf{k} \cdot \mathbf{r}})^\dagger H^\dagger (e^{-i\mathbf{k} \cdot \mathbf{r}})^\dagger \\ = e^{-i\mathbf{k} \cdot \mathbf{r}} H e^{i\mathbf{k} \cdot \mathbf{r}} = H(\mathbf{k}).$$

$H(\mathbf{k}) u(\mathbf{k}, \mathbf{r}) = E u(\mathbf{k}, \mathbf{r})$, where $u(\mathbf{k}, \mathbf{r})$ obeys periodic boundary conditions on the basic cell.

This is a problem in a box \Rightarrow discrete spectrum; tower of eigenvalues $E_n(\mathbf{k})$, where n is some appropriate discrete label.

Moreover, $E_n(\mathbf{k} + \mathbf{g}) = E_n(\mathbf{k})$

Each $E_n(\mathbf{k})$ therefore lies in a band of allowed energies: $E_n^{\min} \leq E_n(\mathbf{k}) \leq E_n^{\max}$.

This shows up the band structure of allowed energy values for an electron in a crystal lattice.

In 1d, the bands of allowed energy do not overlap, and they are interspersed with gaps of forbidden energy. In higher dimensions, the allowed bands of energy may overlap, but gaps of forbidden energy also occur.

Tight Binding Model.

o o o
o o o
o o o
 $V(r) = \sum_{\underline{l}} V_A(r-\underline{l})$

We will assume that we have an eigenstate for the atomic Hamiltonian that is a tightly bound state of the electron.

$H_A = -\frac{\hbar^2}{2m} \nabla^2 + V_A(r).$

$\exists \varphi(r)$ such that $H_A \varphi(r) = E_0 \varphi(r)$, $\varphi(r)$ dies out exponentially in space.

The crystal Hamiltonian is $H = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{\underline{l}} V_A(r-\underline{l})$

When an electron is near one of the atomic sites in the crystal, we expect it to behave more-or-less as if the other atoms were absent. We might guess then that a reasonable approximation to a crystal wavefunction is a superposition of tightly-bound electron wavefunctions: $\Psi(r) = \sum_{\underline{l}} \varphi(r-\underline{l})$, or, $\Psi(k,r) = \sum_{\underline{l}} e^{i\mathbf{k}\cdot\underline{l}} \varphi(r-\underline{l})$. Our reason for this choice is that $\Psi(k,r)$ has the Bloch property: $\Psi(k,r-\underline{l}) = e^{-i\mathbf{k}\cdot\underline{l}} \Psi(k,r)$.

Guess $\Psi(k,r) = \sum_{\underline{l}'} e^{i\mathbf{k}\cdot\underline{l}'} \varphi(r-\underline{l}')$ So, $\Psi(k,r-\underline{l}) = \sum_{\underline{l}'} e^{i\mathbf{k}\cdot\underline{l}'} \varphi(r-\underline{l}-\underline{l}')$
Set $\underline{l}'' = \underline{l} + \underline{l}'$: $\Psi(k,r-\underline{l}) = \sum_{\underline{l}''} e^{i\mathbf{k}\cdot(\underline{l}''-\underline{l})} \varphi(r-\underline{l}'') = e^{-i\mathbf{k}\cdot\underline{l}} \sum_{\underline{l}''} e^{i\mathbf{k}\cdot\underline{l}''} \varphi(r-\underline{l}'')$
So, $\Psi(k,r-\underline{l}) = e^{-i\mathbf{k}\cdot\underline{l}} \Psi(k,r)$.

This satisfies the Bloch condition. We use this guess for the wavefunction to estimate the energy of the state with Bloch wavevector \mathbf{k} .

Assume that we have a large crystal with N atoms. Estimate: $E(\mathbf{k}) = \frac{\int d^3r \Psi^*(\mathbf{k},r) H \Psi(\mathbf{k},r)}{\int d^3r \Psi^*(\mathbf{k},r) \Psi(\mathbf{k},r)}$

Consider denominator.

$\int d^3r \Psi^*(r) \Psi(r) = \sum_{\underline{l}, \underline{l}'} \int d^3r e^{-i\mathbf{k}\cdot\underline{l}} \varphi^*(r-\underline{l}) e^{i\mathbf{k}\cdot\underline{l}'} \varphi(r-\underline{l}') \quad [\text{let } r-\underline{l} \rightarrow r]$
 $= \sum_{\underline{l}, \underline{l}'} \int d^3r e^{-i\mathbf{k}\cdot\underline{l}} e^{i\mathbf{k}\cdot\underline{l}'} \varphi^*(r) \varphi(r+\underline{l}-\underline{l}') = \sum_{\underline{l}, \underline{l}''} e^{i\mathbf{k}\cdot\underline{l}''} \int d^3r \varphi^*(r) \varphi(r-\underline{l}'')$ [where $\underline{l}'' = \underline{l}' - \underline{l}$]
 $= N \sum_{\underline{l}''} e^{i\mathbf{k}\cdot\underline{l}''} \alpha_{\underline{l}''}$, as $\sum_{\underline{l}} 1 = N$, and where $\alpha_{\underline{l}''} = \int d^3r \varphi^*(r) \varphi(r-\underline{l}'')$

If $\underline{l}'' = 0$, $\alpha_0 = \int d^3r \varphi^*(r) \varphi(r) = 1$.

If $\mathbf{k} \cdot \underline{l}'' \neq 0$, we can assume $\alpha_{\underline{l}''}$ is small because wavefunctions centred on different atoms do not overlap strongly.

So, $\int d^3r \Psi^*(r) \Psi(r) = N (1 + \underbrace{\sum_{\underline{l}'' \neq 0} e^{i\mathbf{k}\cdot\underline{l}''} \alpha_{\underline{l}''}}_{\text{small}})$

Now evaluate the numerator.

$\int d^3r \Psi^*(r) H \Psi(r) = \sum_{\underline{l}, \underline{l}'} e^{-i\mathbf{k}\cdot\underline{l}} \int d^3r \varphi^*(r-\underline{l}) \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\underline{l}''} V_A(r-\underline{l}'') \right) e^{i\mathbf{k}\cdot\underline{l}'} \varphi(r-\underline{l}')$
 $= \sum_{\underline{l}, \underline{l}'} e^{-i\mathbf{k}\cdot\underline{l}} \int d^3r \varphi^*(r-\underline{l}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V_A(r-\underline{l}) + \sum_{\underline{l}'' \neq \underline{l}} V_A(r-\underline{l}'') \right) e^{i\mathbf{k}\cdot\underline{l}'} \varphi(r-\underline{l}')$
[Use the fact that $(-\frac{\hbar^2}{2m} \nabla^2 + V_A(r-\underline{l})) \varphi(r-\underline{l}) = E_A \varphi(r-\underline{l})$]
 $= \sum_{\underline{l}, \underline{l}'} e^{-i\mathbf{k}\cdot\underline{l}} e^{i\mathbf{k}\cdot\underline{l}'} \int d^3r \varphi^*(r-\underline{l}) \left(E_A + \sum_{\underline{l}'' \neq \underline{l}} V_A(r-\underline{l}'') \right) \varphi(r-\underline{l}')$
 $= \sum_{\underline{l}, \underline{l}'} e^{i\mathbf{k}\cdot(\underline{l}'-\underline{l})} \int d^3r \varphi^*(r-\underline{l}) \varphi(r-\underline{l}') E_A + \sum_{\underline{l}, \underline{l}' \neq \underline{l}} e^{i\mathbf{k}\cdot(\underline{l}'-\underline{l})} \int d^3r \varphi^*(r-\underline{l}) V_A(r-\underline{l}'') \varphi(r-\underline{l}')$
 $= N (1 + \sum_{\underline{l}'' \neq 0} e^{i\mathbf{k}\cdot\underline{l}''} \alpha_{\underline{l}''}) E_A + [**]$

For $[**]$, let $r-L \rightarrow r$:

$$[**] = \sum_{L', L''} e^{i\mathbf{k} \cdot (L' - L'')} \int d^3r \varphi^*(r) V_A(r - (L' - L)) \varphi(r - (L' - L))$$

Let $L''' = L' - L$, $L'' = L' - L$:

$$[**] = \sum_{L'''} \sum_{L''} e^{i\mathbf{k} \cdot L'''} \int d^3r \varphi^*(r) V_A(r - L''') \varphi(r - L'')$$

$$= N \sum_{L'''} e^{i\mathbf{k} \cdot L'''} \alpha_{L'''} \quad \text{where } \alpha_{L'''} = \sum_{L''} \int d^3r \varphi^*(r) V_A(r - L''') \varphi(r - L'') \quad [\text{small}]$$

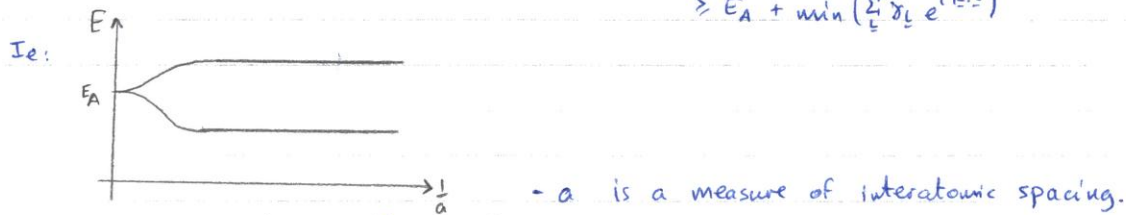
$$\therefore \int d^3r \psi^*(r) H \psi(r) = N \left\{ \left(1 + \sum_{L'' \neq 0} e^{i\mathbf{k} \cdot L''} \alpha_{L''} \right) E_A + \sum_{L''} \alpha_{L''} e^{i\mathbf{k} \cdot L''} \right\}$$

$$\therefore E(\mathbf{k}) = \frac{N \left\{ \left(1 + \sum_{L'' \neq 0} e^{i\mathbf{k} \cdot L''} \alpha_{L''} \right) E_A + \sum_{L''} \alpha_{L''} e^{i\mathbf{k} \cdot L''} \right\}}{N \left(1 + \sum_{L'' \neq 0} e^{i\mathbf{k} \cdot L''} \alpha_{L''} \right)} = E_A + \sum_{L''} \alpha_{L''} e^{i\mathbf{k} \cdot L''} + O(\alpha^2)$$

We see that $E(\mathbf{k})$ is a periodic function of the Bloch wavevector.

$$\mathbf{g} \in \text{reciprocal lattice} : E(\mathbf{k} + \mathbf{g}) = E_A + \sum_{L''} \alpha_{L''} e^{i(\mathbf{k} + \mathbf{g}) \cdot L''} = E_A + \sum_{L''} \alpha_{L''} \cdot 1 \cdot e^{i\mathbf{k} \cdot L''} = E(\mathbf{k})$$

\Rightarrow The atomic level E_A is broadened into a band of allowed energies when the atoms are assembled into a crystal: $E(\mathbf{k}) \leq E_A + \max \left\{ \sum_{L''} \alpha_{L''} e^{i\mathbf{k} \cdot L''} \right\}$
 $\geq E_A + \min \left\{ \sum_{L''} \alpha_{L''} e^{i\mathbf{k} \cdot L''} \right\}$



Atomic energy level \rightarrow allowed band of energy.

Nearly Free Electron Model.

Simplest case: 1 dimension. $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$, $V(x+a) = V(x)$ - assume V is weak.

Assume that we have periodic boundary conditions: $\psi(x+La) = \psi(x)$

Completely Free Electron: $\psi_{\mathbf{k}}(x) = \frac{e^{i\mathbf{k}x}}{\sqrt{La}}$

$$\langle \psi_{\mathbf{k}'} | \psi_{\mathbf{k}} \rangle = \int_0^{La} dx \psi_{\mathbf{k}'}^*(x) \psi_{\mathbf{k}}(x) = \delta_{\mathbf{k}\mathbf{k}'}$$

Because of the periodicity, $\mathbf{k} = \left(\frac{2\pi}{La} \right) \mathbf{n}$, $n = 0, \pm 1, \pm 2, \dots$

We wish to anticipate the appearance of the periodic potential. Identify the Bloch wavenumbers.

Restrict \mathbf{k} to lie in the Brillouin zone: $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$. Any other \mathbf{k} is a restricted \mathbf{k} plus a multiple of $\frac{2\pi}{a}$ (ie, plus a 2π element of the reciprocal lattice)

$$\psi_{\mathbf{k}}(x) = \frac{e^{i\mathbf{k}x}}{\sqrt{La}} \quad \longleftrightarrow \quad \psi_{\mathbf{n}}(k, x) = \frac{e^{i(k + \frac{2\pi n}{a})x}}{\sqrt{La}}$$

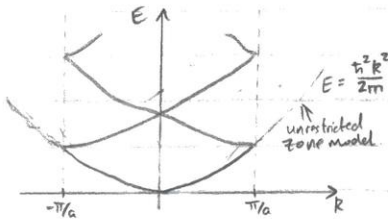
(Unrestricted zone scheme)

(Restricted zone scheme)

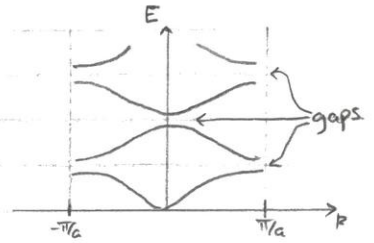
$\psi_n(k, x) = e^{ikx} \cdot \frac{e^{in(\frac{2\pi}{a})x}}{\sqrt{La}}$. This has the structure of a Bloch wavefunction:

$\psi_n(k, x) = e^{ikx} u_n(x)$, where $u_n(x) = \frac{e^{in(\frac{2\pi}{a})x}}{\sqrt{La}}$. $u_n(x+a) = u_n(x)$.
(n-band label)

A graph of the restricted zone energies is:



At points of degeneracy, gaps occur when we switch on the periodic potential:



$E_n(k) = \frac{\hbar^2}{2m} (k + \frac{2n\pi}{a})^2$ - restricted zone model.

Unrestricted Zone Scheme.

$|k\rangle = \frac{e^{ikx}}{\sqrt{La}}$, $E_0(k) = \frac{\hbar^2 k^2}{2m}$, $V(x) = \sum_q V_q e^{iqx}$, $q = \frac{2\pi n}{a}$
 $\Delta E_0(k) = \langle k|V|k\rangle + \sum_{k'} \frac{|\langle k|V|k'\rangle|^2}{E_0(k) - E_0(k')}$

Now, $\langle k|V|k\rangle = \int_0^{La} dx \frac{1}{\sqrt{La}} e^{-ikx} V(x) \frac{1}{\sqrt{La}} e^{ikx} = \frac{1}{La} \int_0^{La} V(x) dx = V_0$.
 $\langle k|V|k'\rangle = \frac{1}{La} \int_0^{La} e^{-i(k-k')x} V(x) dx = \frac{1}{La} \sum_q V_q \int_0^{La} e^{-i(k-k'-q)x} dx$
 $= 0$, unless $k-k'-q$ is zero for some q .

If $k-k'=q$ ($q \in$ reciprocal lattice), then $\langle k|V|k'\rangle = V_q$.

So, finally, $\Delta E_0(k) = V_0 + \sum_q \frac{|V_q|^2}{E_0(k) - E_0(k+q)}$

Actually, nothing much happens unless k is such that $\exists q$ for which $E_0(k+q) = E_0(k)$, i.e. $k = \pm \frac{\pi}{a}$ or $k=0$. For these k , we need to use degenerate perturbation theory.

Neighbourhood of a degeneracy point.

Typically, the states involved are $|\frac{1}{2}q\rangle$ and $|\frac{1}{2}q\rangle$, where $q \in$ Reciprocal lattice.

Let us consider states with wavevectors (unrestricted zone): $-\frac{q}{2} + \epsilon$, $\frac{q}{2} + \epsilon$.

Assume $|\psi\rangle = \alpha_+ |\frac{1}{2}q + \epsilon\rangle + \alpha_- |\frac{1}{2}q + \epsilon\rangle$ + small corrections.

Set $|+\rangle = |\frac{1}{2}q + \epsilon\rangle$, $|-\rangle = |\frac{1}{2}q + \epsilon\rangle$.

Unperturbed energies are: $E_{\pm}^{(0)} = \frac{\hbar^2}{2m} (\pm \frac{q}{2} + \epsilon)^2 \approx \frac{\hbar^2}{2m} q^2 \pm \epsilon \frac{\hbar^2 q}{2m} + \dots$

Hamiltonian is $H = H_0 + V$, $H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$, $V \equiv V(x)$.

$(H_0 + V)|\psi\rangle = E|\psi\rangle$

$(H_0 + V)(\alpha_+ |+\rangle + \alpha_- |-\rangle) = E(\alpha_+ |+\rangle + \alpha_- |-\rangle)$

$\langle +|+\rangle = 1$, $\langle +|-\rangle = 0$, etc.

So, $\langle +|(H_0 + V)(\alpha_+ |+\rangle + \alpha_- |-\rangle) = E \langle +|(\alpha_+ |+\rangle + \alpha_- |-\rangle)$

So $(E_+^{(0)} + \langle +|V|+\rangle)\alpha_+ + \langle +|V|-\rangle\alpha_- = E\alpha_+$

Similarly, $(E_-^{(0)} + \langle -|V|-\rangle)\alpha_- + \langle -|V|+\rangle\alpha_+ = E\alpha_-$

We have two simultaneous equations for α_+ and α_- :

$$\langle +|V|+ \rangle = \langle -|V|- \rangle = V_0, \quad \langle +|V|- \rangle = V_q, \quad \langle -|V|+ \rangle = V_q^*$$

Equations become:
$$\begin{pmatrix} E_+^{(0)} + V_0 - E & V_q \\ V_q^* & E_-^{(0)} + V_0 - E \end{pmatrix} \begin{pmatrix} \alpha_+ \\ \alpha_- \end{pmatrix} = 0$$

Quadratic equation for E ; two roots: $E_{\pm} = V_0 + \frac{1}{2} \left\{ E_+^{(0)} + E_-^{(0)} \pm \sqrt{(E_+^{(0)} - E_-^{(0)})^2 - 4|V_q|^2} \right\}$

As $V \rightarrow 0$, $E_{\pm} \rightarrow E_{\pm}^{(0)}$.

For $V \neq 0$, $E_+ > E_+^{(0)}$, $E_- < E_-^{(0)}$

If $\epsilon(\neq 0)$ is small, $E_+ - E_- > 2|V_q|$. $E_{\pm} = E_{\pm}^{(0)} + V_0 \pm \frac{|V_q|^2}{E_{\pm}^{(0)} - E_{\mp}^{(0)}}$ - ie very close to the original perturbation theory result.

If $\epsilon = 0$, $E_{\pm} = E_{\pm}^{(0)} + V_0 \pm |V_q|$ (energies have separated, hence gap in second diagram)

Insulators, Conductors and Semiconductors

The electrical properties of a crystalline material are determined by the nature of the valence. A material for which the atom has one valence electron will have a half-filled valence band: because of the spin of the electron.

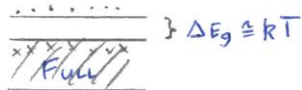
L atoms together $\rightarrow L$ states in the band. But the spin of the electron means that two electrons can be put into each state in the band. This means that the band is only half-filled \Rightarrow conductor.



The existence of nearby accessible states \Rightarrow easy acceleration of electrons.

If we have two valence electrons, the Fermi energy rises above the top of the valence band. \therefore Band is full - no nearby accessible states, difficult to accelerate electrons \Rightarrow insulator.

Semiconductor is an insulator with a small band gap.



- Temperature sensitive conductivity.

Conductivity, $\sigma \sim e^{-\Delta E_g/kT}$