Part II: Applications of Quantum Mechanics - Revision

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1 Scattering in 1D

1.1 Revision from Part IB

Recall that in $1D$ the wavefunctions for scattering from the left and scattering from the right have the forms:

$$\psi_R(x) \sim \begin{cases} e^{ikx} + re^{-ikx} \text{ as } x \to -\infty, \\ te^{ikx} \text{ as } x \to \infty. \end{cases}$$

$$\psi_L(x) \sim \begin{cases} t'e^{-ikx} \text{ as } x \to -\infty, \\ e^{-ikx} + r'e^{ikx} \text{ as } x \to \infty. \end{cases}$$

Definition: The *probability current* is defined by

$$J(x) = -\frac{i\hbar}{2m}\left(\psi'\psi^* - \psi(\psi')^*\right),$$

and can be derived from the equation

$$\frac{\partial|\psi|^2}{\partial t} + \nabla \cdot \mathbf{J} = 0.$$

Theorem: $|r|^2 + |t|^2 = 1$.

Proof: Show that J is independent of x using the Schrödinger equation, and then use compare asymptotic behaviour at $x = \infty$ and $x = -\infty$. □

Theorem: $t' = t,\ r' = -r^*t/t^*$.

Proof: Consider $\psi_R^* - r^*\psi_R$ (idea: try to get one term in asymptotics as $x \to -\infty$). This solves the SE by linearity. Writing out in full shows this is of the form ψ_L; comparing coefficients and using $|r|^2 + |t|^2 = 1$ gives the result. □

1.2 The S-matrix

Definition: Define *ingoing basis states* by: $I_R(x) = e^{ikx}$ as $x \to -\infty$, $I_L(x) = e^{-ikx}$ as $x \to +\infty$, and 0 in the other directions.

Similarly, define *outgoing basis states* by $O_R(x) = e^{ikx}$ as $x \to +\infty$, $O_L(x) = e^{-ikx}$ as $x \to -\infty$.

Writing ψ_R and ψ_L in this basis, we have:

$$\begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix} = \begin{pmatrix} I_R \\ I_L \end{pmatrix} + \begin{pmatrix} t & r \\ r' & t' \end{pmatrix} \begin{pmatrix} O_R \\ O_L \end{pmatrix},$$

where the matrix is called the S-*matrix*.

Theorem: S is unitary.

Proof: Just verify $S^\dagger S = I$ using $|r|^2 + |t|^2 = 1$ and $t' = t$, $r' = -r^*t/t^*$. □

1.3 The parity basis: diagonalising S

Since S is unitary, it can be diagonalised:

Definition: Define the *parity basis* by $\psi_+ = \psi_R + \psi_L$ and $\psi_- = \psi_L - \psi_R$. The transformation matrix taking us from the left/right basis to the parity basis is given by:

$$\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \begin{pmatrix} +1 & +1 \\ -1 & +1 \end{pmatrix} \begin{pmatrix} \psi_R \\ \psi_L \end{pmatrix}.$$

The parity basis gets its name since for a symmetric potential $V(x) = V(-x)$, we have $\psi_R(x) = \psi_L(-x)$, which gives that ψ_+ is an even function and ψ_- is an odd function.

Theorem: The ingoing/outgoing basis states in the parity basis are given by:

$$I_+ \sim e^{-ik|x|}$$
$$I_- \sim \text{sign}(x)e^{-ik|x|}$$

$$O_+ \sim e^{ik|x|}$$
$$O_- \sim -\text{sign}(x)e^{ik|x|}.$$

Proof: Simply use the transformation matrix. □

Theorem: The S-matrix in the parity basis is given by:

$$S^P = \begin{pmatrix} t + \frac{1}{2}(r + r') & \frac{1}{2}(r - r') \\ \frac{1}{2}(r' - r) & t - \frac{1}{2}(r + r') \end{pmatrix}.$$

Proof: Let A be the transformation matrix. Then $S^P = ASA^{-1}$ gives S^P. □

For symmetric potentials, we have $r = r'$, hence the form of S^P reduces to:

$$\begin{pmatrix} t+r & 0 \\ 0 & t-r \end{pmatrix}.$$

Definition: Since S^P is unitary, its eigenvalues have unit modulus. Thus we write $S_{++} = t + r = e^{2i\delta_+(k)}$ and $S_{--} = t - r = e^{2i\delta_-(k)}$ where $\delta_\pm(k)$ are called the *phase shifts*.

1.4 Bound states

Theorem: Poles of the S-matrix lying on the positive imaginary axis correspond to bound states of the potential $V(x)$ (assumed symmetric). S_{++} and ψ_+ give rise to even parity states, and S_{--} and ψ_- give rise to odd parity states.

Proof: Recall that $\psi_+ = I_+ + S_{++}O_+$, so:

$$\psi_+ = \begin{cases} e^{ikx} + S_{++}e^{-ikx} \text{ as } x \to -\infty \\ e^{-ikx} + S_{++}e^{ikx} \text{ as } x \to \infty. \end{cases}$$

Multiplying through by S_{++}^{-1} still gives a solution of the SE by linearity, hence (relabelling ψ_+):

$$\psi_+ = \begin{cases} S_{++}^{-1}e^{ikx} + e^{-ikx} \text{ as } x \to -\infty \\ S_{++}^{-1}e^{-ikx} + e^{ikx} \text{ as } x \to \infty. \end{cases}$$

Setting $S_{++}^{-1} = 0$ and $k = i\lambda$ for some $\lambda > 0$, it is clear we have an even-parity bound state. Similarly for odd-parity bound states. □

1.5 Resonances

A quantum particle trapped in a potential well will have some probability of escaping via *tuneling*.

Definition: We call a particle in such a potential well a *resonance* or *unstable state*.

Theorem: Resonances occur at poles in the S-matrix in the lower half-plane.

Proof: Let the pole occur at $k = k_0 - i\gamma$, $\gamma > 0$. This corresponds to a state with energy:

$$E = \frac{\hbar^2 k^2}{2m} = E_0 - \frac{i\Gamma}{2},$$

where

$$E_0 = \frac{\hbar^2}{2m}(k_0^2 - \gamma^2), \qquad \Gamma = \frac{2\hbar^2\gamma k_0}{m}$$

are the real and (negative twice the) imaginary parts of E. Recall that

$$\psi_+ = \begin{cases} e^{ikx} + S_{++}e^{-ikx} \text{ as } x \to -\infty \\ e^{-ikx} + S_{++}e^{ikx} \text{ as } x \to \infty, \end{cases}$$

and so multiplying through by S_{++}^{-1}, we have (at the pole), the solution of the SE (relabelling ψ_+):

$$\psi_+ = \begin{cases} e^{-ikx} \text{ as } x \to -\infty \\ e^{ikx} \text{ as } x \to \infty. \end{cases}$$

Inserting time-dependence from the the time-dependent SE, we get:

$$\psi_+ = \begin{cases} e^{-ikx}e^{-iEt/\hbar} \text{ as } x \to -\infty \\ e^{ikx}e^{-iEt/\hbar} \text{ as } x \to -\infty. \end{cases}$$

Writing this out with $E = E_0 - i\Gamma/2$ shows that the state is a resonance, since its probability spreads out over time.

We can compute the speed with which the particle escapes by writing the exponent in the form $\gamma(x \pm vt)$; we find the speed is:

$$v = \frac{\Gamma}{2\hbar\gamma}. \quad \square$$

Definition: Γ is called the *width* of the resonance, and $\tau = \hbar/\Gamma$ is called its *half-life*.

Note: A useful expression for S_{++} near a resonance is:

$$S_{++} = \frac{E - E_0 - i\Gamma/2}{E - E_0 + i\Gamma/2},$$

where we get the denominator because we need a pole, and the numerator because we need S_{++} to be pure phase.

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2 Classical scattering in 3D

Consider a plane wave (i.e. a wall of particles) impacting upon a potential:

The incident cross-section is $d\sigma = (\frac{1}{2}(b+db)^2 - \frac{1}{2}b^2)d\phi = bd\phi db$. This scatters into a solid angle $d\Omega = \sin(\theta)d\theta d\phi$ (same $d\phi$ for incoming and outgoing if potential is spherically symmetric). Hence we have:

Definition: The *differential cross-section* is defined by:

$$\left|\frac{d\sigma}{d\Omega}\right| = \frac{b}{\sin(\theta)}\left|\frac{db}{d\theta}\right|.$$

Interpretation: Physically, the differential cross-section is:

$$\frac{d\sigma}{d\Omega} = \frac{\#\text{ of scattered particles per unit time per solid angle}}{\text{incident flux}}.$$

Definition: The *total-cross section* is defined by

$$\sigma_T = \int \frac{d\sigma}{d\Omega} d\Omega.$$

It is the total area of the beam that has been deflected.

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3 Quantum scattering in 3D

3.1 The scattering amplitude

For quantum scattering, the asymptotic form of the wavefunction must be:

$$\psi \sim \underbrace{e^{ikx}}_{\substack{\text{incident}\\ \text{plane wave}}} + \underbrace{f(\theta)\frac{e^{ikr}}{r}}_{\substack{\text{scattered}\\ \text{radial wave}}},$$

where f is some weighting function.

Definition: $f(\theta)$ is called the *scattering amplitude*.

Theorem: The differential cross-section for quantum scattering is given by:

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2.$$

Proof: Recall that the probability current is:

$$\mathbf{J} = -\frac{i\hbar}{2m}\left(\psi^*\nabla\psi - \psi(\nabla\psi)^*\right).$$

Hence

$$\mathbf{J}_{\text{incident}} = \frac{\hbar k}{m}\hat{\mathbf{z}},$$

and $\mathbf{J}_{\text{scattered}}$ can be determined by first finding $\nabla\psi_{\text{scattered}}$ up to $O(1/r^2)$:

$$\nabla\psi_{\text{scattered}} = \frac{ikf(\theta)e^{ikr}}{r}\hat{\mathbf{r}} + O\left(\frac{1}{r^2}\right) \quad \Rightarrow$$

$$\mathbf{J}_{\text{scattered}} = \frac{\hbar k}{m}\frac{|f(\theta)|^2}{r^2}\hat{\mathbf{r}} + O\left(\frac{1}{r^3}\right).$$

Hence the incident flux is:

$$\mathbf{J}_{\text{incident}} \cdot \hat{\mathbf{z}} = \frac{\hbar k}{m},$$

and the number of scatter particles per unit time per solid angle is:

$$\underbrace{(\mathbf{J}_{\text{scattered}} \cdot \hat{\mathbf{r}})dA}_{\substack{\text{flux times}\\ \text{area}}} d\Omega^{-1} = \frac{\hbar k}{m}|f(\theta)|^2,$$

since $dA = r^2 d\Omega$ in the solid angle $d\Omega$. The result follows. □

Corollary: The *total cross-section* is given by:

$$\sigma_T = \int \frac{d\sigma}{d\Omega}\, d\Omega = \int |f(\theta)|^2 d\Omega.$$

3.2 Partial waves

Definition: An expansion *in partial waves* is an expansion of the form

$$\sum_{l=0}^{\infty} R_l(r)P_l(\cos(\theta)),$$

where the P_l are Legendre polynomials.

Theorem: The expansion of the quantum scattering wavefunction

$$\psi \sim e^{ikz} + f(\theta)\frac{e^{ikr}}{r}$$

in partial waves is:

$$\psi \sim \sum_{l=0}^{\infty} \underbrace{\left(\frac{2l+1}{2ik}\right)\left[(-1)^{l+1}\frac{e^{-ikr}}{r} + (1+2if_l)\frac{e^{ikr}}{r}\right]}_{R_l(r)} P_l(\cos(\theta)),$$

where the scattering amplitude $f(\theta)$ has partial wave expansion

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

Proof: Deal with $f(\theta)e^{ikr}/r$ first. Using the partial wave expansion for $f(\theta)$, we have:

$$f(\theta)\frac{e^{ikr}}{r} \sim \sum_{l=0}^{\infty}\frac{2l+1}{k}\frac{e^{ikr}}{r}f_l P_l(\cos(\theta)),$$

is the expansion in partial waves.

Now we deal with e^{ikz}, which is harder. Let $\rho = kr$. Then we have:

$$e^{ikz} = e^{i\rho\cos(\theta)} = \sum_{l=0}^{\infty}(2l+1)u_l(\rho)P_l(\cos(\theta)),$$

and we must find the $u_l(\cos(\theta))$. Use orthogonality of P_l (note normalisation is $2/(2l+1)$). We have (with $\omega = \cos(\theta)$):

$$u_l(\rho) = \frac{1}{2}\int_{-1}^{1} e^{i\rho\omega}P_l(\omega)d\omega.$$

Integrate once by parts to get:

$$u_l(\rho) = \frac{1}{2}\left[\frac{e^{i\rho\omega}P_l(\omega)}{i\rho}\right]_{-1}^{1} + \underbrace{\frac{1}{2i\rho}\int_{-1}^{1} e^{i\rho\omega}\frac{dP_l}{d\omega}d\omega}_{O(1/\rho^2)}$$

$$= \frac{1}{2i\rho}(e^{i\rho} - (-1)^l e^{-i\rho}) + O\left(\frac{1}{\rho^2}\right)$$

using $P_l(1) = 1$ and $P_l(-1) = (-1)^l$. Putting this all together, we get the result. □

3.3 Properties of the expansion

Definition: The *S-matrix elements* are $S_l = 1 + 2if_l$. The *phase shifts* are the δ_l satisfying $S_l = e^{2i\delta_l}$. Hence

$$f_l = \frac{1}{2i}\left(e^{2i\delta_l} - 1\right) = e^{i\delta_l}\sin(\delta_l).$$

Theorem: We have:

$$\sigma_T = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2(\delta_l).$$

Proof: We have

$$\begin{aligned}\sigma_T &= \int |f(\theta)|^2 d\Omega \\ &= 2\pi\int_{-1}^{1}\left|\sum_{l=0}^{\infty}\frac{2l+1}{k}f_l P_l(\omega)\right|^2 d\omega \\ &= \frac{2\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)^2|f_l|^2\int_{-1}^{1}P_l(\omega)^2 d\omega \\ &= \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)|f_l|^2.\end{aligned}$$

Since $f_l = e^{i\delta l}\sin(\delta_l)$, the result follows. □

3.4 The radial Schrödinger equation

Now we have written ψ is a convenient way, we need to determine the $R_l(r)$ in the expansion.

Theorem (Radial SE): The $R_l(r)$ satisfy:

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + k^2\right)(rR_l(r)) = 0,$$

where $U = 2mV/\hbar^2$ and $E = \hbar^2k^2/2m$.

Proof: We substitute the expansion for ψ as

$$\psi \sim \sum_{l=0}^{\infty} R_l(r)P_l(\cos(\theta))$$

into the Schrödinger equation. We need the facts that

$$\nabla^2 = P_r^2 + \frac{\mathbf{L}^2}{r^2},$$

$$P_r = \frac{d}{dr} + \frac{1}{r}$$

and P_l is an $\mathbf{L}^2$ eigenstate with eigenvalue $\hbar^2 l(l+1)$. □

3.5 The BIG picture

The important equations of scattering theory are:

Equations of 3D scattering theory:

The radial SE is:

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + k^2\right)(rR_l(r)) = 0.$$

where $U = 2mV/\hbar^2$, $E = \hbar^2k^2/2m$.

The asymptotic form of the wavefunction ψ is:

$$\sum_{l=0}^{\infty}\underbrace{\left(\frac{2l+1}{2ik}\right)\left[(-1)^{l+1}\frac{e^{-ikr}}{r} + (1+2if_l)\frac{e^{ikr}}{r}\right]}_{R_l(r)}P_l(\cos\theta).$$

The steps to solving a 3D scattering problem are:

1. Solve the radial Schrödinger equation.
2. Compare the form of $R_l(r)$ from the radial Schrödinger equation with the asymptotic form of the wavefunction to determine the f_l, δ_l.

3.6 Detailed example: the hard sphere

Consider

$$V(r) = \begin{cases} \infty \text{ for } r \leq a, \\ 0 \text{ for } r > a. \end{cases}$$

The radial Schrödinger equation is:

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2\right)(rR_l(r)) = 0$$

for $r > a$. Defining $\rho = kr$, the equation reduces to

$$\left(\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + 1\right)(\rho R_l(\rho)) = 0.$$

The solutions are *spherical Bessel functions*:

$$R_l(\rho) = A_l(\cos(\alpha_l)j_l(\rho) - \sin(\alpha_l)n_l(\rho)).$$

Imposing $R_l = 0$ at $r = a$ gives the condition $\cos(\alpha_l)j_l(ka) = \sin(\alpha_l)n_l(ka)$ which can be used to determine α_l.

We now wish to compare R_l to the expected asymptotic form. To do so, we take $\rho \to \infty$ in the above form. Using the asymptotics of the spherical Bessel functions, we get:

$$R_l(\rho) \sim \frac{1}{\rho}\sin\left(\rho - \frac{1}{2}l\pi + \alpha_l\right).$$

The expected form is:

$$\begin{aligned} R_l(\rho) &\sim (-1)^{l+1}\frac{e^{-i\rho}}{\rho} + e^{2i\delta_l}\frac{e^{i\rho}}{\rho} \\ &= \frac{e^{i\delta_l}e^{i\pi l/2}}{\rho}\left[-e^{-i(\rho+\delta_l-\pi l/2)} + e^{i(\rho+\delta_l-\pi l/2)}\right]. \end{aligned}$$

Hence $\alpha_l = \delta_l$. The phase shifts can then be determined from $\cos(\delta_l)j_l(ka) = \sin(\delta_l)n_l(ka)$.

3.7 Scattering length

Definition: For low-momentum scattering, we have in general $\delta_0 \approx -ka_s + O(k^2)$, where we call a_s the *scattering length*.

3.8 Bound states

Theorem: Poles in the S-matrix on the positive imaginary axis correspond to bound states of the potential.

Proof: Same as 1D case. □

Theorem: Divergence of the scattering length is due to bound states in the potential.

Proof: Near a bound state, we have

$$S_0(k) = e^{2i\delta_0} = \frac{i\lambda + k}{i\lambda - k}$$

since bound states are poles on the positive imaginary axis. Hence

$$\begin{aligned} 2i\delta_0 &\approx \log(i\lambda + k) - \log(i\lambda - k) \\ &= \log\left(1 + \frac{k}{i\lambda}\right) - \log\left(1 - \frac{k}{i\lambda}\right) \\ &= \frac{2k}{i\lambda} + O(k^2) \end{aligned}$$

Hence $\delta_0 \approx -k/\lambda$ near a bound state. Thus $a_s \approx 1/\lambda$ near a bound state. A new bound state appears as λ increases past 0 giving a divergent scattering length. As the bound state passes $\lambda = 0$, it is said to be at *threshold*. □

3.9 Resonances

As in 1D, resonances are poles in the S-matrix in the lower half-plane.

Close to a pole, we may write

$$S_0(E) = e^{2i\delta_0} \approx \frac{E - E_0 - i\Gamma/2}{E - E_0 + i\Gamma/2}$$

Taking the real part, we have:

$$\cos(2\delta_0) = \frac{(E-E_0)^2 - \Gamma^2/4}{(E-E_0)^2 + \Gamma^2/4} \Rightarrow \sin^2(\delta_0) = \frac{\Gamma^2}{4(E-E_0)^2 + \Gamma^2}.$$

Hence

$$\sigma_T = \frac{4\pi}{k^2} \cdot \frac{\Gamma^2}{4(E-E_0)^2 + \Gamma^2}.$$

This is called the *Breit-Wigner distribution*. Plotting, we see that a small bump in the distribution corresponds to the existence of a resonance. We now understand that we call Γ the width because it is the characteristic width of the bump.

4 The Born approximation

4.1 The Lippmann-Schwinger equation

Theorem: The Schrödinger equation $(H_0+V)\left|\psi\right\rangle = E\left|\psi\right\rangle$ may be rewritten as

$$\left|\psi\right\rangle = \left|\phi\right\rangle + (E-H_0)^{-1}V\left|\psi\right\rangle$$

where $\left|\phi\right\rangle$ is such that $H_0\left|\phi\right\rangle = E\left|\phi\right\rangle$.

Proof: Trivial. □

To find $(E-H_0)^{-1}$ we seek the Green's function G obeying:

$$\left(E+\frac{\hbar^2}{2m}\nabla^2\right)G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}').$$

Writing $E=\hbar^2k^2/2m$, we need

$$(\nabla^2+k^2)G(\mathbf{r},\mathbf{r}') = \frac{2m}{\hbar^2}\delta(\mathbf{r}-\mathbf{r}'). \qquad (*)$$

Theorem: G can be chosen as:

$$G(\mathbf{r},\mathbf{r}') = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}.$$

Proof: By translational invariance, $G(\mathbf{r},\mathbf{r}') = G(\mathbf{x})$ where $\mathbf{x}=\mathbf{r}-\mathbf{r}'$. Take Fourier transform of $(*)$ to get:

$$(-q^2+k^2)\tilde{G}(\mathbf{q}) = \frac{2m}{\hbar^2} \quad\Rightarrow\quad \tilde{G}(\mathbf{q}) = -\frac{2m}{\hbar^2}\frac{1}{q^2-k^2}.$$

Take inverse Fourier transform:

$$G(\mathbf{x}) = -\frac{2m}{\hbar^2}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\frac{e^{i\mathbf{q}\cdot\mathbf{x}}}{q^2-k^2}$$

$$= -\frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int_0^{2\pi}d\phi\int_{-1}^{+1}d(\cos(\theta))\int_0^{\infty}\frac{dq\; e^{iqx\cos(\theta)}}{q^2-k^2}$$

$$= -\frac{2m}{(2\pi\hbar)^2 ix}\int_0^{\infty} q\left(\frac{e^{iqx}-e^{-iqx}}{q^2-k^2}\right)dq$$

$$= -\frac{2m}{(2\pi\hbar)^2 ix}\int_{-\infty}^{\infty}\frac{qe^{iqx}}{q^2-k^2}dq$$

To remove the singularities in the integrand, consider

$$\int_{-\infty}^{\infty}\frac{qe^{iqx}}{q^2-k^2-i\epsilon}dq$$

as $\epsilon\to 0$. Since $\epsilon\to 0$, we can factorise the denominator as:

$$\int_{-\infty}^{\infty}\frac{qe^{iqx}}{(q-k-i\epsilon)(q+k+i\epsilon)}dq.$$

Now perform contour integral by closing in the upper half plane. Contribution from arc is zero by Jordan's Lemma. By the residue theorem, we get the result. □

4.2 Approximation scheme

Using the Green's function, we can rewrite the Lippmann-Schwinger equation as:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{2m}{\hbar^2}\int d^3\mathbf{r}'\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}).$$

So far, this is exact. To approximate, expand $|\mathbf{r}-\mathbf{r}'|$ using the binomial expansion to get:

$$|\mathbf{r}-\mathbf{r}'| = \sqrt{r^2+r'^2-2\mathbf{r}\cdot\mathbf{r}'} = r - \frac{\mathbf{r}\cdot\mathbf{r}'}{r}.$$

This gives:

$$\psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{2m}{\hbar^2}\frac{1}{4\pi}\left(\int d^3\mathbf{r}'e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')\psi(\mathbf{r}')\right)\frac{e^{ikr}}{r}$$

$$\Rightarrow f(\theta) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3\mathbf{r}'e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}V(\mathbf{r}')\psi(\mathbf{r}').$$

We still have the wavefunction on the right hand side. To remove it, we take the first approximation to $\psi(\mathbf{r})$ as $e^{i\mathbf{k}\cdot\mathbf{r}}$. This gives the *Born approximation*:

$$f(\theta) \approx -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3\mathbf{r}'e^{i\mathbf{q}\cdot\mathbf{r}'}V(\mathbf{r}') = -\frac{m}{2\pi\hbar^2}\tilde{V}(\mathbf{q}),$$

where $\mathbf{q}=\mathbf{k}-k\hat{\mathbf{r}}$ (i.e. momentum loss). The differential cross-section is given by:

$$\frac{d\sigma}{d\Omega} \approx \frac{m^2}{4\pi^2\hbar^4}|\tilde{V}(\mathbf{q})|^2.$$

Note: $\tilde{V}$ is a 3D Fourier transform. We get an integrand of the form $e^{i\mathbf{q}\cdot\mathbf{r}}...r^2\sin(\theta)d\theta d\phi dr$, so we write $\mathbf{q}\cdot\mathbf{r} = qr\cos(\theta)$ in order to integrate.

5 The variational method

5.1 Theory

Theorem: Let $H|n\rangle = E_n|n\rangle$ with $E_0 \leq E_1 \leq ....$ Then for any normalised state $|\psi\rangle$, we have $\langle\psi|H|\psi\rangle \geq E_0$.

Proof: Write

$$|\psi\rangle = \sum_n a_n |n\rangle .$$

Then

$$\langle\psi|H|\psi\rangle = \sum_{m,n=0}^{\infty} a_m^* a_n \langle m|H|n\rangle = \sum_{n=0}^{\infty} |a_n|^2 E_n.$$

Since $\sum |a_n|^2 = 1$ by normalisation, we have:

$$\langle\psi|H|\psi\rangle = E_0 + \sum_{n=0}^{\infty} |a_n|^2 \underbrace{(E_n - E_0)}_{>0} \geq E_0.$$

The *variational method* uses this theorem by taking a family of states $\psi(\alpha)$ and minimising

$$E(\alpha) = \frac{\langle\psi(\alpha)|H|\psi(\alpha)\rangle}{\langle\psi(\alpha)|\psi(\alpha)\rangle}.$$

By above, $E(\alpha) \geq E_0$ for all α, so minimum is a good approximation to E_0 (though no way of telling *how good*).

5.2 Application: bound states

Bound states in a potential with $V(\mathbf{x}) \to 0$ as $|\mathbf{x}| \to \infty$ have $E < 0$. Thus if the variational method gives a negative result, the ground state energy is negative, so there exists a bound state.

For example:

Theorem: Let $V(x)$ be such that $V(x) = 0$ for $|x| > L$. Then there exists a bound state if

$$\int_{-\infty}^{\infty} V(x)\, dx < 0.$$

Proof: Use $\psi(\alpha) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ (i.e. normalised Gaussian). This gives

$$E(\alpha) = \frac{\hbar^2\alpha}{4m} + \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} V(x) e^{-\alpha x^2}\, dx.$$

Let $Q(\alpha) = E(\alpha)/\sqrt{\alpha}$. As $\alpha \to 0^+$, $Q(\alpha)$ becomes negative. So there exists a small α with $E(\alpha) < 0$. □

5.3 Excited states energy

If the potential $V(x)$ has definite parity, we can get an estimate for E_1. We choose $|\psi(\alpha)\rangle$ such that $\langle\psi(\alpha)|0\rangle = 0$ for all α, by choosing $|\psi(\alpha)\rangle$ to have opposite parity to $|0\rangle$. The proof the procedure works is the same as above.

5.4 The virial theorem

From the variational method, it is easy to prove that $E(\alpha)$ is stationary at energy eigenstates $|\psi\rangle$. This allows us to prove:

Theorem: Let kinetic energy be T and potential energy be V. Suppose that $V(\lambda x) = \lambda^n V(x)$ and that $|\psi\rangle$ is an energy eigenstate. Then we have $2\langle\psi|T|\psi\rangle = n\langle\psi|V\psi\rangle$.

Proof: Let $|\psi\rangle$ have energy E. Then

$$\begin{aligned} E &= \int_{-\infty}^{\infty} \psi^* \left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi\right) dx \\ &= \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m}\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x}\, dx + \int_{-\infty}^{\infty} \psi^* V\psi\, dx \quad \text{(by parts)} \\ &= \langle\psi|T|\psi\rangle + \langle\psi|V|\psi\rangle . \end{aligned}$$

Let $\psi(x) \mapsto \alpha^{1/2}\psi(\alpha x)$ (the $\alpha^{1/2}$ is needed for normalisation). Then:

$$E(\alpha) = \alpha^2 \langle\psi|T|\psi\rangle + \alpha^{-n}\langle\psi|V|\psi\rangle .$$

Using $E(\alpha)$ stationary at energy eigenstates, we have that when $\alpha = 1$, $\frac{\partial E}{\partial\alpha} = 0$, and the result follows. □

5.5 Examples of variational method

When doing questions using the variational method, always try to write the Hamiltonian so that $\psi(\alpha)$ is an eigenstate of part of the Hamiltonian. This dramatically eases calculation.

6 One-dimensional band structure

6.1 The tight-binding model in 1D

Assumptions of model:

- Assume electrons are bound at particular lattice sites with state $|n\rangle$ at the nth site.
- Assume there is a non-negligible probability of jumping to at furthest the two sites to the left and right.
- Periodically identify $|1\rangle = |N+1\rangle$ (put lattice on a circle).

Then the Hamiltonian is:

$$H = E_0 \sum_{n=1}^{N} |n\rangle \langle n| - t \sum_{n=1}^{N} \left(|n\rangle \langle n+1| + |n+1\rangle \langle n| \right),$$

where t is called the *hopping parameter*.

Solution of Schrödinger: Write

$$|\psi\rangle = \sum_n \psi_n |n\rangle .$$

Substituting into $H|\psi\rangle = E|\psi\rangle$, we get:

$$E_0\psi_n - t(\psi_{n+1} + \psi_{n-1}) = E\psi_n.$$

Solutions are of the form

$$\psi_n = \frac{e^{ikna}}{\sqrt{N}},$$

where the lattice spacing is a and $\sqrt{N}$ is included for normalisation.

States are labelled by $ka \in [-\pi, \pi)$, since $n \in \mathbb{Z}$. Thus $k \in [-\pi/a, \pi/a)$.

Definition: $[-\pi/a, \pi/a)$ is called the *Brillouin zone*.

Features of model:

- The energy is $E(k) = E_0 - 2t\cos(ka)$, so energy lies in a *band*.
- Periodicity implies $e^{ikNa} = 1$, hence
$$k \in \frac{2\pi\mathbb{Z}}{Na},$$
thus *momentum is quantised*.
- The number of states in the Brillouin zone is
$$\frac{\text{length of zone}}{\text{possible momenta}} = \frac{2\pi/a}{2\pi/Na} = N.$$
- At low momenta, $E(k) \approx E_0 - 2t + ta^2k^2$. $E_0 - 2t$ is an irrelevant constant. We can compare ta^2k^2 with $\hbar^2k^2/2m$ to deduce the particle has an *effective mass* $m^* = \hbar^2/2ta^2$ in the presence of the lattice.

6.2 Nearly-free: perturbative approach

Assumptions of model:

- Electrons move on a continuous line.
- The potential is treated as a perturbation to a free electron.
- The potential is assumed periodic with period a.
- We impose a periodic boundary condition by putting the electron on a circle of circumference L. Then the number of lattice sites is L/a.

Solution of Schrödinger: Solve via perturbation theory. The unperturbed states are plane waves:

$$\langle x|k\rangle = \frac{e^{ikx}}{\sqrt{L}}$$

with energies $E_0(k) = \hbar^2k^2/2m$. By orthonormality, we have:

$$\langle k|k'\rangle = \frac{1}{L}\int_{-\infty}^{\infty} e^{i(k'-k)x}dx = \delta_{k,k'}.$$

Since every state has degeneracy 2, we may need degenerate perturbation theory. To check, we investigate mixing of the states $|k\rangle$ and $|k'\rangle$. We have:

$$\langle k|V|k'\rangle = \frac{1}{L}\int_{-\infty}^{\infty} \sum_{n=-\infty}^{\infty} V_n e^{i(k'-k+2\pi n/a)x}\, dx,$$

where V_n are the Fourier coefficients of $V(x)$ (allowed since V_n periodic with period a - also note $V_n^* = V_n$ to guarantee $V(x)$ real). Hence

$$\langle k|V|k'\rangle = \sum_{n=-\infty}^{\infty} V_n \delta_{(k-k'),2\pi n/a}.$$

So we get mixing iff $k - k' = 2\pi n/a$. Since degeneracy only occurs for $k' = -k$, we get mixing iff $k = \pi n/a$ (i.e. k is at the edge of the Brillouin zone).

Thus we get the following three cases:

Case 1 - $|k| \ll \pi/a$: We can use non-degenerate perturbation theory. We have:

$$E(k) = \frac{\hbar^2k^2}{2m} + \underbrace{\langle k|V|k\rangle}_{\substack{\text{irrelevant} \\ \text{constant } V_0}} + \underbrace{\sum_{k'\neq k} \frac{|\langle k'|V|k\rangle|^2}{E_0(k) - E_0(k')}}_{\text{non-zero iff } k = k' + 2\pi n/a} + \ldots .$$

If $k = k' + 2\pi n/a$, $E_0(k)$ and $E_0(k')$ are far apart, so second order term negligible (denominator large). Hence up to a constant, spectrum unchanged - electron 'doesn't see' the lattice.

Case 2 - $k = n\pi/a$: We need degenerate perturbation theory. The degenerate subspace is $\mathrm{span}\{|k\rangle, |k'\rangle \equiv |-k\rangle\}$; we need to diagonalise H in this degenerate subspace.

The matrix of H in the degenerate subspace is:

$$\begin{pmatrix} \langle k|H|k\rangle & \langle k|H|k'\rangle \\ \langle k'|H|k\rangle & \langle k'|H|k'\rangle \end{pmatrix} = \begin{pmatrix} E_0(k)+V_0 & V_n \\ V_n^* & E_0(k')+V_0 \end{pmatrix}.$$

The eigenvalues obey $(E_0(k)+V_0-E)^2-|V_n|^2=0$, hence

$$E = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} + V_0 \pm |V_n|.$$

So we get a 'jump' in the energy spectrum when $k = n\pi/a$.

Case 3 - $k = n\pi/a + \delta$, $|\delta| \ll 1$: This is the case when k is 'close' to the edge of the Brillouin zone. We again need degenerate perturbation theory, since when states have energy very close to one another, they mix.

The state $|k\rangle = |n\pi/a+\delta\rangle$ will mix with $|-n\pi/a+\delta\rangle$. Using the matrix from above, with $k \mapsto n\pi/a+\delta$ and $k' \mapsto -n\pi/a+\delta$, we get the eigenvalue equation

$$(E_0(k)+V_0-E)(E_0(k')+V_0-E) - |V_n|^2 = 0.$$

Solving for E, we have:

$$E = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2}+\delta^2\right) + V_0 \pm \sqrt{|V_n|^2 + \left(\frac{\hbar^2}{2m}\cdot\frac{2n\pi\delta}{a}\right)^2}.$$

Using the binomial expansion, we see the leading order non-constant term is $O(\delta^2)$, hence near the edge of the Brillouin zone, the energy behaves quadratically.

Summary:

- The spectrum is virtually unchanged when $|k| \ll \pi/a$.
- The energy splits when $k = n\pi/a$. The size of the gap is $2|V_n|$.
- The spectrum is quadratic at the edges.

Combining this information allows us to sketch the band structure:

Definition: The region of k-space corresponding to the nth band is called the nth Brillouin zone.

6.3 Nearly-free: Floquet matrix approach

This is another way of deriving the band structure for nearly-free electrons.

Let $\psi_1(x)$ and $\psi_2(x)$ be two linearly independent solutions of the SE with a periodic potential $V(x) = V(x+a)$. Since the equation is invariant under the translation $x \mapsto x+a$, $\psi_1(x+a)$ and $\psi_2(x+a)$ must also be solutions to the SE.

Definition: Let

$$\begin{pmatrix}\psi_1(x+a)\\ \psi_2(x+a)\end{pmatrix} = F(E)\begin{pmatrix}\psi_1(x)\\ \psi_2(x)\end{pmatrix}, \qquad (*)$$

where $F(E)$ is a matrix (this must be possible since $\psi_1(x)$ and $\psi_2(x)$ are LI so form a basis for the solution space of the equation). We call $F(E)$ the *Floquet matrix*.

Theorem: The Floquet matrix has the following properties:

(i) $\det(F(E)) = 1$;

(ii) $\mathrm{tr}(F(E))$ is real.

Proof: To prove (i), differentiate $(*)$ with respect to x to get

$$\begin{pmatrix}\psi_1'(x+a)\\ \psi_2'(x+a)\end{pmatrix} = F(E)\begin{pmatrix}\psi_1'(x)\\ \psi_2'(x)\end{pmatrix}.$$

We can write this equation and $(*)$ together as a matrix equation:

$$W(x+a) = F(E)W(x),$$

where

$$W(x) = \begin{pmatrix}\psi_1(x) & \psi_1'(x)\\ \psi_2(x) & \psi_2'(x)\end{pmatrix}.$$

We have that $\det(W)$ is independent of x (show using $\partial_x \det(W)$ and the SE). Thus $\det(W(x)) = \det(W(x+a))$ so $\det(F(E)) = 1$.

To prove (ii), simply note that we may always pick ψ_1 and ψ_2 to be real (simply take real parts and they remain solutions to SE), hence $F(E)$ has real entries, and hence the trace is real. Similarity transformations preserve the trace too if we want to pick ψ_1 and ψ_2 complex. □

6.4 Using the Floquet matrix

From the above Theorem, the Floquet matrix has characteristic equation $\lambda^2 - (\mathrm{tr}(F))\lambda + 1 = 0$. There are two types of solution to this equation:

1. If $|\mathrm{tr}(F)| < 2$, then the roots $\lambda_\pm$ are complex and have equal magnitude (since they are complex conjugates). Hence $\lambda_+ = e^{ika}$ and $\lambda_- = e^{-ika}$ for some $k \in \mathbb{R}$, $|k| < \pi/a$. So the eigenstates obey $\psi_\pm(x+a) = e^{\pm ika}\psi_\pm(x)$. These correspond to plane wave states, spread throughout the lattice. These are the bands in the spectrum.

2. If $|\mathrm{tr}(F)| > 2$, then the roots $\lambda_\pm$ are real an so $\lambda_+ = e^{\mu a}$ and $\lambda_- = e^{-\mu a}$ for some μ. Thus $\psi_\pm(x) = e^{\pm\mu a}\psi_\pm(x)$. Thus there always exists a state that diverges as $x \to \infty$ or $x \to -\infty$. Thus these states are not normalisable and thus unphysical. This is where the gaps in the spectrum occur.

Hence Floquet theory recovers the band structure.

Example: Suppose we want to find the eigenstates of the potential

$$V(x) = -\frac{\hbar^2\lambda}{m}\sum_{n=-\infty}^{\infty}\delta(x-na).$$

We use Floquet theory. Observe $\psi_1(x) = \sinh(kx)$ and $\psi_2(x) = \cosh(kx)$ both solve the SE with energy $-\hbar^2k^2/2m$, in the region $-a < x < 0$.

We attempt to extend these solutions to $0 < x < a$. Writing

$$\psi_1(x) = \begin{cases}\sinh(kx) \text{ for } -a < x < 0\\ A\sinh(kx) + B\cosh(kx) \text{ for } 0 < x < a\end{cases}$$

and applying continuity and the jump condition gives $A = 1$ and $B = 0$. Similarly we can extend $\psi_2(x)$. This gives the Floquet matrix:

$$\begin{pmatrix}\cosh(ka) & \sinh(ka)\\ -\frac{2\lambda}{k}\cosh(ka) + \sinh(ka) & -\frac{2\lambda}{k}\sinh(ka) + \cosh(ka)\end{pmatrix}.$$

The condition for a band is $|\mathrm{tr}(F)|^2 < 2$, i.e.

$$\left(\cosh(ka) - \frac{\lambda}{k}\sinh(ka)\right)^2 < 1.$$

6.5 Impurities and bound states

Suppose we modify the potential in the above example to

$$V(x) = -\frac{\hbar^2\lambda}{m}\sum_{n=-\infty, n\neq 0}^{\infty}\delta(x-na) - \frac{\hbar^2\gamma}{m}\delta(x),$$

i.e. we introduced an impurity at $x = 0$.

For $x > 0$, nothing has changed. So the Floquet matrix still takes us from $0 < x < a$, to $a < x < 2a$, etc. Thus we seek an eigenvector of F with eigenvalue c such that $|c| < 1$, so that $\psi(x + a) = c\psi(x)$ for all $x > 0$. We can use parity to extend to $x < 0$, then match at the origin.

From the theory, we know such an eigenvalue c exists if $|\mathrm{tr}(F)|^2 > 2$. Let its eigenstate on $0 < x < a$ be $\psi = Ae^{\mu x} + Be^{-\mu x}$. Extend to $-a < x < 0$ as follows.

We write

$$\psi(x) = \begin{cases}Ae^{\mu x} + Be^{-\mu x} \text{ for } 0 < x < a,\\ Ae^{-\mu x} + Be^{\mu x} \text{ for } -a < x < 0,\end{cases}$$

by parity. Continuity at $x = 0$ is automatically satisfied. Using the jump condition at $x = 0$, we find $(A - B)\mu = -\gamma(A + B)$. WLOG $A = \mu - \gamma$ (it's a normalisation constant), so $B = \mu + \gamma$. Thus

$$\psi \propto \begin{cases}(\mu-\gamma)e^{\mu x} + (\mu+\gamma)e^{-\mu x} \text{ for } 0 < x < a,\\ (\mu-\gamma)e^{-\mu x} + (\mu+\gamma)e^{\mu x} \text{ for } -a < x < 0.\end{cases}$$

Recall that since this is an eigenstate for $F(E)$ on $0 < x < a$, we must have:

$$F(E)\begin{pmatrix}\mu-\gamma\\ \mu+\gamma\end{pmatrix} = c\begin{pmatrix}\mu-\gamma\\ \mu+\gamma\end{pmatrix}.$$

Conversely, if this condition holds, all the matching conditions at $x = 0$ hold. So this is a necessary and sufficient condition for the existence of a bound state.

6.6 Bloch's Theorem in 1D

Definition: Define the translation operator by $T_l\psi(x) = \psi(x + l)$.

Theorem: The translation operator obeys:

(i) T_l is unitary;

(ii) $\{T_l\}$ forms an Abelian group;

(iii) $T_l = e^{il\hat{p}/\hbar}$.

Proof: For (i), we have

$$(\phi, T_l\psi) = \langle\phi|T_l|\psi\rangle = \int dx\ \phi^* T_l\psi = \int dx\ \phi^*(x)\psi(x+l)$$
$$= \int dx\ \phi(x-l)^*\psi(x) = \int dx (T_{-l}\phi)^*\psi = (T_{-l}\phi, \psi).$$

by a simple substitution. Hence $T_l^\dagger = T_{-l} = T_l^{-1}$. So done.

(ii) is obvious. (iii) is just Taylor's theorem,

$$e^{il\hat{p}/\hbar}\psi(x) = \left(1 + l\frac{\partial}{\partial x} + \frac{l^2}{2}\frac{\partial^2}{\partial x^2} + ...\right)\psi(x) = \psi(x+l). \quad \square$$

Definition: A system is called *invariant under discrete translations* if $[H, T_l] = 0$ for all $l = na$, $n \in \mathbb{Z}$, for some a.

This is distinct from translational symmetry, when $[H, T_l] = 0$ for all l, i.e. $[H, \hat{p}] = 0$.

Theorem: If a system has discrete translational symmetry (say period a), we can label eigenstates by some $k \in [-\pi/a, \pi/a)$.

Proof: Since we have discrete translational symmetry, we can simultaneously diagonalise H and T_a. Since T_a is unitary, all its eigenvalues are phases $e^{\theta(a)}$, for some $\theta(a)$, dependent on a.

We have that T_{na} has eigenvalue $e^{i\theta(an)}$ and T_a^n has eigenvalue $e^{i\theta(a)n}$; these must be the same to respect the group structure. Choosing $\theta(a) = ak$ for some k fulfils that requirement.

Based on this, we can label eigenstates by k:

$$T_a\psi_k(x) = \psi_k(x+a) = e^{ika}\psi_k(x).$$

Because e^{ika} is a phase, k is defined only up to $2\pi/a$, i.e. $k \equiv k + 2\pi/a$. Thus we can restrict k to lie in the range $k \in [-\pi/a, \pi/a)$, i.e. the Brillouin zone, as required. □

Theorem (Bloch's Theorem): In a periodic potential, $V(x) = V(x+a)$, all energy eigenstates can be written as

$$\psi_k(x) = e^{ikx}u_k(x),$$

where $u_k(x)$ is periodic, $u_k(x+a) = u_k(x)$, and $k \in [-\pi/a, \pi/a)$.

Proof: Take $\psi_k(x)$ to be an eigenstate of T_a. Then $T_a\psi_k(x) = \psi_k(x+a)$ and $T_a\psi_k(x) = e^{ika}\psi_k(x)$, so that $\psi_k(x+a) = e^{ika}\psi_k(x)$.

Define $u_k(x) = e^{-ikx}\psi_k(x)$. Then $u_k(x)$ is certainly periodic with period a: $u_k(x+a) = e^{-ik(x+a)}\psi_k(x+a) = e^{-ikx}\psi_k(x) = u_k(x)$. So we're done. □

Slogan: A lattice only affects plane wave states e^{ikx} by multiplying them by a periodic function.

Definition: $p = \hbar k$ is called the *crystal momentum*. It is conserved modulo $2\pi/a$, e.g. if particles collide their initial and final momentum can only differ by $2\pi n/a$.

Also, our revision of the range of k means we change the way we draw the nearly-free electron bands; we now use the *reduced zone scheme*:

7 3D lattices

7.1 Bravais lattices

Definition: A *Bravais lattice* is a periodic array of points defined by integer sums of linearly independent basis vectors, $\mathbf{a}_i$, i.e.

$$\Lambda = \{\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 | n_i \in \mathbb{Z}\}.$$

The vectors $\mathbf{a}_i$ are called *primitive unit vectors*. A *primitive unit cell* is a region of space which, when translated by the primitive lattice vectors, tessellates all of space.

Theorem: All primitive unit cells have volume $V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$.

Proof: We can relate two choices of primitive lattice vectors $\mathbf{a}_i'$ and $\mathbf{a}_i$ by a transformation matrix M, i.e. $\mathbf{a}_i' = M\mathbf{a}_i$. Since the $\mathbf{a}_i'$ must be integer combinations of the $\mathbf{a}_i$ and vice-versa, M and M^{-1} are matrices of integers. Hence $\det(M), \det(M^{-1}) \in \mathbb{Z}$. But $\det(M)\det(M^{-1}) = \det(MM^{-1}) = 1$, so $|\det(M)| = 1$. So preserves volume. □

Definition: The *Wigner-Seitz cell* for the lattice Λ is

$$\Gamma = \{\mathbf{x} : |\mathbf{x}| < |\mathbf{x} - \mathbf{r}| \text{ for all } \mathbf{r} \in \Lambda \backslash \{\mathbf{0}\}\}.$$

It is the collection of all points closer to the origin than to any of the other lattice points.

The important lattices in nature are:

Cubic lattice: $\mathbf{a}_1 = a\hat{\mathbf{x}}$, $\mathbf{a}_2 = a\hat{\mathbf{y}}$, $\mathbf{a}_3 = a\hat{\mathbf{z}}$. The Wigner-Seitz cell is also a cube, of volume a^3, centred on some lattice point.

Body-centred cubic lattice: $\mathbf{a}_1 = a\hat{\mathbf{x}}$, $\mathbf{a}_2 = a\hat{\mathbf{y}}$, $\mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. Equivalently, $\mathbf{a}_1 = \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, $\mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$, $\mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$. This is a cube with an extra point in the middle. The volume of its Wigner-Seitz cell is $V^3/2$.

Face-centred cubic lattice: $\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}})$, $\mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}})$, $\mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}})$. This is a cube with an extra point on the centre of each face. The Wigner-Seitz cell has volume $V = a^3/4$.

7.2 Reciprocal lattices

Definition: The *reciprocal* or *dual* lattice of Λ is

$$\Lambda^* = \{\mathbf{k} = \sum n_i \mathbf{b}_i : n_i \in \mathbb{Z}\},$$

where the $\mathbf{b}_i$ satisfy $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. Since dimensionally we have $[\mathbf{a}_i] = L \Rightarrow [\mathbf{b}_j] = L^{-1}$, Λ^* is a momentum-space lattice.

Theorem: In 3D, we have

$$\mathbf{b}_i = \frac{2\pi}{V} \cdot \frac{1}{2}\epsilon_{ijk}\mathbf{a}_j \times \mathbf{a}_k,$$

where V is the volume of the primitive unit cell. Conversely,

$$\mathbf{a}_i = \frac{2\pi}{V^*} \cdot \frac{1}{2}\epsilon_{ijk}\mathbf{b}_j \times \mathbf{b}_k,$$

where V^* is the volume of the reciprocal primitive unit cell.

Proof: Consider just $\mathbf{b}_1$. We have $\mathbf{a}_2 \cdot \mathbf{b}_1 = \mathbf{a}_3 \cdot \mathbf{b}_1 = 0$. So $\mathbf{b}_1$ is orthogonal to both $\mathbf{a}_2$ and $\mathbf{a}_3$. Hence it lies along the line parallel to $\mathbf{a}_2 \times \mathbf{a}_3$, i.e. $\mathbf{b}_1 = K\, \mathbf{a}_2 \times \mathbf{a}_3$.

We now just need to find K. We need $\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$, hence $KV = 2\pi$. Thus $K = 2\pi/V$.

The remaining relationships follow by symmetry. In particular, we need the $\frac{1}{2}\epsilon_{ijk}$ because the ϵ_{ijk} picks up both $\mathbf{a}_j \times \mathbf{a}_k$ and $-\mathbf{a}_k \times \mathbf{a}_j = \mathbf{a}_j \times \mathbf{a}_k$. □

Theorem: We have $e^{i\mathbf{k}\cdot\mathbf{r}} = 1$ for all $\mathbf{r} \in \Lambda$ and $\mathbf{k} \in \Lambda^*$.

Proof: For integers n_i and m_j we have:

$$\exp\left(i(n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3) \cdot (m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3)\right)$$
$$= \exp(i(n_1m_1 + n_2m_2 + n_3m_3) \cdot 2\pi) = 1. \ \square$$

Definition: The *Brillouin zone* is the Wigner-Seitz cell of the reciprocal lattice. The nth *Brillouin zone* is the set of points in the reciprocal lattice for which the origin is the nth closest point.

Theorem: The nth Brillouin zone can be mapped into the first zone, without overlap except on the bounding surfaces, to completely cover the first zone.

Proof: Define the map θ from the nth Brillouin zone to the first Brillouin zone by $\theta(\mathbf{k}) = \mathbf{k} - \mathbf{q_k}$, where $\mathbf{q_k}$ is the closest element of Λ^* to $\mathbf{k}$.

We need to show: (i) this maps into the first Brillouin zone; (ii) the map is surjective; (iii) the map is injective, with overlap only on the boundaries.

To show (i), let $\theta(\mathbf{k}) = \mathbf{k} - \mathbf{q_k}$. Let $\mathbf{q}$ be the closest element of Λ^* to $\mathbf{k} - \mathbf{q_k}$. By periodicity, $\mathbf{q}$ is the closest dual lattice vector to $\mathbf{k}$, translated by $-\mathbf{q_k}$, i.e. $\mathbf{q} = \mathbf{q_k} - \mathbf{q_k} = \mathbf{0}$. So $\theta(\mathbf{k})$ is in the first Brillouin zone.

For (ii), let $\mathbf{k}$ be in the first Brillouin zone, and let $\mathbf{q}$ be the nth closest dual lattice point to $\mathbf{k}$ (choosing $\mathbf{q}$ from a selection if necessary). Then $\mathbf{q} + \mathbf{k}$ has closest dual lattice point $\mathbf{q}$ by periodicity, so $\theta(\mathbf{q} + \mathbf{k}) = \mathbf{k}$.

Finally, for (iii), suppose that $\theta(\mathbf{y}) = \theta(\mathbf{z}) = \mathbf{x}$. Let $\theta(\mathbf{y}) = \mathbf{y} - \mathbf{u} = \mathbf{x}$ and $\theta(\mathbf{z}) = \mathbf{z} - \mathbf{v} = \mathbf{x}$, and define $\mathbf{w} = \mathbf{v} - \mathbf{u} \in \Lambda^*$. Then $\mathbf{w} = \mathbf{z} - \mathbf{y} \Rightarrow \mathbf{z} = \mathbf{y} + \mathbf{w}$.

Now let $\mathbf{y}_n$ be the nth closest dual lattice point to $\mathbf{y}$. By periodicity, $\mathbf{y}_n + \mathbf{w}$ is the nth closest dual lattice point to $\mathbf{z}$. Since both $\mathbf{y}$ and $\mathbf{z}$ are in the nth Brillouin zone, their nth closest point must be $\mathbf{0}$ or a vector equidistant to $\mathbf{0}$.

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8 3D band structure

8.1 The tight-binding model in 3D

The 3D tight-binding Hamiltonian is

$$H = E_0 \sum_{\mathbf{r}\in\Lambda} |\mathbf{r}\rangle\langle\mathbf{r}| - \sum_{\mathbf{r}\in\Lambda}\sum_{\mathbf{a}} t_{\mathbf{a}} \left(|\mathbf{r}\rangle\langle\mathbf{r}+\mathbf{a}| + |\mathbf{r}+\mathbf{a}\rangle\langle\mathbf{r}|\right),$$

where '$\mathbf{a}$' are the nearest-neighbour sites to the origin (be careful not to double count - if we include $\mathbf{a}$, we mustn't use $-\mathbf{a}$). This is solved by

$$|\psi(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}} |\mathbf{r}\rangle,$$

which gives the spectrum as

$$E(\mathbf{k}) = E_0 - 2\sum_{\mathbf{a}} t_{\mathbf{a}} \cos(\mathbf{k}\cdot\mathbf{a}).$$

8.2 Bloch's Theorem in 3D

Theorem (Bloch's Theorem): An electron moving in a periodic potential $V(\mathbf{x})$ with the periodicity of the lattice Λ has energy eigenstates of the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}} u_{\mathbf{k}}(\mathbf{x}),$$

where $u_{\mathbf{k}}$ has the periodicity of the lattice.

Proof: Same as in 1D. Introduce the translation operator $T_{\mathbf{r}}$. We have $[T_{\mathbf{r}}, H] = 0$ for all $\mathbf{r} \in \Lambda$, so they are simultaneously diagonalisable. Choose $\psi_{\mathbf{k}}(\mathbf{x})$ to be an eigenstate of $T_{\mathbf{r}}$ with eigenvalue $e^{i\mathbf{k}\cdot\mathbf{r}}$. The proof then proceeds as in 1D. □

8.3 Fourier transforms for lattices

We want to study the nearly-free electron model in 3D. We will need the Fourier transform:

$$\tilde{V}(\mathbf{k}) = \int d^3\mathbf{x}\, e^{-i\mathbf{k}\cdot\mathbf{x}} V(\mathbf{x}).$$

Theorem: $\tilde{V}(\mathbf{k}) = 0$ unless $\mathbf{k} \in \Lambda^*$.

Proof: We have:

$$\begin{aligned}\tilde{V}(\mathbf{k}) &= \sum_{\mathbf{r}\in\Lambda} \int_\Gamma d^3\mathbf{x}\, e^{-i\mathbf{k}\cdot(\mathbf{x}+\mathbf{r})} V(\mathbf{x}+\mathbf{r}) \\ &= \underbrace{\sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}}_{\Delta(\mathbf{k})} \int_\Gamma d^3\mathbf{x}\, e^{-i\mathbf{k}\cdot\mathbf{x}} V(\mathbf{x}),\end{aligned}$$

where Γ is the Wigner-Seitz cell.

For any $\mathbf{r}_0 \in \Lambda$, we also have:

$$\Delta(\mathbf{k}) = \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)} = e^{-i\mathbf{k}\cdot\mathbf{r}_0} \sum_{\mathbf{r}\in\Lambda} e^{i\mathbf{k}\cdot\mathbf{r}} = e^{-i\mathbf{k}\cdot\mathbf{r}_0}\Delta(\mathbf{k}).$$

Hence $\Delta(\mathbf{k}) = 0$ unless $e^{-i\mathbf{k}\cdot\mathbf{r}_0}$ for all $\mathbf{r}_0 \in \Lambda$, i.e. $\mathbf{k} \in \Lambda^*$. □

Theorem (Stronger version): We can write

$$\tilde{V}(\mathbf{k}) = \underbrace{\left(V^* \sum_{\mathbf{q}\in\Lambda^*} \delta(\mathbf{k}-\mathbf{q})\right)}_{\Delta(\mathbf{k})} \underbrace{\int_\Gamma d^3\mathbf{x}\, e^{-i\mathbf{k}\cdot\mathbf{x}} V(\mathbf{x})}_{S(\mathbf{k})}.$$

where V^* is the volume of the Brillouin zone, and Γ is the Wigner-Seitz cell. $S(\mathbf{k})$ is called the *structure factor*.

Proof: We follow the same proof as above, but this time we try to determine the explicit form of $\Delta(\mathbf{k})$. Write $\mathbf{k} = \sum k_i \mathbf{b}_i$ and $\mathbf{r} = \sum n_i \mathbf{a}_i$ where the n_i are integers and k_i are *not necessarily integers*. Then

$$\Delta(\mathbf{k}) = \sum_{\mathbf{r}\in\Lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} = \sigma(k_1)\sigma(k_2)\sigma(k_3)$$

where

$$\sigma(k) = \sum_{n=-\infty}^{\infty} e^{-2\pi i k n}.$$

Expand the *Dirac comb function* in a Fourier series:

$$\sum_{n=-\infty}^{\infty} \delta(k-n) = \sum_{n=-\infty}^{\infty} c_n e^{-2\pi i k n}.$$

Then

$$\sum_{n=-\infty}^{\infty} \int_{-1/2}^{1/2} \delta(k-n) e^{2\pi i k m} dk = c_m \quad \Rightarrow \quad c_m = 1.$$

Hence we have found $\sigma(k)$ explicitly. Thus $\Delta(\mathbf{k})$ is non-vanishing if and only if the k_i are integers, i.e. $\mathbf{k} \in \Lambda^*$. So we have:

$$\Delta(\mathbf{k}) = \sigma(k_1)\sigma(k_2)\sigma(k_3) = V^* \sum_{\mathbf{q}\in\Lambda^*} \delta(\mathbf{k}-\mathbf{q}).$$

We can invert this above Fourier transform to get:

$$V(\mathbf{x}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{x}} \Delta(\mathbf{k}) S(\mathbf{k}) = \sum_{\mathbf{q}\in\Lambda^*} e^{i\mathbf{q}\cdot\mathbf{x}} V_{\mathbf{q}},$$

for constants $V_{\mathbf{q}}$, i.e. a Fourier series for $V(\mathbf{x})$. We are now ready to analyse the nearly-free electron model in 3D.

8.4 Nearly-free electrons in 3D

As in 1D, treat $V(\mathbf{x})$ as a perturbation to free electrons with wavefunction

$$\langle \mathbf{x}|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{x}},$$

and energy $E = \hbar^2\mathbf{k}^2/2m$. We now decide whether to use degenerate perturbation theory by computing $\langle \mathbf{k}|V|\mathbf{k}'\rangle$.

Theorem: $\langle \mathbf{k}|V|\mathbf{k}'\rangle = 0$ unless $\mathbf{k} - \mathbf{k}' \in \Lambda^*$.

Proof: We have:

$$\langle \mathbf{k}|V|\mathbf{k}'\rangle = \int d^3\mathbf{x}\, e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}} V(\mathbf{x}) = \tilde{V}(\mathbf{k}-\mathbf{k}'),$$

hence done by earlier work. □

As in 1D, we get cases:

Case 1 - far from edge of Brillouin zone: For $|\mathbf{k}|$ small, $|\mathbf{k}\rangle$ and $|\mathbf{k}+\mathbf{q}\rangle$ have wildly different energy for $\mathbf{q} \in \Lambda^*$. Hence non-degenerate perturbation theory is valid. As in 1D, we find the spectrum unchanged, i.e. $E \approx \hbar^2|\mathbf{k}|^2/2m$.

Case 2 - close to edge of Brillouin zone: Suppose $|\mathbf{k}\rangle$ and $|\mathbf{k}+\mathbf{q}\rangle$ have the same energy. Then $|\mathbf{k}|^2 = |\mathbf{k}+\mathbf{q}|^2$ which implies $2\mathbf{k}\cdot\mathbf{q} + |\mathbf{q}|^2 = 0$. This is satisfied for $\mathbf{k} = -\frac{1}{2}\mathbf{q} + \mathbf{k}_\perp$, where $\mathbf{k}_\perp \cdot \mathbf{q} = 0$, i.e. when $\mathbf{k}$ is on the perpendicular bisector of the origin and the lattice point, i.e. on the edge of the Brillouin zone as expected.

The result is that a band opens up in the spectrum at the edge of the Brillouin zone. Energies at the edges of the first Brillouin zone are slightly lower than they should be, and energies at the edges of the second Brillouin zone that touch the first are slightly higher than they should be.

8.5 Example: 2D square lattice

Consider a 2D square lattice of spacing a and potential

$$V = 2A(\cos(\gamma x) + \cos(\gamma y)),$$

where $\gamma = 2\pi/a$. One state on the edge of the Brillouin zone is $\mathbf{k} = (\gamma/2, 0)$. The states $(-\gamma/2, 0)$, $(0, \gamma/2)$ and $(0, -\gamma/2)$ all have the same energies in the absence of the perturbation. However, only $\mathbf{k} = (\gamma/2, 0)$ and $\mathbf{k}' = (-\gamma/2, 0)$ differ by a dual lattice vector.

In this degenerate subspace, we have

$$\begin{pmatrix} \langle \mathbf{k}|H|\mathbf{k}'\rangle & \langle \mathbf{k}|H|\mathbf{k}'\rangle \\ \langle \mathbf{k}'|H|\mathbf{k}\rangle & \langle \mathbf{k}'|H|\mathbf{k}'\rangle \end{pmatrix} = \begin{pmatrix} E_{\mathbf{k}} + V_{(0,0)} & V_{(\gamma,0)} \\ V_{(-\gamma,0)} & E_{\mathbf{k}'} + V_{(0,0)} \end{pmatrix}.$$

This gives energies:

$$E = \frac{\hbar^2\gamma^2}{8m} \pm A,$$

showing that a gap has opened up. We can perform a similar analysis at the corners. We get a diagram that looks like:

8.6 Number of states in the Brillouin zone

Theorem: Consider a finite lattice Λ with N lattice sites. The number of states in the Brillouin zone is N.

Proof: Consider a lattice $\mathbf{r} = \sum n_i \mathbf{a}_i$, with $0 \leq n_i \leq N_i$. For N_i very large, $N \approx N_1 N_2 N_3$. Imposing periodic boundary conditions on the wavefunction, we have $\psi(\mathbf{x} + N_i\mathbf{a}_i) = \psi(\mathbf{x})$.

Without loss of generality, let ψ be a Bloch state. Then $\psi(\mathbf{x} + N_i\mathbf{a}_i) = e^{iN_i\mathbf{a}_i\cdot\mathbf{k}}\psi(\mathbf{x})$. Hence periodicity forces:

$$e^{iN_i\mathbf{a}_i\cdot\mathbf{k}} = 1 \quad \Rightarrow \quad \mathbf{k} = \sum_i \frac{m_i\mathbf{b}_i}{N_i},$$

where $m_i \in \mathbb{Z}$ and $\mathbf{b}_i$ are reciprocal lattice vectors.

Thus for $\mathbf{k}$ to be in the first Brillouin zone, need $m_i \in \{0, 1, ...N_i - 1\}$, i.e. there are $N_1N_2N_3 \approx N$ possible states in the first Brillouin zone. □

9 Scattering off a lattice

9.1 The Laue condition

The wavefunction for scattering at the origin is

$$\psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k};\mathbf{k}')\frac{e^{ikr}}{r},$$

where we have an incident wave of momentum $\mathbf{k}$ and scattering amplitude f ($\mathbf{k}' = k\hat{\mathbf{r}}$ is momentum of outgoing wave).

Shift the potential so it is now localised at $\mathbf{R}$. Then:

$$\begin{aligned}\psi(\mathbf{r}) &\sim e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} + f(\mathbf{k};\mathbf{k}')\frac{e^{ik|\mathbf{r}-\mathbf{R}|}}{|\mathbf{r}-\mathbf{R}|} \\ &\approx e^{-i\mathbf{k}\cdot\mathbf{R}}\left(e^{i\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k};\mathbf{k}')e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}}\frac{e^{ikr}}{r}\right),\end{aligned}$$

where we have expanded $|\mathbf{r} - \mathbf{R}| = \sqrt{r^2 + R^2 - 2\mathbf{r}\cdot\mathbf{R}} \approx r - \hat{\mathbf{r}}\cdot\mathbf{R}$, and used $\mathbf{k}' = k\hat{\mathbf{r}}$.

For a lattice localised at multiple $\mathbf{R}$, we get a total scattering amplitude:

$$f_\Lambda = f(\mathbf{k};\mathbf{k}')\sum_{\mathbf{R}\in\Lambda} e^{i\mathbf{q}\cdot\mathbf{R}},$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. Hence there is *zero scattering* unless $\mathbf{q} \in \Lambda^*$. This is the *Laue condition*.

9.2 The Bragg condition

Suppose that $\mathbf{Q} = \mathbf{k} - \mathbf{k}' \in \Lambda^*$, i.e. there is scattering. Let $\mathbf{k}\cdot\mathbf{k}' = k^2\cos(\theta)$. Taking the square of the condition $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ gives:

$$\mathbf{k}^2 + \mathbf{k}'^2 - 2\mathbf{k}\cdot\mathbf{k}' = \mathbf{Q}^2 \quad \Rightarrow \quad 2k^2(1 - \cos(\theta)) = \mathbf{Q}^2$$

$$\Rightarrow \quad 2k\sin\left(\frac{1}{2}\theta\right) = Q.$$

Define the *Bragg planes* of the lattice Λ by the set of $\mathbf{a} \in \Lambda$ such that $\mathbf{a}\cdot\mathbf{Q} = 2\pi n$ for n an integer. Let the distance between successive planes be $d = 2\pi/Q$. Let $\lambda = 2\pi/k$ be the incoming wavelength. Then we have derived the condition:

$$n\lambda = 2d\sin(\theta/2).$$

This is called the *Bragg condition* for scattering.

Interpretation: Suppose two waves scatter off two consecutive Bragg planes, as shown in the figure below. The extra distance that one has to travel compared to the other is $2x = 2d\sin(\theta/2)$. So the Bragg condition states: *the extra distance travelled must be the wavelength*, or *waves must interfere constructively for scattering to occur*.

10 Electron dynamics in solids

We now study bulk behaviour of many electrons. We ignore all interactions between electrons.

10.1 Fermi definitions

Electrons are fermions, so by the Pauli exclusion principle, no two electrons may occupy the same state.

Consider putting electrons in a box. Their energy is $E = \hbar^2|\mathbf{k}|^2/2m$. Filling up energy levels from the bottom, the first electron can be put in state $\mathbf{k} = \mathbf{0}$ and spin up, the second can put in state $\mathbf{k} = \mathbf{0}$ and spin down, the third can be put in state $\mathbf{k} = (1, 0, 0)$ and spin up, etc.

Definition: As this procedure goes on, we fill up a ball in momentum space. This is called the *Fermi sea*. The boundary of the Fermi sea is called the *Fermi surface*. States on the Fermi surface are said to have *Fermi momentum* $\hbar k_F$ and *Fermi energy* $E = \hbar^2 k_F^2/2m$.

10.2 Metals and insulators

In the presence of a lattice, we know:

- The energy levels split into bands.
- Each band accommodates $2N$ electrons (2 from spin, number of states in Brillouin zone is N).
- Each atom donates Z electrons called *valence electrons*. Z is called the *valency*. So in total we have ZN electrons.

We consider the two cases of $Z = 1$ and $Z = 2$. We have:

Case 1 - $Z = 1$: There are N electrons. They fill up half of the Brillouin zone. The Fermi sea looks like:

The existence of a Fermi surface in the first Brillouin zone means that if the system is perturbed slightly (e.g. an electric field is applied) the electrons can respond by moving into unoccupied states at little energy cost.

Definition: Materials with a Fermi surface are called *metals*.

Case 2 - $Z = 2$: There are now $2N$ electrons. We spill over into the first Brillouin zone for weak lattices:

For strong lattices, i.e. when the minimum energy $E_{\min}$ in the second Brillouin zone is greater than the maximum energy $E_{\max}$ in the first Brillouin zone, we get the case:

There is now no Fermi surface. Hence there is a large energy gap everywhere to the next available state - so electrons don't move when small perturbations are applied.

Definition: Materials with no Fermi surface are called *insulators*.

11 The semi-classical equations

11.1 Velocity, currents and effective mass

Theorem: The velocity of electrons in a lattice is

$$\mathbf{v} = \frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}}.$$

Proof: The velocity is given by

$$\mathbf{v} = \frac{1}{m}\langle\psi| - i\hbar\nabla|\psi\rangle\,.$$

From Bloch's Theorem, $\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x})$ for $\mathbf{k}$ in the Brillouin zone. The SE gives $H\psi_{\mathbf{k}} = E(\mathbf{k})\psi_{\mathbf{k}}$, so $H_{\mathbf{k}}u_{\mathbf{k}} = E(\mathbf{k})u_{\mathbf{k}}$, where

$$H_{\mathbf{k}} = \frac{\hbar^2}{2m}(-i\nabla + \mathbf{k})^2 + V(\mathbf{x}).$$

Consider $H_{\mathbf{k}+\mathbf{q}}$ for small $\mathbf{q}$. Then

$$H_{\mathbf{k}+\mathbf{q}} = H_{\mathbf{k}} + \frac{\partial H_{\mathbf{k}}}{\partial \mathbf{k}}\cdot\mathbf{q} + \dots\,.$$

View this as a small perturbation of $H_{\mathbf{k}}$. Then from first order perturbation theory, the change in energy is:

$$\Delta E = \langle u_{\mathbf{k}}|\frac{\partial H_{\mathbf{k}}}{\partial \mathbf{k}}\cdot\mathbf{q}|u_{\mathbf{k}}\rangle\,.$$

This must agree with the exact result:

$$E(\mathbf{k}+\mathbf{q}) = E(\mathbf{k}) + \frac{\partial E}{\partial \mathbf{k}}\cdot\mathbf{q} + \dots\,.$$

Hence we have

$$\frac{\partial E}{\partial \mathbf{k}} = \langle u_{\mathbf{k}}|\frac{\partial H}{\partial \mathbf{k}}|u_{\mathbf{k}}\rangle$$

$$= \frac{\hbar^2}{m}\langle u_{\mathbf{k}}|(-i\nabla + \mathbf{k})|u_{\mathbf{k}}\rangle = \frac{\hbar^2}{m}\langle\psi_{\mathbf{k}}| - i\nabla|\psi_{\mathbf{k}}\rangle = \hbar\mathbf{v}.\ \square$$

Theorem: A filled band carries no electric current, $\mathbf{J} = -e\mathbf{v}$, or heat current.

Proof: The total electric current is (2 included for spin degeneracy):

$$\mathbf{j} = -\frac{2e}{\hbar}\int_{\Gamma}\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\partial E}{\partial \mathbf{k}} = 0,$$

since this is a total derivative, and Γ, the Brillouin zone, is a torus.

Similarly, the total heat current is given by

$$\mathbf{j}_E = 2\int_{\Gamma}\frac{d^3\mathbf{k}}{(2\pi)^3}\underbrace{E\mathbf{v}}_{\substack{\text{energy}\\ \text{carried}}} = \frac{2}{2\hbar}\int_{\Gamma}\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\partial(E^2)}{\partial \mathbf{k}} = 0.\quad\square$$

Definition: The *effective mass tensor* is defined to be

$$m^*_{ij} = \hbar^2\left(\frac{\partial^2 E}{\partial k^i \partial k^j}\right)^{-1}.$$

For isotropic systems, this reduces to

$$m^* = \hbar^2\left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}.$$

This comes from expanding around the minimum energy of a band, $E = E_{\min} + (\hbar^2/2m)|\mathbf{k} - \mathbf{k}_{\min}|^2$.

11.2 The semi-classical equations

In the semi-classical approximation we work with average momentum $\mathbf{k}$ and average position $\mathbf{x}$. We assume that when we apply an external force, $\mathbf{F} = -\nabla U(\mathbf{x})$, the energy is $E = E(\mathbf{k}) + U(\mathbf{x})$.

Theorem: We have Newton's equation,

$$\hbar\frac{d\mathbf{k}}{dt} = -\nabla U = \mathbf{F}.$$

Proof: Differentiate $E(\mathbf{k}) + U(\mathbf{x})$ wrt to t; the result must be zero by energy conservation. We get:

$$0 = \frac{\partial E}{\partial \mathbf{k}}\cdot\frac{d\mathbf{k}}{dt} + \frac{\partial U}{\partial \mathbf{x}}\cdot\frac{d\mathbf{x}}{dt} \quad\Rightarrow\quad 0 = \mathbf{v}\cdot\left(\frac{d\mathbf{k}}{dt}\hbar + \nabla U\right).\ \square$$

Theorem: Newton's equation may be written as

$$m^*\frac{d\mathbf{v}}{dt} = \mathbf{F}.$$

Proof: We have:

$$m^*\frac{d\mathbf{v}}{dt} = \frac{m^*}{\hbar}\frac{d}{dt}\left(\frac{\partial E}{\partial \mathbf{k}}\right) = \frac{m^*}{\hbar}\frac{d\mathbf{k}}{dt}\cdot\frac{\partial}{\partial \mathbf{k}}\left(\frac{\partial E}{\partial \mathbf{k}}\right) = \hbar\frac{d\mathbf{k}}{dt} = \mathbf{F},$$

using the definition of effective mass. $\square$

In summary:

The semi-classical equations:

$$\mathbf{v} = \frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}},$$

$$\hbar\frac{d\mathbf{k}}{dt} = -\nabla U = \mathbf{F},$$

$$m^*\frac{d\mathbf{v}}{dt} = -\nabla U = \mathbf{F}.$$

11.3 Example: motion in a magnetic field

Consider electrons of charge $-e$ and energy $E(\mathbf{k})$ moving in a constant magnetic field $\mathbf{B}$. The semi-classical equations give:

$$\hbar\frac{d\mathbf{k}}{dt} = -e\mathbf{v}\times\mathbf{B}, \quad \mathbf{v} = \frac{1}{\hbar}\frac{\partial\mathbf{E}}{\partial\mathbf{k}}.$$

We can show that $\mathbf{k}\cdot\mathbf{B}$ is constant using the semi-classical equations, so the k-space orbits are in a plane perpendicular to $\mathbf{B}$.

We can also show that E is constant, hence the $\mathbf{k}$-space trajectories are surface of constant energy; we conclude the orbits in momentum space are around Fermi surfaces in planes perpendicular to $\mathbf{B}$.

To get the orbits in real space, we note $\hat{\mathbf{B}}\times\hbar\dot{\mathbf{k}} = -e\hat{\mathbf{B}}\times(\dot{\mathbf{r}}\times\mathbf{B}) = -eB\dot{\mathbf{r}}_\perp$, via a vector identity for the vector triple product, where $\mathbf{r}_\perp = \mathbf{r} - (\mathbf{r}\cdot\hat{\mathbf{B}})\hat{\mathbf{B}}$.

Theorem: The time taken to orbit the Fermi surface is

$$T = \frac{\hbar^2}{eB}\frac{\partial A(E)}{\partial E}\bigg|_{\mathbf{k}\cdot\mathbf{B}},$$

where $A(E)$ is the cross-sectional area of the Fermi surface with Fermi energy E.

Proof: The time taken to go between $\mathbf{k}_1$ and $\mathbf{k}_2$ is:

$$t_2 - t_1 = \int_{\mathbf{k}_1}^{\mathbf{k}_2}\frac{1}{|\dot{\mathbf{k}}|}d\mathbf{k} = \frac{\hbar^2}{eB}\int_{\mathbf{k}_1}^{\mathbf{k}_2}\left|\frac{\partial E}{\partial\mathbf{k}_\perp}\right|^{-1}d\mathbf{k},$$

by the real-space equation of motion above. Consider a second orbit at a higher energy, with difference in energy ΔE given by:

$$\Delta E = \left|\frac{\partial E}{\partial\mathbf{k}_\perp}\right|\Delta(\mathbf{k}).$$

The time taken to traverse the orbit is

$$t_2 - t_1 = \frac{\hbar^2}{eB}\frac{1}{\Delta E}\int_{\mathbf{k}_1}^{\mathbf{k}_2}\Delta(\mathbf{k})\,d\mathbf{k},$$

where the integral is the area of the strip between the two orbits. As $\Delta E\to 0$, we recover the result. □

11.4 Holes

If we have a completely filled band, and remove one electron, the vacancy acts like a particle in its own right.

Definition: This particle is called a *hole*.

The energy of a hole is $E_{\text{hole}}(\mathbf{k}) = -E(\mathbf{k})$ where $E(\mathbf{k})$ is the energy of the electron with the same momentum as the hole. Taylor-expanding, we get $m^*_{\text{hole}} = -m^*$.

Finally, the momentum of the hole if $\mathbf{k}_{\text{hole}} = -\mathbf{k}$, and the hole velocity is

$$\mathbf{v}_{\text{hole}} = \frac{1}{\hbar}\frac{\partial E_{\text{hole}}}{\partial\mathbf{k}_{\text{hole}}} = \frac{1}{\hbar}\frac{\partial E}{\partial\mathbf{k}} = +\mathbf{v}.$$

Substituting these into the semi-classical equations of motion, we get:

$$m^*_{\text{hole}}\frac{d\mathbf{v}_{\text{hole}}}{dt} = -\mathbf{F} = +e\mathbf{E},$$

for a hole in an electric field, say. Thus *holes look like positive charge carriers*.

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12 Phonons

12.1 Monatomic lattices

Consider a 1D lattice with spacing a where atoms are free to move, say with position x_n. Assume the potential is

$$\sum_n V(x_n - x_{n-1}).$$

Taylor expand about $x_n = na$ (the equilibrium position), writing $u_n = x_n - na$ for the small deviation. Then to second order the Hamiltonian is:

$$H = \sum_n\frac{p_n^2}{2m} + \frac{\lambda}{2}\sum_n(u_n - u_{n-1})^2.$$

This gives the equations of motion:

$$m\ddot{u}_n = -\lambda(2u_n - u_{n-1} - u_{n+1}).$$

Trial $u_n = Ae^{-i(\omega t + kna)}$, with $k\in[-\pi/a,\pi/a)$ and impose the periodic boundary condition $u_{n+N} = u_n$. We find the dispersion relation:

$$\omega = 2\sqrt{\frac{\lambda}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|.$$

At small k, we get $\omega\approx ak\sqrt{\lambda/m}$, i.e. the speed of sound in the crystal is $c_s = a\sqrt{\lambda/m}$.

12.2 Diatomic lattices

Consider a chain of atoms of alternating masses m and M, spacing a. As before, we find the equations of motion:

$$M\ddot{u}_{2n} = -\lambda(2u_{2n} - u_{2n-1} - u_{2n+1}),$$
$$m\ddot{u}_{2n+1} = -\lambda(2u_{2n+1} - u_{2n} - u_{2n+2}).$$

Trial $u_{2n} = Ae^{-i\omega t - 2ikna}$ and $u_{2n+1} = Be^{-i\omega t - 2ikna}$ (2's in exponent next to a now since effectively periodic with period $2a$). Substituting into the equations of motion, we obtain the eigenvalue problem:

$$\begin{pmatrix} m\omega^2 - 2\lambda & \lambda(1+e^{-2ika}) \\ \lambda(1+e^{2ika}) & M\omega^2 - 2\lambda\end{pmatrix}\begin{pmatrix}A\\B\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix}.$$

Solve by requiring the determinant of the matrix to be zero. This gives two dispersion relations,

$$\omega_{\pm}^2 = \frac{\lambda}{mM}\left(m + M \pm \sqrt{(m-M)^2 + 4mM\cos^2(ka)}\right).$$

The $+$ branch is called the *optical branch* and the $-$ branch is called the *acoustic branch*.

These names come from the eigenvectors associated to these eigenvalues - the acoustic branch has eigenvector $(1, 1)$ so atoms oscillate in sync (longitudinal), whilst the optical branch has eigenvector $(M, -m)$ so the atoms oscillate out of phase (transverse).

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13 Particles in a magnetic field

13.1 Gauge fields

Recall from Part IB Electromagnetism that:

$$\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}$$

where ϕ and $\mathbf{A}$ are called *gauge fields*. Recall that $\mathbf{A}$ and ϕ are not unique; under a *gauge transformation*:

$$\phi \mapsto \phi - \frac{\partial \alpha}{\partial t}, \quad \mathbf{A} \mapsto \mathbf{A} + \nabla\alpha,$$

the electric and magnetic fields remain unchanged. This is a redundancy in our description of the system. Only quantities which are *gauge invariant* are physically meaningful.

Notice that the canonical momentum, $\mathbf{p} = m\dot{\mathbf{x}} + q\mathbf{A}$, is unphysical, as it is altered under a gauge transformation $\mathbf{p} \mapsto q\nabla\alpha$. However, the *mechanical momentum*, $\boldsymbol{\pi} = \mathbf{p} - q\mathbf{A}$ *is* gauge invariant.

13.2 The Schrödinger equation

From the classical theory, we know that the Hamiltonian for a particle of charge q moving in an electromagnetic field is:

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi.$$

Hence the Schrödinger equation is:

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(-i\hbar\nabla - q\mathbf{A}\right)^2\psi + q\phi\psi.$$

Theorem: Provided $\psi \mapsto e^{iq\alpha/\hbar}\psi$ under a gauge transformation, the Schrödinger equation is gauge invariant.

Proof: Define *covariant derivatives* by:

$$\mathcal{D}_t\psi = \frac{\partial\psi}{\partial t} + \frac{iq}{\hbar}\phi\psi,$$

$$\mathcal{D}_i\psi = \frac{\partial\psi}{\partial x_i} - \frac{iq}{\hbar}A_i\psi.$$

An exercise in differentiation shows $\mathcal{D}_t\psi \mapsto e^{iq\alpha/\hbar}\mathcal{D}_t\psi$ under a gauge transformation, and $\mathcal{D}_i\psi \mapsto e^{iq\alpha/\hbar}\mathcal{D}_i\psi$ too. In particular, $\mathcal{D}_i(\mathcal{D}_i\psi) \mapsto e^{iq\alpha/\hbar}\mathcal{D}_i\psi$, since $\mathcal{D}_i\psi$ transforms like the wavefunction under gauge transformation.

In terms of the covariant derivatives, the Schrödinger equation may be written

$$i\hbar\mathcal{D}_t\psi = -\frac{\hbar^2}{2m}\mathcal{D}^2\psi,$$

which is manifestly gauge invariant by the above. □

13.3 Landau levels

Consider the SE in a constant magnetic field $\mathbf{B} = (0, 0, B)$.

Definition: *Landau gauge* is defined by $\mathbf{A} = (0, Bx, 0)$.

Working in Landau gauge, the Hamiltonian becomes:

$$H = \frac{1}{2m}(\hat{p}_x^2 + (\hat{p}_y - qB\hat{x})^2 + \hat{p}_z^2).$$

Solution via wavefunctions: Trial $\psi = e^{ik_y y + ik_z z}\chi(x)$ in the SE. Since $\hat{p}_y\psi = \hbar k_y\psi$ and $\hat{p}_z\psi = \hbar k_z\psi$, we get:

$$H\psi = \frac{1}{2m}\left((\hbar k_y - qB\hat{x})^2 + \hbar^2 k_z^2 + \hat{p}_x^2\right)\psi = E\psi.$$

In particular, the z direction decouples, and we can instead consider the problem:

$$\tilde{H}\chi(x) = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\chi(x),$$

where

$$\tilde{H} = \frac{1}{2m}\hat{p}_x^2 + \frac{m\omega_B^2}{2}(\hat{x} - k_y l_B^2)^2,$$

with $l_B^2 = \hbar/qB$ (the *magnetic length* squared) and $\omega_B = qB/m$ (the *cyclotron frequency*).

This is simply a harmonic oscillator (albeit not centred at the origin). So the energy spectrum is:

$$E_n = \hbar\omega_B\left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m},$$

for $n = 0, 1, 2...$.

Definition: The levels $\hbar\omega_B\,(n + 1/2)$ are called *Landau levels*.

The associated wavefunctions come from the harmonic oscillator:

$$\psi_{n,k_y,k_z} \sim e^{ik_y y + ik_z z} H_n(x - k_y l_B^2) e^{-(x-k_y l_B^2)/2l_B^2},$$

and hence the wavefunctions are localised near $k_y l_B^2$ in the x-direction. This allows us to show:

Theorem: The number of states in an area A is

$$\frac{qBA}{2\pi\hbar}.$$

Proof: Set $k_z = 0$ and restrict to a finite part of the plane of width L_x and length L_y, both finite.

Since L_y is finite, momentum k_y is quantised in units $2\pi/L_y$. Since L_x is finite, the wavefunctions may only be localised near $0 \leq k_y l_B^2 \leq L_x$.

Hence the number of states is:

$$N = \underbrace{\int_0^{L_x/l_B^2} dk}_{\text{possible space}} \Big/ \underbrace{\frac{2\pi}{L_y}}_{\substack{\text{space } k_y \\ \text{takes up}}} = \frac{L_x L_y}{2\pi l_B^2} = \frac{qBA}{2\pi\hbar}. \quad \square$$

Solution via raising and lowering operators: We define raising and lowering operators via:

$$a = \frac{1}{\sqrt{2q\hbar B}}(\pi_x + i\pi_y), \quad a^\dagger = \frac{1}{\sqrt{2q\hbar B}}(\pi_x - i\pi_y).$$

These obey the commutation relation $[a, a^\dagger] = 1$. Also, we may write

$$H = \frac{q\hbar B}{m} a^\dagger a - \frac{q\hbar B}{2m} + \frac{p_z^2}{2m},$$

and after decoupling the z-direction, we can solve for the spectrum via the standard method for a harmonic oscillator.

13.4 The Arahonov-Bohm effect

Consider a particle moving on a fixed circle around a solenoid, at fixed radius r. Although $\mathbf{B} = \mathbf{0}$ on the circle, we have $\mathbf{A} \neq \mathbf{0}$ on the circle, by Part IB Electromagnetism:

$$\oint \mathbf{A} \cdot d\mathbf{x} = \iint \mathbf{B} \cdot d\mathbf{S} = \Phi,$$

the total magnetic flux through the solenoid. Choose gauge with $A_r = 0$, $A_z = 0$ and

$$A_\phi = \frac{\Phi}{2\pi r}.$$

The Hamiltonian becomes

$$H = \frac{1}{2m}(p_\phi - qA_\phi)^2 = \frac{1}{2mr^2}\left(-i\hbar\frac{\partial}{\partial\phi} - q\frac{\Phi}{2m}\right)^2.$$

The energy eigenstates are

$$\psi = \frac{1}{\sqrt{2\pi r}} e^{in\phi},$$

where $n \in \mathbb{Z}$ so that ψ is single-valued. The corresponding eigenvalues are:

$$E = \frac{1}{2\pi r^2}\left(\hbar n - \frac{q\Phi}{2\pi}\right)^2 = \frac{\hbar^2}{2mr^2}\left(n - \frac{\Phi}{\Phi_0}\right)^2,$$

where $\Phi_0 = 2\pi\hbar/q$ is called the *quantum of flux*. Note that if Φ/Φ_0 is an integer, the spectrum is unchanged; however, if it is *not*, we can always detect the fractional part - even though there is no magnetic field outside of the solenoid!

Interpretation: The particle knows about non-local information because it is a quantum particle. Namely, it 'knows about':

$$\oint \mathbf{A} \cdot d\mathbf{x},$$

which *is* a gauge-invariant quantity, and hence physical.

13.5 Spin in a magnetic field

For particles in a magnetic field with spin, we get the coupling term in the Hamiltonian:

$$-\frac{gq}{2m}\mathbf{S} \cdot \mathbf{B},$$

where g is a dimensionless number, approximately equal to 2. This is derived in Quantum Field Theory.

Example: For a particle of charge e and spin $1/2$, with $g = 2$ moving in the magnetic field $\mathbf{B} = (0, 0, B)$, we can write the Hamiltonian as:

$$H = \frac{1}{2m}Q^2,$$

where $Q = \pi_x\sigma_x + \pi_y\sigma_y$, where $\boldsymbol{\sigma}$ are the Pauli matrices. This is easiest to see by working backwards from the result, and recalling $\sigma_x\sigma_y = -i\sigma_z$, $\sigma_y\sigma_x = i\sigma_z$, and evaluating the commutator

$$[\pi_x, \pi_y] = i\hbar qB.$$