

Postgraduate Lectures

1. Time Independent Green's functions

a) Formalism

Green's functions are defined as the solutions of the inhomogeneous equation:

$$[z - \mathcal{L}(\mathbf{r})] G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}') \quad (1.1)$$

where $z = \lambda + is$ is a complex variable and $\mathcal{L}(\mathbf{r})$ is a time-independent, linear, Hermitian operator with eigenfunctions $\phi_n(\mathbf{r})$ and

$$\mathcal{L}(\mathbf{r})\phi_n(\mathbf{r}) = \lambda_n\phi_n(\mathbf{r}) \quad (1.2)$$

$\phi_n(\mathbf{r})$ and $G(\mathbf{r}, \mathbf{r}'; z)$ satisfy the same boundary conditions on the surface of the domain Ω . The set $\{\phi_n\}$ can be considered orthonormal and complete i.e.

$$\int_{\Omega} \phi_n^*(\mathbf{r})\phi_m(\mathbf{r}) d\mathbf{r} = \delta_{nm} \quad (1.3a)$$

$$\sum_n \phi_n(\mathbf{r})\phi_n^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (1.3b)$$

Note that the sum \sum and integral \int operations are more or less interchangeable depending on the nature of the operator \mathcal{L} , continuum or tight binding, and its spectrum, continuous or discrete. It is useful to consider an abstract vector space and use Dirac's notation

$$\phi_n(\mathbf{r}) \equiv \langle \mathbf{r} | \phi_n \rangle \quad (1.4a)$$

$$\delta(\mathbf{r} - \mathbf{r}') \mathcal{L}(\mathbf{r}) \equiv \langle \mathbf{r} | \mathcal{L} | \mathbf{r}' \rangle \quad (1.4b)$$

$$G(\mathbf{r}, \mathbf{r}'; z) \equiv \langle \mathbf{r} | \mathcal{G}(z) | \mathbf{r}' \rangle \quad (1.4c)$$

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \quad (1.4d)$$

$$\int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| = 1 \quad (1.4e)$$

$$(z - \mathcal{L}) \mathcal{G}(z) = 1 \quad (1.4f)$$

$$\mathcal{L} | \phi_n \rangle = \lambda_n | \phi_n \rangle \quad (1.4g)$$

$$\langle \phi_n | \phi_m \rangle = \delta_{nm} \quad (1.4h)$$

$$\sum_n | \phi_n \rangle \langle \phi_n | = 1 \quad (1.4i)$$

We can revert to the \mathbf{r} -representation by taking the $\langle \mathbf{r} |, | \mathbf{r}' \rangle$ matrix element, thus

$$\langle \mathbf{r} | (z - \mathcal{L}) \mathcal{G}(z) | \mathbf{r}' \rangle = \langle \mathbf{r} | 1 | \mathbf{r}' \rangle = \langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \quad (1.5a)$$

$$\begin{aligned} zG(\mathbf{r}, \mathbf{r}'; z) - \langle \mathbf{r} | \mathcal{L} \mathcal{G}(z) | \mathbf{r}' \rangle &= zG(\mathbf{r}, \mathbf{r}'; z) - \int d\mathbf{r}'' \langle \mathbf{r} | \mathcal{L} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | \mathcal{G}(z) | \mathbf{r}' \rangle \\ &= zG(\mathbf{r}, \mathbf{r}'; z) - \mathcal{L}(\mathbf{r})G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad (1.5b)$$

If $z \neq \{\lambda_n\}$ then we can write

$$\mathcal{G}(z) = \frac{1}{z - \mathcal{L}} \quad (1.6)$$

Multiplying (1.6) by (1.4i) and using $F(\mathcal{L}) | \phi_n \rangle = F(\lambda_n) | \phi_n \rangle$ gives

$$\begin{aligned} \mathcal{G}(z) &= \frac{1}{z - \mathcal{L}} \sum_n | \phi_n \rangle \langle \phi_n | \\ &= \sum_n \frac{1}{z - \mathcal{L}} | \phi_n \rangle \langle \phi_n | \\ &= \sum_n \frac{| \phi_n \rangle \langle \phi_n |}{z - \lambda_n} \\ G(\mathbf{r}, \mathbf{r}'; z) &= \sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z - \lambda_n} \end{aligned} \quad (1.7)$$

Since \mathcal{L} is hermitian, all its eigenvalues $\{\lambda_n\}$ are real. Hence $\mathcal{G}(z)$ is an analytic function everywhere on the complex plain except at those points which correspond to the eigenvalues of \mathcal{L} . $\mathcal{G}(z)$ has poles at the discrete eigenvalues of \mathcal{L} . The converse is also true.

If the spectrum is continuous, i.e. there is a range of values of λ such that every value in that range is an eigenvalue of \mathcal{L} , $\mathcal{G}(\lambda)$ is not well defined. If we try to define it by a limiting procedure we find that the side limits $\lim_{s \rightarrow 0^+} \mathcal{G}(\lambda \pm is)$ exist but are different from one another. This is a *branch cut* of $\mathcal{G}(z)$ along the real z -axis.

In disordered systems there are other possibilities besides discrete and continuous spectra (see later).

We can define 2 Green's functions as follows

$$\mathcal{G}^+(\lambda) = \lim_{s \rightarrow 0^+} \mathcal{G}(\lambda + is) \quad (1.8a)$$

$$\mathcal{G}^-(\lambda) = \lim_{s \rightarrow 0^+} \mathcal{G}(\lambda - is) \quad (1.8b)$$

From (1.7) we obtain the results

$$G^*(\mathbf{r}, \mathbf{r}'; z) = G(\mathbf{r}', \mathbf{r}; z^*) \quad (1.9a)$$

$$G^-(\mathbf{r}, \mathbf{r}'; \lambda) = [G^+(\mathbf{r}', \mathbf{r}; \lambda)]^* \quad (1.9b)$$

$$\text{Re } G^-(\mathbf{r}, \mathbf{r}; \lambda) = \text{Re } G^+(\mathbf{r}, \mathbf{r}; \lambda) \quad (1.9c)$$

$$\text{Im } G^-(\mathbf{r}, \mathbf{r}; \lambda) = -\text{Im } G^+(\mathbf{r}, \mathbf{r}; \lambda) \quad (1.9d)$$

Using the identity

$$\lim_{y \rightarrow 0^+} \frac{1}{x \pm iy} = \text{P} \frac{1}{x} \mp i\pi\delta(x) \quad (1.10)$$

we can define

$$\tilde{\mathcal{G}}(\lambda) = \mathcal{G}^+(\lambda) - \mathcal{G}^-(\lambda) \quad (1.11a)$$

$$\tilde{G}(\mathbf{r}, \mathbf{r}'; \lambda) = -2\pi i \sum_n \delta(\lambda - \lambda_n) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \quad (1.11b)$$

Integrating the diagonal elements over \mathbf{r} gives

$$G^\pm(\mathbf{r}, \mathbf{r}; \lambda) = \text{P} \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r})}{\lambda - \lambda_n} \mp i\pi \sum_n \delta(\lambda - \lambda_n) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}) \quad (1.12a)$$

$$\text{Tr } G^\pm(\lambda) = \text{P} \sum_n \frac{1}{\lambda - \lambda_n} \mp i\pi \sum_n \delta(\lambda - \lambda_n) \quad (1.12b)$$

$\sum_n \delta(\lambda - \lambda_n)$ is the density of states (DOS) at λ , $N(\lambda)$; $N(\lambda) d\lambda$ is the number of states in the interval $[\lambda, \lambda + d\lambda]$. The quantity

$$\rho(\mathbf{r}; \lambda) \equiv \sum_n \delta(\lambda - \lambda_n) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}) \quad (1.13)$$

is the DOS per unit volume, and $N(\lambda) = \int \rho(\mathbf{r}; \lambda) d\mathbf{r}$ Hence

$$\begin{aligned} \rho(\mathbf{r}; \lambda) &= \mp \frac{1}{\pi} \text{Im } G^\pm(\mathbf{r}, \mathbf{r}; \lambda) \\ &= \frac{-1}{2\pi i} \tilde{G}(\mathbf{r}, \mathbf{r}; \lambda) \end{aligned} \quad (1.14a)$$

$$N(\lambda) = \mp \frac{1}{\pi} \text{Im } \text{Tr } G^\pm(\lambda) \quad (1.14b)$$

Another important relationship is

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; z) &= \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{z - \lambda_n} \\ &= \int_{-\infty}^{+\infty} d\lambda \sum_n \delta(\lambda - \lambda_n) \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{z - \lambda} \\ &= \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\lambda \frac{\tilde{G}(\mathbf{r}, \mathbf{r}'; \lambda)}{z - \lambda} \end{aligned} \quad (1.15)$$

In particular

$$G(\mathbf{r}, \mathbf{r}; z) = \int_{-\infty}^{+\infty} d\lambda \frac{\rho(\mathbf{r}; \lambda)}{z - \lambda} \quad (1.16)$$

Thus the real and imaginary parts of \mathcal{G} are not independent of one another. (1.16) is an example of a *Kramers–Kronig* relation. One more important property is

$$\frac{dG(\mathbf{r}, \mathbf{r}'; z)}{dz} = - \int d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}''; z) G(\mathbf{r}'', \mathbf{r}'; z) \quad (1.17a)$$

$$\begin{aligned} &= - \int d\mathbf{r}'' \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}'')}{z - \lambda_n} \sum_m \frac{\phi_m(\mathbf{r}'') \phi_m^*(\mathbf{r}')}{z - \lambda_m} \\ &= - \sum_n \frac{\phi_n(\mathbf{r})}{z - \lambda_n} \sum_m \frac{\phi_m^*(\mathbf{r}')}{z - \lambda_m} \int d\mathbf{r}'' \phi_n^*(\mathbf{r}'') \phi_m(\mathbf{r}'') \\ &= - \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{(z - \lambda_n)^2} \\ &= \frac{d}{dz} \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{z - \lambda_n} \\ \frac{dG(\mathbf{r}, \mathbf{r}; \lambda)}{d\lambda} &= - \langle \mathbf{r} | (\lambda - \mathcal{L})^{-2} | \mathbf{r} \rangle \\ &< 0 \quad \lambda \neq \{\lambda_n\} \end{aligned} \quad (1.17b)$$

knowledge of the Green's function permits us to solve the general *inhomogeneous* equation

$$[z - \mathcal{L}(\mathbf{r})] u(\mathbf{r}) = f(\mathbf{r}) \quad (1.18)$$

where $u(\mathbf{r})$ satisfies the same boundary conditions as G and ϕ . By operating with \mathcal{G} on (1.18) we obtain the solution

$$u(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}'; z) f(\mathbf{r}') d\mathbf{r}' \quad z \neq \{\lambda_n\} \quad (1.19a)$$

$$= \int G^\pm(\mathbf{r}, \mathbf{r}'; \lambda) f(\mathbf{r}') d\mathbf{r}' + \phi(\mathbf{r}) \quad z = \{\lambda_n\} \quad (1.19b)$$

where λ_n belongs to the branch cut, the continuous spectrum, of \mathcal{L} , and $\phi(\mathbf{r})$ is a solution of the corresponding homogeneous equation. If z coincides with a discrete eigenvalue of \mathcal{L} , say λ_n , there is no solution of (1.18) unless $f(\mathbf{r})$ is orthogonal to all eigenfunctions $\phi(\mathbf{r})$ corresponding to λ_n .

If $u(\mathbf{r})$ describes the response of a system to a source $f(\mathbf{r})$, then $G(\mathbf{r}, \mathbf{r}')$ describes the response of the same system to a unit point source located at \mathbf{r}' . Note that because of (1.9) this response is essentially the same as that at \mathbf{r}' due to a point source at \mathbf{r} . (19) implies that the response to $f(\mathbf{r})$ can be expressed as the sum of the responses to point sources distributed according to $f(\mathbf{r})$.

b) Example 1

Consider the case $\mathcal{L}(\mathbf{r}) = -\nabla^2$ and the domain Ω extends over the whole 3 dimensional space. Then the eigenfunctions of \mathcal{L} are

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (1.20a)$$

with eigenvalues

$$\lambda_n = \mathbf{k}^2 \quad (1.20b)$$

where \mathbf{k} is real. The spectrum is continuous, from 0 to $+\infty$.

The Green's function can be obtained either by solving the defining equation

$$(z + \nabla^2) G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}') \quad (1.21)$$

or from the solution of the homogeneous eigenvalue problem using (1.7)

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; z) &= \sum_{\mathbf{k}} \frac{\langle \mathbf{r} | \mathbf{k} \rangle \langle \mathbf{k} | \mathbf{r}' \rangle}{z - \mathbf{k}^2} \\ &= \int \frac{d\mathbf{k}}{(2\pi)^d} \frac{e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')}}{z - \mathbf{k}^2} \end{aligned} \quad (1.22)$$

where d is the dimensionality.

Consider the 3-dimensional case $d = 3$. If $\rho = \mathbf{r} - \mathbf{r}'$ and θ is the angle between \mathbf{k} and ρ we can write (1.22) as

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; z) &= \frac{1}{4\pi^2} \int_0^\infty \frac{\mathbf{k}^2 d\mathbf{k}}{z - \mathbf{k}^2} \int_0^\pi d\theta \sin \theta e^{i\mathbf{k} \cdot \rho \cos \theta} \\ &= \frac{1}{4\pi^2} \int_0^\infty \frac{\mathbf{k}^2 d\mathbf{k}}{z - \mathbf{k}^2} \frac{e^{+i\mathbf{k} \cdot \rho} - e^{-i\mathbf{k} \cdot \rho}}{i\mathbf{k} \cdot \rho} \\ &= \frac{1}{4i\pi^2 \rho} \int_{-\infty}^{+\infty} \frac{k e^{i\mathbf{k} \cdot \rho}}{z - \mathbf{k}^2} d\mathbf{k} \end{aligned} \quad (1.23)$$

the integration path can be closed in the upper half plane. Unless z is real and nonnegative, one of the poles, $+\sqrt{z}$, has a positive imaginary part and the other, $-\sqrt{z}$, has a negative imaginary part and lies outside the integration contour. Hence

$$G(\mathbf{r}, \mathbf{r}'; z) = -\frac{e^{i\sqrt{z}|\mathbf{r}-\mathbf{r}'|}}{4\pi |\mathbf{r}-\mathbf{r}'|} \quad \text{Im } \sqrt{z} > 0 \quad (1.24)$$

For $z = \lambda$ and $\lambda > 0$ G is not well defined, but the side limits are

$$G^\pm(\mathbf{r}, \mathbf{r}'; \lambda) = -\frac{e^{\pm i\sqrt{\lambda}|\mathbf{r}-\mathbf{r}'|}}{4\pi |\mathbf{r}-\mathbf{r}'|} \quad \sqrt{\lambda} \geq 0, \quad \lambda \geq 0 \quad (1.25)$$

For $z = \lambda$ and $\lambda < 0$ we obtain

$$G(\mathbf{r}, \mathbf{r}'; \lambda) = -\frac{e^{-\sqrt{\lambda}|\mathbf{r}-\mathbf{r}'|}}{4\pi |\mathbf{r}-\mathbf{r}'|} \quad \sqrt{\lambda} > 0, \quad \lambda \geq 0 \quad (1.26)$$

and for $z = 0$ we have

$$G(\mathbf{r}, \mathbf{r}'; 0) = -\frac{1}{4\pi |\mathbf{r}-\mathbf{r}'|} \quad (1.27)$$

which is the Green's function corresponding to *Laplace's* equation

$$\nabla^2 G(\mathbf{r}, \mathbf{r}'; 0) = \delta(\mathbf{r} - \mathbf{r}') \quad (1.28)$$

By applying (1.19b) we can find the general solution of *Poisson's* equation

$$\nabla^2 V(\mathbf{r}) = -\frac{1}{\epsilon_0} \rho(\mathbf{r}) \quad (1.29a)$$

$$\begin{aligned} V(\mathbf{r}) &= \int G(\mathbf{r}, \mathbf{r}'; z) \frac{-1}{\epsilon_0} \rho(\mathbf{r}') d\mathbf{r}' + C \\ &= \frac{1}{\epsilon_0} \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + C \end{aligned} \quad (1.29b)$$

The constant has been added since the general eigenfunction of $-\nabla^2$ with eigenvalue 0 is a constant. (1.29) is the basic result of electrostatics.

c) Example 2

Now consider the 1-dimensional case

$$\left(z + \frac{d^2}{dx^2} \right) G(x, x'; z) = \delta(x - x') \quad (1.30)$$

For $x \neq x'$ the solution must be that of the homogeneous equation

$$G = Ae^{+i\sqrt{z}x} + Be^{-i\sqrt{z}x} \quad (1.31)$$

With $\text{Im} \sqrt{z} > 0$ only the + solution is finite as $x - x' \rightarrow +\infty$ and only the - solution for $x - x' \rightarrow -\infty$. By integrating (1.30) we find

$$G(x' - , x'; z) = G(x' + , x'; z) \quad (1.32a)$$

$$\left. \frac{dG}{dx} \right|_{x=x'-} = \left. \frac{dG}{dx} \right|_{x=x'+} + 1 \quad (1.32b)$$

We can thus determine the coefficients A and B to obtain

$$G(x, x'; z) = \frac{e^{i\sqrt{z}|x-x'|}}{2i\sqrt{z}} \quad \text{Im} \sqrt{z} > 0 \quad (1.33)$$

For $z = \lambda \geq 0$ we have for the side limits

$$G^\pm(x, x'; \lambda) = \mp \frac{i}{2\sqrt{\lambda}} e^{\pm i\sqrt{\lambda}|x-x'|} \quad \lambda \geq 0 \quad \sqrt{\lambda} > 0 \quad (1.34)$$

whereas for $z = -|\lambda|$ we obtain

$$G(x, x'; -|\lambda|) = -\frac{1}{2\sqrt{|\lambda|}} e^{-\sqrt{|\lambda|}|x-x'|} \quad \lambda < 0 \quad \sqrt{|\lambda|} > 0 \quad (1.35)$$

and for the 1-D Laplace's equation, $z = 0$,

$$G(x, x'; 0) = \frac{1}{2} |x - x'| + \text{const} \quad (1.36)$$

2. Time-Dependent Green's Functions

a) First-Order Case

The Green's function $g(\mathbf{r}, \mathbf{r}', t - t')$ associated with the 1st order (in time) P.D.E's

$$\left[\frac{i}{c} \frac{\partial}{\partial t} - \mathcal{L}(\mathbf{r}) \right] \phi(\mathbf{r}, t) = 0 \quad (2.1a)$$

$$\left[\frac{i}{c} \frac{\partial}{\partial t} - \mathcal{L}(\mathbf{r}) \right] \psi(\mathbf{r}, t) = f(\mathbf{r}, t) \quad (2.1b)$$

is defined by

$$\left[\frac{i}{c} \frac{\partial}{\partial t} - \mathcal{L}(\mathbf{r}) \right] g(\mathbf{r}, \mathbf{r}', t, t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (2.2)$$

subject to the same boundary conditions as ϕ and ψ . For the moment assume that c is a positive constant. The operator $\mathcal{L}(\mathbf{r})$ is as in section 1.

Expressing $g(\mathbf{r}, \mathbf{r}', \tau)$, where $\tau = t - t'$ via its Fourier transform we obtain

$$g(\tau) = \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} e^{-i\omega'\tau} g(\omega') \quad (2.3a)$$

$$\left(\frac{\omega}{c} - \mathcal{L} \right) g(\omega) = \delta(\mathbf{r} - \mathbf{r}') \quad (2.3b)$$

$$g(\omega) = G\left(\frac{\omega}{c}\right) \quad (2.3c)$$

where $G(z)$ is the Green's function discussed in section 1. As before it may be necessary to use a limiting procedure to define $g(\tau)$.

$$g^\pm(\tau) = \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} G^\pm\left(\frac{\omega'}{c}\right) e^{-i\omega'\tau} \quad (2.4)$$

In analogy with the previous procedure we can also define

$$\tilde{g}(\tau) = g^+(\tau) - g^-(\tau) \quad (2.5)$$

Note \tilde{g} is integrated along a line just above the real axis and back just below. This contour thus contains all the eigenvalues of $\mathcal{L}(\mathbf{r})$. However $g^\pm(\tau)$ requires its integral to be closed around either the upper or the lower half plane. This is chosen such that the exponential becomes negligible well away from the real axis. Thus the appropriate choice is the lower (upper) half plane for $\tau > 0$ ($\tau < 0$).

The g 's obey the relationships

$$g^\pm = \pm \Theta(\pm\tau) \tilde{g}(\tau) \quad (2.6a)$$

$$g^-(\mathbf{r}, \mathbf{r}', \tau) = [g^+(\mathbf{r}', \mathbf{r}, -\tau)]^* \quad (2.6b)$$

We can write $\tilde{g}(\tau)$ as

$$\begin{aligned} \tilde{g}(\tau) &= \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} e^{-i\omega'\tau} \tilde{G}\left(\frac{\omega'}{c}\right) \\ &= -2\pi i \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} e^{-i\omega'\tau} \sum_n \delta\left(\frac{\omega'}{c} - \lambda_n\right) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \\ &= -ic \sum_n e^{-ic\lambda_n\tau} \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \end{aligned} \quad (2.7)$$

The corresponding operator $\tilde{g}(\tau)$ is then

$$\begin{aligned} \tilde{g}(\tau) &= -ic \sum_n e^{-ic\lambda_n\tau} |\phi_n\rangle \langle \phi_n| \\ &= -ice^{-i\mathcal{L}\tau} \end{aligned} \quad (2.8)$$

where

$$U(t-t') = e^{-ic\mathcal{L}(t-t')} = \frac{i}{c}\tilde{g}(t-t') \quad (2.9)$$

is the time–evolution operator or a propagator because

$$|\phi(t)\rangle = U(t-t')|\phi(t')\rangle \quad (2.10)$$

Note also that

$$\tilde{g}(\mathbf{r}, \mathbf{r}', 0) = -ic\delta(\mathbf{r} - \mathbf{r}') \quad (2.11a)$$

$$U(t_1 - t_2) = U(t_1 - t_3)U(t_3 - t_2) \quad (2.11b)$$

By combining (2.9) and (2.10) we obtain

$$\phi(\mathbf{r}, t) = \frac{i}{c} \int \tilde{g}(\mathbf{r}, \mathbf{r}', t-t')\phi(\mathbf{r}', t') d\mathbf{r}' \quad (2.12)$$

The solution of the inhomogeneous equation, $\psi(\mathbf{r}, t)$, can be expressed as

$$\psi(\mathbf{r}, t) = \phi(\mathbf{r}, t) + \int d\mathbf{r}' dt' g^+(\mathbf{r}, \mathbf{r}', t-t')f(\mathbf{r}', t') \quad (2.13a)$$

$$= \phi(\mathbf{r}, t) + \int d\mathbf{r}' \int_{-\infty}^t dt' \tilde{g}(\mathbf{r}, \mathbf{r}', t-t')f(\mathbf{r}', t') \quad (2.13b)$$

This is best proved by substitution of (2.13) in (2.1) and using (2.2). If we had used $g^-(\tau)$ instead of $g^+(\tau)$ the resulting $\psi(\mathbf{r}, t)$ would have satisfied (2.1b). We have excluded this solution using the physical argument that the response of the system at a time t depends only on what the source was in the past ($t' < t$).

b) Example

Consider again the case $\mathcal{L} = -\nabla^2$. It suffices to calculate $\tilde{g}(\tau)$. Using (2.7) and $\phi_n(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{\Omega}$ and $\lambda_n = k^2$ we get

$$\begin{aligned} \tilde{g}(\mathbf{r}, \mathbf{r}', \tau) &= -ic \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot (\mathbf{r}-\mathbf{r}')}}{\Omega} e^{-ick^2\tau} \\ &= -ic \int \frac{d^d k}{(2\pi)^d} e^{i\mathbf{k} \cdot \boldsymbol{\rho} - ick^2\tau} \end{aligned} \quad (2.14)$$

where $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}'$ and d is the dimensionality. Using $\mathbf{k} \cdot \boldsymbol{\rho} = \sum_{i=1}^d k_i \rho_i$ and $k^2 = \sum_{i=1}^d k_i^2$ we can rewrite (2.14) as

$$\begin{aligned} \tilde{g}(\mathbf{r}, \mathbf{r}', \tau) &= -ic \prod_{i=1}^d \int_{-\infty}^{+\infty} \frac{dk_i}{2\pi} e^{ik_i \rho_i - ick_i^2\tau} \\ &= -ic \prod_{i=1}^d \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{\frac{i\rho_i^2}{4c\tau}} e^{-ic\tau k^2} \\ &= -ic \prod_{i=1}^d e^{\frac{i\rho_i^2}{4c\tau}} \frac{1}{2\pi} \sqrt{\frac{\pi}{ic\tau}} \\ &= -ic \left(\frac{1}{4\pi ic\tau} \right)^{\frac{d}{2}} e^{\frac{i\rho^2}{4c\tau}} \end{aligned} \quad (2.15)$$

where $\sqrt{\pi/ic\tau}$ is the square root with a positive real part. (2.15) and (2.12) allow us to study the time evolution of a wave–packet.

If we choose $c = -i\kappa$ where κ is a positive constant, and $\mathcal{L} = \nabla^2$ we obtain the diffusion equation $-\partial\phi/\kappa\partial t + \nabla^2\phi = 0$. Again for causality reasons we need $g^+(\tau)$ only. It is more convenient to consider the *Laplace* transform, rather than the *Fourier* transform. The final result, obtained by substituting $c \mapsto -i\kappa$ in (2.15), is

$$g^+(\mathbf{r}, \mathbf{r}', t-t') = -\kappa\Theta(t-t') \left(\frac{1}{4\pi\kappa(t-t')} \right)^{\frac{d}{2}} \exp\left(\frac{-(\mathbf{r}-\mathbf{r}')^2}{4\kappa(t-t')} \right) \quad (2.16)$$

Note that $g^+ \mapsto -\kappa\delta(\mathbf{r}-\mathbf{r}')$ as $t-t' \mapsto 0^+$. As t increases, g^+ describes the diffusion of a local initial pulse. Note that the average diffusion range increases as $\sqrt{t-t'}$.

c) Second-Order Case

The second-order differential equation gives

$$\left[-\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \mathcal{L}(\mathbf{r}) \right] \phi(\mathbf{r}, t) = 0 \quad (2.17a)$$

$$\left[-\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \mathcal{L}(\mathbf{r}) \right] \psi(\mathbf{r}, t) = f(\mathbf{r}, t) \quad (2.17b)$$

$$\left[-\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \mathcal{L}(\mathbf{r}) \right] g(\mathbf{r}, \mathbf{r}', t - t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (2.17c)$$

subject to the same boundary conditions on ϕ , ψ , and g . As before we express $g(\tau)$ as a Fourier transform of $g(\omega)$

$$g(\tau) = \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} e^{-i\omega'\tau} g(\omega') \quad (2.18a)$$

$$g(\omega) = G\left(\frac{\omega^2}{c^2}\right) \quad (2.18b)$$

Since $G(z)$ has all its singularities on the real z -axis, $g(\omega)$ is analytic everywhere on the complex ω plane except on the real or imaginary axes. However on physical grounds we can restrict ourselves to the case where all the eigenfrequencies ω_n are real. Then the singularities of $G(z)$ are all on the positive real z -semiaxis.

Again near a branch cut it may be necessary to use a limiting procedure to define $g(\omega)$. There are 4 cases

$$\begin{aligned} g^+(\omega') &= \lim_{s \rightarrow 0^+} G\left(\frac{\omega'^2}{c^2} + is\right) \\ &= G^+\left(\frac{\omega'^2}{c^2}\right) = \lim_{s \rightarrow 0^+} g(\omega' + is\bar{\epsilon}(\omega')) \end{aligned} \quad (2.19a)$$

$$g^R(\omega') = \lim_{s \rightarrow 0^+} G\left(\frac{\omega'^2}{c^2} + is\bar{\epsilon}(\omega')\right) = \lim_{s \rightarrow 0^+} g(\omega' + is) \quad (2.19b)$$

$$g^A(\omega') = \lim_{s \rightarrow 0^+} G\left(\frac{\omega'^2}{c^2} - is\bar{\epsilon}(\omega')\right) = \lim_{s \rightarrow 0^+} g(\omega' - is) \quad (2.19c)$$

$$\begin{aligned} g^-(\omega') &= \lim_{s \rightarrow 0^+} G\left(\frac{\omega'^2}{c^2} - is\right) \\ &= G^-\left(\frac{\omega'^2}{c^2}\right) = \lim_{s \rightarrow 0^+} g(\omega' - is\bar{\epsilon}(\omega')) \end{aligned} \quad (2.19d)$$

where

$$\bar{\epsilon}(x) = \begin{cases} 1 & \text{if } x > 0 \\ -1 & \text{if } x < 0 \end{cases} \quad (2.20)$$

and ω' is real. These are referred to as the *causal* (a), *retarded* (b), and *advanced* (c) Green's functions. The fourth case is not independent and can be derived from $g^R + g^A = g^+ + g^-$.

We can also define 3 different \tilde{g} 's as

$$\tilde{g}^> = g^+ - g^A \quad (2.21a)$$

$$\tilde{g}^< = g^+ - g^R \quad (2.21b)$$

$$\tilde{g} = g^R - g^A = \tilde{g}^> - \tilde{g}^< \quad (2.21c)$$

Note that the \tilde{g} 's satisfy the homogeneous equation (2.17a) rather than (2.17c).

As before by noting that the path for the various g 's can be closed in the upper (or lower) half plane when τ is larger (smaller) than zero we have

$$g^+(\tau) = \Theta(\tau)\tilde{g}^>(\tau) + \Theta(-\tau)\tilde{g}^<(\tau) \quad (2.22a)$$

$$g^R(\tau) = \Theta(\tau)\tilde{g}(\tau) \quad (2.22b)$$

$$g^A(\tau) = -\Theta(-\tau)\tilde{g}(\tau) \quad (2.22c)$$

$$g^-(\tau) = -\Theta(\tau)\tilde{g}^<(\tau) - \Theta(-\tau)\tilde{g}^>(\tau) \quad (2.22d)$$

It can also be shown

$$\begin{aligned}
\tilde{g}^>(\mathbf{r}, \mathbf{r}', \tau) &= \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega\tau} \tilde{G} \left(\frac{\omega^2}{c^2} \right) \\
&= - \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega\tau} 2\pi i \sum_n \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \delta \left(\frac{\omega^2}{c^2} - \lambda_n \right) \\
&= \frac{-ic}{2} \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\sqrt{\lambda_n}} e^{-ic\sqrt{\lambda_n}\tau}
\end{aligned} \tag{2.23}$$

where $\sqrt{\lambda_n} \geq 0$. Similarly

$$\tilde{g}^< = \frac{-ic}{2} \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\sqrt{\lambda_n}} e^{ic\sqrt{\lambda_n}\tau} \tag{2.24}$$

and also

$$\tilde{g}^<(\mathbf{r}, \mathbf{r}', \tau) = - [\tilde{g}^>(\mathbf{r}', \mathbf{r}, \tau)]^* \tag{2.25a}$$

$$\tilde{g}(\mathbf{r}, \mathbf{r}', \tau) = -c \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\sqrt{\lambda_n}} \sin(c\sqrt{\lambda_n}\tau) \tag{2.25b}$$

$$\tilde{g}(\tau) = -c \frac{\sin(c\sqrt{\mathcal{L}}\tau)}{\sqrt{\mathcal{L}}} \quad \text{in operator form} \tag{2.25c}$$

Consider now the expression

$$|\phi(t)\rangle = -\frac{1}{c^2} [\tilde{g}(t-t') |\dot{\phi}(t')\rangle + \dot{\tilde{g}}(t-t') |\phi(t')\rangle] \tag{2.26a}$$

$$\begin{aligned}
\phi(\mathbf{r}, t) &= -\frac{1}{c^2} \int d\mathbf{r}' \tilde{g}(\mathbf{r}, \mathbf{r}', t-t') \dot{\phi}(\mathbf{r}', t') \\
&\quad - \frac{1}{c^2} \int d\mathbf{r}' \dot{\tilde{g}}(\mathbf{r}, \mathbf{r}', t-t') \phi(\mathbf{r}', t')
\end{aligned} \tag{2.26b}$$

where the dot denotes differentiation with respect to t and $\dot{\phi}(t')$ is $d\phi/dt$ for $t = t'$. Since $\tilde{g}(t-t')$ satisfies the homogeneous equation (2.17a) so does $\phi(\mathbf{r}, t)$. Also $\phi(t) \rightarrow \phi(t')$ and $\dot{\phi}(t) \rightarrow \dot{\phi}(t')$ as $t \rightarrow t'$. Thus this determines the solution of (2.17a) for time t in terms of $\phi(t')$ and $\dot{\phi}(t')$ at time t' . Then

$$\psi(\mathbf{r}, t) = \phi(\mathbf{r}, t) + \int d\mathbf{r}' dt' g^R(\mathbf{r}, \mathbf{r}', t-t') f(\mathbf{r}', t') \tag{2.27a}$$

$$= \phi(\mathbf{r}, t) + \int d\mathbf{r}' \int_{-\infty}^t dt' \tilde{g}(\mathbf{r}, \mathbf{r}', t-t') f(\mathbf{r}', t') \tag{2.27b}$$

satisfies the inhomogeneous equation (2.17b) where $\phi(\mathbf{r}, t)$ is the general solution of (2.17a). g^R is used because the response can only depend on the source at times $t' \leq t$.

c) Example (2nd Order)

Consider again the case $\mathcal{L} = -\nabla^2$ in 3-D for which $G^\pm(\lambda)$ are given by (1.25). Substituting in (2.23) we get

$$\tilde{g}^>(\rho, \tau) = -\frac{1}{4\pi\rho} \int_0^\infty \frac{d\omega}{2\pi} e^{-i\omega\tau} (e^{+i\omega\rho/c} - e^{-i\omega\rho/c}) \quad (2.28a)$$

$$\tilde{g}^<(\rho, \tau) = -\frac{1}{4\pi\rho} \int_0^\infty \frac{d\omega}{2\pi} e^{+i\omega\tau} (e^{+i\omega\rho/c} - e^{-i\omega\rho/c}) \quad (2.28b)$$

where $\rho = \mathbf{r} - \mathbf{r}'$. Subtracting we get

$$\begin{aligned} \tilde{g}(\rho, \tau) &= \frac{1}{4\pi\rho} \int_0^\infty \frac{d\omega}{2\pi} (e^{+i\omega\rho/c} - e^{-i\omega\rho/c}) (e^{+i\omega\tau} - e^{-i\omega\tau}) \\ &= \frac{1}{4\pi\rho} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} (e^{i\omega(\rho/c+\tau)} - e^{i\omega(\rho/c-\tau)}) \\ &= \frac{1}{4\pi\rho} \left[\delta\left(\frac{\rho}{c} + \tau\right) - \delta\left(\frac{\rho}{c} - \tau\right) \right] \\ &= \frac{c}{4\pi\rho} [\delta(\rho + c\tau) - \delta(\rho - c\tau)] \end{aligned} \quad (2.29)$$

Using (2.29) and (2.22) we obtain

$$g^R(\mathbf{r}, \mathbf{r}', t - t') = -\frac{c}{4\pi|\mathbf{r} - \mathbf{r}'|} \delta(|\mathbf{r} - \mathbf{r}'| - c(t - t')) \quad (2.30a)$$

$$g^A(\mathbf{r}, \mathbf{r}', t - t') = -\frac{c}{4\pi|\mathbf{r} - \mathbf{r}'|} \delta(|\mathbf{r} - \mathbf{r}'| + c(t - t')) \quad (2.30b)$$

Then the solution of the inhomogeneous wave equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \psi(\mathbf{r}, t) = f(\mathbf{r}, t)$$

is from (2.27)

$$\begin{aligned} \psi(\mathbf{r}, t) &= \phi(\mathbf{r}, t) - \frac{1}{4\pi} \int d\mathbf{r}' dt' \delta\left(\frac{\rho}{c} - (t - t')\right) \frac{f(\mathbf{r}', t')}{\rho} \\ &= \phi(\mathbf{r}, t) - \frac{1}{4\pi} \int d\mathbf{r}' \frac{f\left(\mathbf{r}', t - \frac{|\mathbf{r} - \mathbf{r}'|}{c}\right)}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \quad (2.31)$$

which is the basic result of electromagnetic theory.

3. Application to Free Quantum–Mechanical Particles

a) General Relations

The one–particle time–independent Schrödinger equation and its Green's function have the form

$$[E - \mathcal{H}(\mathbf{r})] \psi(\mathbf{r}) = 0 \quad (3.1a)$$

$$[E - \mathcal{H}(\mathbf{r})] \mathcal{G}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}') \quad (3.1b)$$

where $\mathcal{H}(\mathbf{r})$ is the Hamiltonian in the \mathbf{r} –representation and $G(\mathbf{r}, \mathbf{r}'; E)$ satisfies the same boundary conditions as $\psi(\mathbf{r})$. From section 1. it is clear that

$$\mathcal{L}(\mathbf{r}) \rightarrow \mathcal{H}(\mathbf{r}) \quad (3.2a)$$

$$\lambda \rightarrow E \quad (3.2b)$$

$$\lambda + is = z \rightarrow z = E + is \quad (3.2c)$$

$$\lambda_n \rightarrow E_n \quad (3.2d)$$

$$\phi_n(\mathbf{r}) \rightarrow \phi_n(\mathbf{r}) \quad (3.2e)$$

Thus G is related to the eigenvalues, E_n , and eigenfunctions, ϕ_n , of \mathcal{H} by

$$G(\mathbf{r}, \mathbf{r}'; z) = \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{z - E_n} \quad (3.3a)$$

$$\mathcal{G}(z) = \sum_n \frac{|\phi_n\rangle \langle \phi_n|}{z - E_n} = \frac{1}{z - \mathcal{H}} \quad (3.3b)$$

The singularities of $\mathcal{G}(z)$ are on the real axis and

- 1) The poles of $\mathcal{G}(z)$ coincide with the discrete eigenvalues of \mathcal{H} , and vice versa.
- 2) The residue at each pole E_n of $G(\mathbf{r}, \mathbf{r}'; z)$ is $\sum_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}')$ where \sum_i is over the f_n degenerate eigenstates corresponding to E_n .
- 3) The degeneracy f_n can be found by integrating the residue of the diagonal matrix element $G(\mathbf{r}, \mathbf{r}; E_n)$ over \mathbf{r} i.e.,

$$\begin{aligned} f_n &= \int d^3r \text{Res } G(\mathbf{r}, \mathbf{r}; E_n) \\ &= \text{Tr Res } \mathcal{G}(E_n) \end{aligned} \quad (3.4)$$

For a non–degenerate state $f_n = 1$ and

$$\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') = \text{Res } G(\mathbf{r}, \mathbf{r}'; E_n) \quad (3.5a)$$

$$|\phi_n(\mathbf{r})| = \sqrt{[\text{Res } G(\mathbf{r}, \mathbf{r}; E_n)]} \quad (3.5b)$$

$$p_n(\mathbf{r}) = -i \ln \left\{ \frac{\text{Res } G(\mathbf{r}, 0; E_n)}{\sqrt{[\text{Res } G(\mathbf{r}, \mathbf{r}; E_n) \cdot \text{Res } G(0, 0; E_n)]}} \right\} \quad (3.5c)$$

where $p_n(\mathbf{r})$ is the phase of $\phi(\mathbf{r})$ (assuming $p_n(0) = 0$).

- 4) The branch cuts of $\mathcal{G}(z)$ along the real z –axis coincide with the continuous spectrum of \mathcal{H} and vice versa.
- 5) The density of states per unit volume is given by

$$\rho(\mathbf{r}; E) = \mp \frac{1}{\pi} \text{Im } G^\pm(\mathbf{r}, \mathbf{r}; E) \quad (3.6)$$

- 6) The density of states $N(E)$ is given by

$$\begin{aligned} N(E) &= \int d\mathbf{r} \rho(\mathbf{r}; E) \\ &= \mp \frac{1}{\pi} \text{Tr Im } \mathcal{G}^\pm(E) \end{aligned} \quad (3.7)$$

7) The time-dependent Schrödinger equation gives

$$\left(i\hbar \frac{\partial}{\partial t} - \mathcal{H} \right) |\psi(t)\rangle = 0 \quad (3.8a)$$

$$|\psi(t)\rangle = \mathcal{U}(t-t_0) |\psi(t_0)\rangle \quad (3.8b)$$

$$\mathcal{U}(t-t_0) = \exp\left(-i \frac{(t-t_0)\mathcal{H}}{\hbar}\right) \quad (3.8c)$$

$$\begin{aligned} &= i\hbar \tilde{g}(t-t_0) \\ &= i\hbar \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t_0)} \tilde{\mathcal{G}}(\hbar\omega) \end{aligned} \quad (3.8d)$$

$$\psi(\mathbf{r}, t) = i\hbar \int \tilde{g}(\mathbf{r}, \mathbf{r}', t-t_0) \psi(\mathbf{r}', t_0) d\mathbf{r}' \quad (3.8e)$$

b) The Free-Particle Case, $\mathcal{H}_0 = p^2/2m$.

We denote the free-particle Hamiltonian by \mathcal{H}_0 where

$$\mathcal{H}_0 = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \quad (3.9)$$

and $\mathcal{G}_0(z)$ is the corresponding Green's function

$$\left(z + \frac{\hbar^2}{2m} \nabla_r^2 \right) G_0(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}') \quad (3.10)$$

Hence

$$G_0(\mathbf{r}, \mathbf{r}'; z) = \frac{2m}{\hbar^2} G\left(\mathbf{r}, \mathbf{r}'; \frac{2mz}{\hbar^2}\right) \quad (3.11)$$

where $G(\mathbf{r}, \mathbf{r}'; z)$ is the Green's function corresponding to the operator $\mathcal{L} = -\nabla^2$. Thus we have for G_0
3-D Case

$$G_0(\mathbf{r}, \mathbf{r}'; E) = -\frac{m}{2\pi\hbar^2} \frac{e^{-k_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad E \leq 0 \quad (3.12a)$$

$$G_0^\pm(\mathbf{r}, \mathbf{r}'; E) = -\frac{m}{2\pi\hbar^2} \frac{e^{\pm ik_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad E \geq 0 \quad (3.12b)$$

$$k_0 = \sqrt{\frac{2m|E|}{\hbar^2}} \geq 0 \quad (3.12c)$$

$\tilde{\mathcal{G}}_0(z)$ has a branch cut along the +ve E -axis corresponding to the continuous spectrum of \mathcal{H}_0 . Then

$$\tilde{G}(\mathbf{r}, \mathbf{r}'; E) = G^+(\mathbf{r}, \mathbf{r}'; E) - G^-(\mathbf{r}, \mathbf{r}'; E) \quad (3.13a)$$

$$= -2\pi i \frac{m}{2\pi^2\hbar^2} \frac{\sin(k_0|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \Theta(E) \quad (3.13b)$$

$$\begin{aligned} \rho_0(\mathbf{r}; E) &= \frac{\tilde{G}_0(\mathbf{r}, \mathbf{r}'; E)}{-2\pi i} \\ &= \frac{mk_0}{2\pi^2\hbar^2} \Theta(E) \\ &= \Theta(E) \frac{m^{\frac{3}{2}}}{\sqrt{2\pi^2\hbar^3}} \sqrt{E} \end{aligned} \quad (3.13c)$$

¶ $\hbar = h/2\pi$, where h is Planck's constant

1-D Case

$$G_0(x, x'; E) = -\frac{m}{\hbar^2 k_0} e^{k_0 |r-r'|} \quad E < 0 \quad (3.14a)$$

$$G_0^\pm(x, x'; E) = \mp \frac{im}{\hbar^2 k_0} e^{\pm ik_0 |r-r'|} \quad E < 0 \quad (3.14b)$$

$$\tilde{G}_0(x, x'; E) = -2\pi i \Theta(E) \frac{m}{\pi \hbar^2 k_0} \cos(k_0 |x-x'|) \quad (3.14c)$$

$$\begin{aligned} \rho_0(x; E) &= \frac{\tilde{G}_0(x, x; E)}{-2\pi i} \\ &= \Theta(E) \frac{m}{\pi \hbar^2 k_0} \\ &= \Theta(E) \frac{\sqrt{m}}{\sqrt{2\pi\hbar}} \frac{1}{\sqrt{E}} \end{aligned} \quad (3.14d)$$

Note that the behaviour of $\rho(\mathbf{r}; E)$, and hence of $\tilde{G}(E)$ and $G^\pm(E)$, at the band edge $E \rightarrow 0+$ depends crucially on the dimensionality. In general

$$\lim_{E \rightarrow E_B^+} \rho(E) \sim (E - E_B)^{\frac{d-2}{2}} \quad (3.15a)$$

$$\lim_{E \rightarrow E_B^+} G^\pm(\mathbf{r}, \mathbf{r}'; E) \sim \begin{cases} \text{const.} & \text{in 3-D} \\ -\ln(z) & \text{in 2-D} \\ \frac{1}{\sqrt{z}} & \text{in 1-D} \end{cases} \quad (3.15b)$$

4. Perturbation Theory

a) Time-Independent Case

Suppose that the one-particle Hamiltonian, \mathcal{H} , can be separated into an unperturbed part, \mathcal{H}_0 , and a perturbation, \mathcal{H}_1 where

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \quad (4.1)$$

Assuming we can solve for the Green's function \mathcal{G}_0 of \mathcal{H}_0 , how can we find \mathcal{G} of \mathcal{H} ? Noting that

$$\mathcal{G}_0(z) = (z - \mathcal{H}_0)^{-1} \quad (4.2a)$$

$$\mathcal{G}(z) = (z - \mathcal{H})^{-1} \quad (4.2b)$$

we proceed as follows

$$\begin{aligned} \mathcal{G} &= [z - \mathcal{H}_0 - \mathcal{H}_1]^{-1} \\ &= [\mathcal{G}_0^{-1} - \mathcal{H}_1]^{-1} \\ [\mathcal{G}_0^{-1} - \mathcal{H}_1] \mathcal{G} &= \mathcal{I} \\ [\mathcal{I} - \mathcal{G}_0 \mathcal{H}_1] \mathcal{G} &= \mathcal{G}_0 \\ \mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G} \end{aligned} \quad (4.3)$$

This is often called *Dyson's equation*. It is the starting point for almost everything that follows. Note that (4.3) can be expanded to give

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \dots \quad (4.4a)$$

$$= \mathcal{G}_0 + (\mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \dots) \mathcal{H}_1 \mathcal{G}_0 \quad (4.4b)$$

$$= \mathcal{G}_0 + \mathcal{G} \mathcal{H}_1 \mathcal{G}_0 \quad (4.4c)$$

In the \mathbf{r} -representation (4.3) becomes

$$G(\mathbf{r}, \mathbf{r}'; z) = G_0(\mathbf{r}, \mathbf{r}'; z) + \int d\mathbf{r}_1 d\mathbf{r}_2 G_0(\mathbf{r}, \mathbf{r}_1; z) H_1(\mathbf{r}_1, \mathbf{r}_2) G(\mathbf{r}_2, \mathbf{r}'; z) \quad (4.5)$$

Often $H_1(\mathbf{r}_1, \mathbf{r}_2)$ is a local potential which can be written $\delta(\mathbf{r}_1 - \mathbf{r}_2)V(\mathbf{r}_1)$; then (4.5) becomes

$$G(\mathbf{r}, \mathbf{r}'; z) = G_0(\mathbf{r}, \mathbf{r}'; z) + \int d\mathbf{r}_1 G_0(\mathbf{r}, \mathbf{r}_1; z)V(\mathbf{r}_1)G(\mathbf{r}_1, \mathbf{r}'; z) \quad (4.6)$$

which is a linear inhomogeneous integral equation with a kernel of the form $G_0(\mathbf{r}, \mathbf{r}_1; z)V(\mathbf{r}_1)$.

In the \mathbf{k} -representation we can write

$$G(\mathbf{k}, \mathbf{k}'; z) = G_0(\mathbf{k}, \mathbf{k}'; z) + \sum_{\mathbf{k}_1, \mathbf{k}_2} G_0(\mathbf{k}, \mathbf{k}_1; z)H_1(\mathbf{k}_1, \mathbf{k}_2)G(\mathbf{k}_2, \mathbf{k}'; z) \quad (4.7)$$

where we have used the relations

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{\Omega}} \quad (4.8a)$$

$$\sum_{\mathbf{k}} = \Omega \int \frac{d\mathbf{k}}{(2\pi)^d} \quad (4.8b)$$

Next we introduce the t -matrix $T(z)$ which can be defined via

$$\mathcal{G}(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)T(z)\mathcal{G}_0(z) \quad (4.9)$$

By comparing (4.9) with (4.3) and (4.4) we see that

$$\begin{aligned} T &= \mathcal{H}_1 + \mathcal{H}_1(\mathcal{G}_0 + \mathcal{G}_0\mathcal{H}_1\mathcal{G}_0 + \dots)\mathcal{H}_1 \\ &= \mathcal{H}_1 + \mathcal{H}_1\mathcal{G}\mathcal{H}_1 \end{aligned} \quad (4.9a)$$

$$\begin{aligned} &= \mathcal{H}_1 + \mathcal{H}_1\mathcal{G}_0(\mathcal{H}_1 + \mathcal{H}_1\mathcal{G}_0\mathcal{H}_1 + \dots) \\ &= \mathcal{H}_1 + \mathcal{H}_1\mathcal{G}_0T \end{aligned} \quad (4.9b)$$

$$\begin{aligned} &= \mathcal{H}_1 + (\mathcal{H}_1 + \mathcal{H}_1\mathcal{G}_0\mathcal{H}_1 + \dots)\mathcal{G}_0\mathcal{H}_1 \\ &= \mathcal{H}_1 + T\mathcal{G}_0\mathcal{H}_1 \end{aligned} \quad (4.9c)$$

Clearly all the reservations about the behaviour of $\mathcal{G}(z)$ close to the real axis also apply to $T(z)$. Thus $T(z)$ is undefined where z is equal to a discrete eigenvalue of \mathcal{H} , and we must define $T^\pm(E)$ close to a branch cut (a continuum).

As before (4.9) will become an integral equation in either \mathbf{r} or \mathbf{k} representations. Thus

$$T(\mathbf{k}, \mathbf{k}'; z) = H_1(\mathbf{k}, \mathbf{k}') + \sum_{\mathbf{k}_1, \mathbf{k}_2} H_1(\mathbf{k}, \mathbf{k}_1)G_0(\mathbf{k}_1, \mathbf{k}_2; z)T(\mathbf{k}_2, \mathbf{k}'; z) \quad (4.10)$$

$$H_1(\mathbf{k}, \mathbf{k}') \equiv \langle \mathbf{k} | \mathcal{H}_1 | \mathbf{k}' \rangle = \frac{1}{\Omega} \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}'} \mathcal{H}_1(\mathbf{r}, \mathbf{r}')$$

$$G_0(\mathbf{k}_1, \mathbf{k}_2; z) \equiv \langle \mathbf{k}_1 | \mathcal{G}_0(z) | \mathbf{k}_2 \rangle = \frac{1}{\Omega} \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i\mathbf{k}_1 \cdot \mathbf{r}_1 + i\mathbf{k}_2 \cdot \mathbf{r}_2} G_0(\mathbf{r}_1, \mathbf{r}_2; z)$$

$$T(\mathbf{k}, \mathbf{k}'; z) \equiv \langle \mathbf{k} | T(z) | \mathbf{k}' \rangle = \frac{1}{\Omega} \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}'} T(\mathbf{r}, \mathbf{r}'; z)$$

In the usual case when $\mathcal{H}_1(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')V(\mathbf{r})$ and $G_0(\mathbf{r}, \mathbf{r}'; z)$ is a function of $\mathbf{r} - \mathbf{r}'$ only. This simplifies to

$$\begin{aligned} H_1(\mathbf{k}, \mathbf{k}') &= V(\mathbf{k} - \mathbf{k}') \frac{1}{\Omega} \\ V(\mathbf{q}) &= \int d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} \quad \mathbf{q} = \mathbf{k} - \mathbf{k}' \\ G_0(\mathbf{k}_1, \mathbf{k}_2; z) &= \delta_{\mathbf{k}_1, \mathbf{k}_2} G_0(\mathbf{k}_1; z) \\ G_0(\mathbf{k}_1; z) &= \int d\mathbf{p} G_0(\mathbf{p}; z) e^{-i\mathbf{k}_1 \cdot \mathbf{p}} \quad \mathbf{p} = \mathbf{r} - \mathbf{r}' \\ T(\mathbf{k}, \mathbf{k}'; z) &= V(\mathbf{k} - \mathbf{k}') + \int \frac{d\mathbf{k}_1}{(2\pi)^d} V(\mathbf{k} - \mathbf{k}_1) G_0(\mathbf{k}_1; z) T(\mathbf{k}_1, \mathbf{k}'; z) \end{aligned} \quad (4.11)$$

where $T'(\mathbf{k}, \mathbf{k}'; z) = \Omega T(\mathbf{k}, \mathbf{k}'; z)$.

From $\mathcal{G}(z)$ (or $T(z)$) we can find the *discrete* eigenvalues of \mathcal{H} and the corresponding eigenvectors. In the *continuous* case, only the DOS can be obtained directly from $\mathcal{G}(z)$. However we can write the time-independent Schrödinger equation in the form

$$(E - \mathcal{H}_0) |\psi\rangle = \mathcal{H}_1 |\psi\rangle \quad (4.12)$$

which can be considered as an inhomogeneous equation whose solution is

$$|\psi^\pm\rangle = |\phi\rangle + \mathcal{G}_0^\pm(E) \mathcal{H}_1 |\psi^\pm\rangle \quad (4.13)$$

where $|\phi\rangle$ is the general solution of $(E - \mathcal{H}_0) = 0$ and ψ^\pm are associated with \mathcal{G}_0^\pm respectively. In the \mathbf{r} -representation this becomes an integral equation

$$\psi^\pm(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}_1 d\mathbf{r}_2 G_0^\pm(\mathbf{r}, \mathbf{r}_1; E) H_1(\mathbf{r}_1, \mathbf{r}_2) \psi^\pm(\mathbf{r}_2) \quad (4.14a)$$

$$= \phi(\mathbf{r}) + \int d\mathbf{r}_1 G_0^\pm(\mathbf{r}, \mathbf{r}_1; E) V(\mathbf{r}_1) \psi^\pm(\mathbf{r}_1) \quad (4.14b)$$

where (4.14b) applies in the usual case of a local potential. (4.14) is the *Lippmann–Schwinger* equation. If E does not belong to the spectrum of \mathcal{H} (4.14) becomes homogeneous, $\phi(\mathbf{r}) = 0$.

$$\psi(\mathbf{r}) = \int d\mathbf{r}_1 G_0(\mathbf{r}, \mathbf{r}_1; E) V(\mathbf{r}_1) \psi(\mathbf{r}_1) \quad (4.15)$$

By iterating (4.14) and using (4.9a) we obtain

$$\begin{aligned} |\psi^\pm\rangle &= |\phi\rangle + \mathcal{G}_0^\pm |\phi\rangle + \mathcal{G}_0^\pm \mathcal{H}_1 \mathcal{G}_0^\pm \mathcal{H}_1 |\phi\rangle + \dots \\ &= |\phi\rangle + \mathcal{G}_0^\pm T^\pm |\phi\rangle \end{aligned} \quad (4.16)$$

By multiplying (4.4) from the left or right by \mathcal{H}_1 we have

$$\mathcal{H}_1 \mathcal{G} = T \mathcal{G}_0 \quad \text{or} \quad \mathcal{G} \mathcal{H}_1 = \mathcal{G}_0 T \quad (4.17)$$

which when substituted into (4.16) gives

$$|\psi^\pm\rangle = |\phi\rangle + \mathcal{G}^\pm \mathcal{H}_1 |\phi\rangle \quad (4.18)$$

Comparing (4.16) with (4.13) gives

$$T^\pm |\phi\rangle = \mathcal{H}_1 |\psi^\pm\rangle \quad (4.19)$$

b) Time-Dependent Case

Using similar procedures on the time-dependent Schrödinger equation

$$\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H}_0\right) |\psi(t)\rangle = \mathcal{H}_1(t) |\psi(t)\rangle \quad (4.20)$$

where $\mathcal{H}_1(t)$ may be time-dependent. From the general solution of an inhomogeneous equation we have

$$|\psi^\pm(t)\rangle = |\phi(t)\rangle + \int_{-\infty}^{+\infty} dt' \mathcal{G}_0^\pm(t-t') \mathcal{H}_1(t') |\psi^\pm(t')\rangle \quad (4.21)$$

On physical grounds we keep the $|\psi^+(t)\rangle$ solution because it is causal; the effects of $\mathcal{H}_1(t)$ appear after $\mathcal{H}_1(t)$ has been applied.

Iterating (4.21) gives

$$\begin{aligned} |\psi^+(t)\rangle &= |\phi(t)\rangle + \int dt_1 \mathcal{G}_0^+(t-t_1) \mathcal{H}_1(t_1) |\phi(t_1)\rangle \\ &\quad + \int dt_1 dt_2 \mathcal{G}_0^+(t-t_1) \mathcal{H}_1(t_1) \mathcal{G}_0^+(t_1-t_2) \mathcal{H}_1(t_2) |\phi(t_2)\rangle + \dots \end{aligned} \quad (4.22)$$

Assuming $\mathcal{H}_1(t) = 0$ for $t \leq t_0$ and $|\phi_0(t)\rangle$ is an eigenfunction of \mathcal{H}_0 , say $|\phi_n\rangle$, we have

$$\begin{aligned} |\phi(t)\rangle &= \exp\left(-i\frac{E_n(t-t_0)}{\hbar}\right) |\phi_n\rangle \\ &= \exp\left(-i\frac{\mathcal{H}_0(t-t_0)}{\hbar}\right) |\phi_n\rangle \\ &= i\hbar \mathcal{G}_0(t-t_0) |\phi_n\rangle \end{aligned} \quad (4.23)$$

Under these initial conditions (4.22) can be written as

$$\begin{aligned} |\psi^+(t)\rangle &= \mathcal{A}(t, t_0) |\phi_n\rangle \\ \mathcal{A}(t, t_0) &= i\hbar \mathcal{G}_0(t-t_0) + i\hbar \int_{t_0}^t dt_1 \mathcal{G}_0(t-t_1) \mathcal{H}_1(t_1) \mathcal{G}_0(t_1-t_0) \\ &\quad + i\hbar \int_{t_0}^t dt_1 dt_2 \mathcal{G}_0(t-t_1) \mathcal{H}_1(t_1) \mathcal{G}_0^+(t_1-t_2) \mathcal{H}_1(t_2) \mathcal{G}_0(t_2-t_0) + \dots \end{aligned} \quad (4.24a)$$

$$(4.24b)$$

The probability amplitude for a transition from state $|\phi_n\rangle$ to the state $|\phi_m\rangle$ as a result of $\mathcal{H}_1(t)$ acting during an interval $[t_0, t]$ can be calculated from (4.24) as

$$\begin{aligned} \langle\phi_m|\mathcal{A}(t, t_0)|\phi_n\rangle &= \exp\left(-i\frac{E_m t + E_n t_0}{\hbar}\right) [\langle\phi_m|\phi_n\rangle \\ &\quad + \frac{-i}{\hbar} \int_{t_0}^t dt_1 \langle\phi_m|\exp\left(i\frac{\mathcal{H}_0 t_1}{\hbar}\right) \mathcal{H}_1(t_1) \exp\left(-i\frac{\mathcal{H}_0 t_1}{\hbar}\right) |\phi_n\rangle \\ &\quad + \frac{-i}{\hbar} \int_{t_0}^t dt_1 dt_2 \langle\phi_m|\exp\left(i\frac{\mathcal{H}_0 t_1}{\hbar}\right) \mathcal{H}_1(t_1) \mathcal{G}_0^+(t_1-t_2) \mathcal{H}_1(t_2) \\ &\quad \times \exp\left(-i\frac{\mathcal{H}_0 t_2}{\hbar}\right) |\phi_n\rangle + \dots] \end{aligned} \quad (4.25)$$

We define the operator $\mathcal{S}(t, t_0)$ as follows

$$\mathcal{S}(t, t_0) \equiv \exp\left(i\frac{\mathcal{H}_0 t}{\hbar}\right) \mathcal{A}(t, t_0) \exp\left(-i\frac{\mathcal{H}_0 t}{\hbar}\right) \quad (4.26)$$

so that $\langle \phi_m | \mathcal{S}(t, t_0) | \phi_n \rangle$ is the quantity in parenthesis in (4.25) which can be rewritten as

$$\begin{aligned} \langle \phi_m | \mathcal{S}(t, t_0) | \phi_n \rangle &= \delta_{mn} + \frac{-i}{\hbar} \int_{t_0}^t dt_1 e^{i\omega_{mn}t_1} \langle \phi_m | \mathcal{H}_1(t_1) | \phi_n \rangle \\ &+ \frac{-i}{\hbar} \int_{t_0}^t dt_1 dt_2 \int \frac{d\omega}{2\pi} e^{it_1(\omega_m - \omega)} e^{it_2(\omega - \omega_n)} \\ &\times \langle \phi_m | \mathcal{H}_1(t_1) \mathcal{G}_0^+(\hbar\omega) \mathcal{H}_1(t_2) | \phi_n \rangle + \dots \end{aligned} \quad (4.27)$$

where $\omega_n = E_n/\hbar$ and $\omega_{mn} = \omega_m - \omega_n$.

(4.27) implies that the probability amplitude of a transition between two *different* states as a result of $\mathcal{H}_1(t)$ acting during an infinite period, $-\infty \rightarrow +\infty$ is

$$\langle \phi_m | \mathcal{S} | \phi_n \rangle = \frac{-i}{\hbar} \int_{-\infty}^{+\infty} dt_1 e^{i\omega_{mn}t_1} \langle \phi_m | \mathcal{H}_1(t_1) | \phi_n \rangle + \dots \quad (4.28)$$

where

$$\mathcal{S} \equiv \lim_{\substack{t \rightarrow +\infty \\ t_0 \rightarrow -\infty}} \mathcal{S}(t, t_0) \quad (4.29)$$

is the so called *S-matrix*. This is the basic result of time-dependent perturbation theory.

For the case where \mathcal{H}_1 is time-independent we obtain for $\langle \phi_m | \mathcal{S} | \phi_n \rangle$

$$\begin{aligned} \langle \phi_m | \mathcal{S} | \phi_n \rangle &= \delta_{mn} + \langle \phi_m | \mathcal{H}_1 | \phi_n \rangle \frac{-1}{\hbar} \int_{-\infty}^{+\infty} dt_1 e^{i\omega_{mn}t_1} \\ &+ \frac{-i}{\hbar} \int \frac{d\omega}{2\pi} \langle \phi_m | \mathcal{H}_1 \mathcal{G}_0^+(\hbar\omega) \mathcal{H}_1 | \phi_n \rangle \\ &\times \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2 e^{it_1(\omega_m - \omega)} e^{it_2(\omega - \omega_n)} + \dots \\ &= \delta_{mn} - 2\pi i \delta(E_n - E_m) [\langle \phi_m | \mathcal{H}_1 | \phi_n \rangle + \langle \phi_m | \mathcal{H}_1 \mathcal{G}_0^+(E_n) \mathcal{H}_1 | \phi_n \rangle + \dots] \\ &= \delta_{mn} - 2\pi i \delta(E_n - E_m) \langle \phi_m | T^+(E_n) | \phi_n \rangle \end{aligned} \quad (4.30)$$

where we have used the relation

$$\int_{-\infty}^{+\infty} dt \exp\left(i \frac{Et}{\hbar}\right) = 2\pi\hbar \delta(E) \quad (4.31)$$

The transition probability is then

$$\begin{aligned} |\langle \phi_m | \mathcal{S} | \phi_n \rangle|^2 &= \frac{1}{\hbar^2} |\langle \phi_m | \mathcal{H}_1 | \phi_n \rangle|^2 \int dt_1 dt_2 e^{i\omega_{mn}t_1 - i\omega_{mn}t_2} + \dots \\ &= \frac{1}{\hbar^2} |\langle \phi_m | \mathcal{H}_1 | \phi_n \rangle|^2 \int_{-\infty}^{+\infty} dt' e^{i\omega_{mn}t'} \int_{-\infty}^{+\infty} dt + \dots \\ &= \frac{2\pi}{\hbar} |\langle \phi_m | \mathcal{H}_1 | \phi_n \rangle|^2 \delta(E_n - E_m) \int_{-\infty}^{+\infty} dt + \dots \end{aligned} \quad (4.32)$$

so that the transition probability per unit time, W_{mn} , is given by

$$W_{mn} = \frac{2\pi}{\hbar} |\langle \phi_m | \mathcal{H}_1 | \phi_n \rangle|^2 \delta(E_n - E_m) + \dots \quad (4.33a)$$

$$= \frac{2\pi}{\hbar} |\langle \phi_m | T^+(E_n) | \phi_n \rangle|^2 \delta(E_n - E_m) \quad (4.33b)$$

which is the well known *Fermi's golden rule*. Note that the higher order terms are included automatically by replacing \mathcal{H}_1 by $T^+(E_n)$.

Since $|\phi_n\rangle$ is normalised, then $|\psi^+(t)\rangle$ is also normalised, hence

$$1 = \langle \psi^+(t) | \psi^+(t) \rangle = \langle \phi_n | \mathcal{A}^\dagger(t, t_0) \mathcal{A}(t, t_0) | \phi_n \rangle \quad (4.34)$$

and for the S -matrix we have

$$\mathcal{S}^\dagger \mathcal{S} = \mathcal{S} \mathcal{S}^\dagger = 1 \quad (4.35)$$

which can be expressed in terms of the t -matrix using (4.30)

$$\begin{aligned} & \langle \phi_n | T^+(E_n) | \phi_l \rangle - \langle \phi_n | T^-(E_n) | \phi_l \rangle \\ &= -2\pi i \sum_m \langle \phi_n | T^-(E_n) | \phi_m \rangle \langle \phi_m | T^-(E_n) | \phi_l \rangle \delta(E_m - E_n) \end{aligned} \quad (4.36)$$

This is equivalent to the *optical theorem* of scattering theory.

It is convenient to rewrite the expression for \mathcal{S} in the so-called interaction picture.

$$\begin{aligned} \mathcal{S} &= 1 + \frac{-1}{\hbar} \int_{-\infty}^{+\infty} dt_1 \mathcal{H}_1^I(t_1) \\ &+ \left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{+\infty} dt_1 \mathcal{H}_1^I(t_1) \int_{-\infty}^{t_1} dt_2 \mathcal{H}_1^I(t_2) + \dots \end{aligned} \quad (4.37a)$$

$$\mathcal{H}_1^I(t) \equiv e^{i\mathcal{H}_0 t/\hbar} \mathcal{H}_1(t) e^{-i\mathcal{H}_0 t/\hbar} \quad (4.37b)$$

where we have used the relation

$$\begin{aligned} \mathfrak{g}_0^+(t_1 - t_2) &= \Theta(t_1 - t_2) \mathfrak{g}_0(t_1 - t_2) \\ &= \Theta(t_1 - t_2) \frac{-i}{\hbar} e^{-i\mathcal{H}_0(t_1 - t_2)/\hbar} \end{aligned} \quad (4.38)$$

Note that the restrictions on the intermediate integrations in (4.37) can be dropped if the n th term is divided by $n!$. Also, in writing products of \mathcal{H}_1^I 's it is essential to preserve the original order of the operators. To make this ordering explicit we define the time-ordered product of operators \mathcal{H}_1^I as

$$T [\mathcal{H}_1^I(t_1) \dots \mathcal{H}_1^I(t_j) \dots] = \mathcal{H}_1^I(t_1) \mathcal{H}_1^I(t_2) \dots \mathcal{H}_1^I(t_{n-1}) \mathcal{H}_1^I(t_n) \quad (4.39)$$

where $t_1 > t_2 > \dots > t_{n-1} > t_n$. Thus (4.37a) becomes

$$\begin{aligned} \mathcal{S} &= \sum_{n=0}^{\infty} \left(\frac{-i}{\hbar}\right)^n \frac{1}{n!} \int dt_1 dt_2 \dots dt_n T [\mathcal{H}_1^I(t_1) \dots \mathcal{H}_1^I(t_n)] \\ &= T \exp \left(-\frac{i}{\hbar} \int dt \mathcal{H}_1^I(t) \right) \end{aligned} \quad (4.40)$$

which is just a compact way of writing the sum.

c) Application to Scattering Theory

We consider $\mathcal{H}_0 = p^2/2m = -\hbar^2 \nabla^2/2m$, and $H_1(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')V(\mathbf{r})$ is of finite extent (i.e. $V(\mathbf{r})$ decays fast enough as $\mathbf{r} \rightarrow \infty$). Here \mathcal{H} has a continuous spectrum from 0 to $+\infty$, but may develop discrete eigenvalues below zero.

The problem of physical interest for $E > 0$ is scattering. An incident particle of energy $E = \hbar^2 k^2/2m$ described by $\exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{\Omega}$ is influenced by the perturbation $V(\mathbf{r})$ and its wave function is modified. We must find the asymptotic behaviour as $\mathbf{r} \rightarrow \infty$. From (4.16) we have

$$\psi^\pm(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{r}} + \frac{1}{\sqrt{\Omega}} \int d\mathbf{r}_1 d\mathbf{r}_2 G_0^\pm(\mathbf{r}, \mathbf{r}_1) T^\pm(\mathbf{r}_1, \mathbf{r}_2) e^{i\mathbf{k} \cdot \mathbf{r}_2} \quad (4.41)$$

Using the expression for the 3-D G_0^\pm obtained earlier we can write

$$\sqrt{\Omega} \psi^\pm(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{2m}{4\pi\hbar^2} \int d^3 r_1 d^3 r_2 \frac{e^{\pm i\mathbf{k}|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} T^\pm(\mathbf{r}_1, \mathbf{r}_2) e^{i\mathbf{k} \cdot \mathbf{r}_2} \quad (4.42)$$

where $k = \sqrt{2mE/\hbar^2}$. For large \mathbf{r} we can write

$$\begin{aligned} \sqrt{\Omega} \psi^\pm(\mathbf{r}) &\xrightarrow{r \rightarrow \infty} e^{i\mathbf{k} \cdot \mathbf{r}} \\ &\quad - \frac{m}{2\pi\hbar^2} \frac{e^{\pm ikr}}{r} \int d^3 r_1 d^3 r_2 e^{\mp i\mathbf{k}_f \cdot \mathbf{r}_1} \langle \mathbf{r}_1 | T^\pm(E) | \mathbf{r}_2 \rangle e^{i\mathbf{k} \cdot \mathbf{r}_2} \\ &= e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{m}{2\pi\hbar^2} \frac{e^{\pm ikr}}{r} \langle \pm \mathbf{k}_f | T'^\pm(E) | \mathbf{k} \rangle \end{aligned} \quad (4.43)$$

where \mathbf{k}_f is a vector of length k in the direction of \mathbf{r} , and $T' = \Omega T$.

In (4.43) ψ^- must be excluded as it describes a physically unacceptable incoming spherical wave. The quantity of importance is the *scattering amplitude* $f(\mathbf{k}_f, \mathbf{k})$ which is defined by

$$\psi(\mathbf{r}) \xrightarrow{r \rightarrow \infty} \text{const.} \left[e^{i\mathbf{k} \cdot \mathbf{r}} + f(\mathbf{k}_f, \mathbf{k}) \frac{e^{ikr}}{r} \right] \quad (4.44a)$$

$$f(\mathbf{k}_f, \mathbf{k}) = -\frac{m}{2\pi\hbar^2} \langle \mathbf{k}_f | T'^+(E) | \mathbf{k} \rangle \quad (4.44b)$$

Thus the t -matrix is essentially the scattering amplitude, which is directly related to the scattering cross section

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= |f|^2 \\ &= \frac{m^2}{4\pi^2\hbar^4} \left| \langle \mathbf{k}_f | T'^+(E) | \mathbf{k} \rangle \right|^2 \end{aligned} \quad (4.45)$$

Substituting (4.44) into (4.11) we obtain

$$f(\mathbf{k}_f, \mathbf{k}) = -\frac{m}{2\pi\hbar^2} V(\mathbf{k}_f - \mathbf{k}) + \int \frac{d^3 \mathbf{k}_1}{(2\pi)^3} \frac{V(\mathbf{k}_f - \mathbf{k})}{E - \frac{\hbar^2 k_1^2}{2m} + i\epsilon} f(\mathbf{k}_1, \mathbf{k}) \quad (4.46)$$

Thus to 1st order in V

$$f(\mathbf{k}_f, \mathbf{k}) \approx -\frac{m}{2\pi\hbar^2} V(\mathbf{k}_f - \mathbf{k}) \quad (4.47)$$

where $V(\mathbf{q})$ is the Fourier transform of $V(\mathbf{r})$. This is the *Born approximation* for the scattering amplitude.

Another derivation of (4.45): The probability per unit time for the transition $\mathbf{k} \rightarrow \mathbf{k}_f$, $W_{\mathbf{k}_f, \mathbf{k}}$, times the number of final states divided by the solid angle 4π and by the flux $\mathbf{j} = \mathbf{v}/\Omega$ of the incoming particle.

$$\frac{d\sigma}{d\Omega} = \frac{\Omega}{4\pi v} \int dE_f N(E_f) W_{\mathbf{k}_f, \mathbf{k}} \quad (4.48)$$

Using (4.33) we obtain the total cross section

$$\begin{aligned}
\sigma &= \int d\Omega \frac{d\sigma}{d\Omega} & (4.49a) \\
&= \frac{\Omega}{v} \sum_{\mathbf{k}_f} W_{\mathbf{k}_f \mathbf{k}} \\
&= \frac{\Omega}{v} \frac{2\pi}{\hbar} \sum_{\mathbf{k}_f} |\langle \mathbf{k}_f | T^+(E) | \mathbf{k} \rangle|^2 \delta(E_f - E) \\
&= \frac{2\pi\Omega}{\hbar v} \sum_{\mathbf{k}_f} \langle \mathbf{k} | T^-(E) | \mathbf{k}_f \rangle \langle \mathbf{k}_f | T^+(E) | \mathbf{k} \rangle \delta(E_f - E) \\
&= \frac{2\pi}{\hbar v} \frac{\Omega i}{2\pi} [\langle \mathbf{k} | T^+(E) | \mathbf{k} \rangle - \langle \mathbf{k} | T^-(E) | \mathbf{k} \rangle] \\
&= -\frac{2\Omega}{\hbar v} \text{Im} \langle \mathbf{k} | T^+(E) | \mathbf{k} \rangle \\
&= \frac{4\pi}{k} \text{Im} f(\mathbf{k}, \mathbf{k}) & (4.49b)
\end{aligned}$$

which is the *optical theorem* which connects the total cross section with the forward scattering amplitude.

As an example consider the case where $V(\mathbf{r})$ is an attractive Coulomb potential $V(\mathbf{r}) = -e^2/4\pi\epsilon_0 r$. Then f is given by

$$\begin{aligned}
f &= \frac{-t\Gamma(1-it) \exp(2it \ln \sin(\frac{1}{2}\theta))}{\Gamma(1+it) 2k \sin^2(\frac{1}{2}\theta)} \\
k &= \sqrt{\frac{2mE}{\hbar^2}} \quad \text{Im } k \geq 0 & (4.50) \\
t &= \frac{me^2}{4\pi\epsilon_0 \hbar^2 k}
\end{aligned}$$

where θ is the angle between \mathbf{k} and \mathbf{k}_f . The poles of f occur when the argument of $\Gamma(1-it)$ is a nonpositive integer, i.e. when $1-it = -p$ where $p = 0, 1, 2, \dots$, or $it = 1+p = n$ and $n = 1, 2, 3, \dots$. Thus the discrete eigenenergies are

$$E_n = -\frac{e^4 m}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \quad n = 1, 2, \dots \quad (4.51)$$

which is the standard result (in SI units). If the potential is repulsive we must replace i by $-i$. In this case the argument in the Γ function in the numerator in (4.50) cannot become a non-positive integer; thus f has no poles, just as we would expect for a repulsive potential.

5. Tight-Binding Hamiltonians

a) Introduction

Consider the so-called tight-binding Hamiltonian of the form

$$\mathcal{H} = \sum_l |l\rangle \varepsilon_l \langle l| + \sum_{lm} |l\rangle V_{lm} \langle m| \quad (5.1)$$

where each state $|l\rangle$ is an atomic-like orbital centred at the site l . The sites $\{l\}$ form a lattice. For the moment we shall consider the periodic case where the Hamiltonian is invariant under translation by any vector l .

The eigenfunctions obey *Bloch's theorem*

$$\Psi_{nk}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{ik \cdot \mathbf{r}} u_{nk}(\mathbf{r}) \quad (5.2a)$$

$$\Psi_{nk}(\mathbf{r} + l) = e^{ik \cdot l} \Psi_{nk}(\mathbf{r}) \quad (5.2b)$$

where $u_{nk}(\mathbf{r})$ is a periodic function and k is restricted to a finite region of space, the *Brillouin zone*.

It is useful to introduce *Wannier functions* associated with the band index n and the lattice site l defined as

$$w_n(\mathbf{r} - l) = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot l} \Psi_{nk}(\mathbf{r}) \quad (5.3)$$

These functions form a complete set for all n and l . Any operator can be expressed in the Wannier representation. It may happen that the eigenenergies associated with a particular band index n_0 are well separated from the rest. In this case the matrix elements of \mathcal{H} between $w_{n_0}(\mathbf{r} - l)$ and $w_n(\mathbf{r} - m)$, where $n \neq n_0$, may be smaller than $|\varepsilon_n - \varepsilon_{n_0}|$. Then these small matrix elements may be omitted and the band n_0 is decoupled from the rest. In what follows we work within this subspace and for simplicity omit the subscript n_0 to obtain

$$w(\mathbf{r} - l) = \langle \mathbf{r} | l \rangle \quad (5.4a)$$

$$\langle l | \mathcal{H} | m \rangle = \varepsilon_l \delta_{lm} + V_{lm} \quad (5.4b)$$

In the usual notation (with $V_{ll} = 0$). Since \mathcal{H} is periodic we can write

$$\varepsilon_l = \varepsilon_0 \quad (5.5a)$$

$$V_{l,m} = V_{l,-m} \quad (5.5b)$$

We shall consider also the case of 2 interpenetrating sublattices where

$$\varepsilon_{\mathbf{i}} = \begin{cases} \varepsilon_1 & \text{if } \mathbf{i} \in \text{sublattice 1.} \\ \varepsilon_2 & \text{if } \mathbf{i} \in \text{sublattice 2.} \end{cases} \quad (5.6)$$

For simplicity we assume only nearest neighbour interactions

$$V_{\mathbf{i}\mathbf{j}} = \begin{cases} V & \mathbf{i}, \mathbf{j} \text{ nearest neighbours} \\ 0 & \text{otherwise.} \end{cases} \quad (5.7)$$

Usually in the literature V is assumed positive. It is actually physically more realistic to consider V negative, since this guarantees that the energy k increases as E increases. The Green's functions for the 2 cases are related by

$$G(\mathbf{l}, \mathbf{m}; E + is, \{\varepsilon_i\}, V) = -G(\mathbf{l}, \mathbf{m}; -E - is, \{-\varepsilon_i\}, -V) \quad (5.8)$$

From Bloch's Theorem we have

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_l e^{ik \cdot l} |l\rangle \quad (5.9)$$

By substituting (5.9) into \mathcal{H} we can derive the eigenenergies

$$E(\mathbf{k}) = \varepsilon_0 + \begin{cases} V \sum_l e^{ik \cdot l} & \text{general case} \\ 2V \cos(ka) & \text{1-D} \\ 2V [\cos(k_1 a) + \cos(k_2 a)] & \text{2-D square lattice} \\ 2V \sum_{d=1}^3 \cos(k_d a) & \text{3-D simple cubic lattice} \end{cases} \quad (5.10)$$

In all cases $-\pi/a < k \leq \pi/a$ which is the first Brillouin zone. Remember that the number of distinct k -vectors in the Brillouin zone is equal to the number of unit cells in the crystal. Note that the bands go from $-ZV \leq E \leq ZV$, where Z is the number of nearest neighbours. Thus the band width is given by $2ZV$, but is often quoted as ZV .

c) Green's functions

The Green's function can be written

$$\mathcal{G}(z) = \sum_{\mathbf{k}} \frac{|\mathbf{k}\rangle\langle\mathbf{k}|}{z - E(\mathbf{k})} \quad (5.11a)$$

$$G(\mathbf{l}, \mathbf{m}; z) = \sum_{\mathbf{k}} \frac{\langle\mathbf{l}|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{m}\rangle}{z - E(\mathbf{k})} \quad (5.11b)$$

$$= \frac{\Omega}{N(2\pi)^d} \int_{BZ} d\mathbf{k} \frac{e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{m})}}{z - E(\mathbf{k})} \quad (5.11c)$$

$$G(\mathbf{l}, \mathbf{l}; z) = \frac{\Omega}{N(2\pi)^d} \int_{BZ} \frac{d\mathbf{k}}{z - E(\mathbf{k})} \quad (5.11d)$$

Note in particular that

$$\begin{aligned} \lim_{z \rightarrow \infty} G(\mathbf{l}, \mathbf{l}; z) &= \int \frac{dE \rho(E)}{z - E} \\ &\xrightarrow{z \rightarrow \infty} \frac{\int \rho(E) dE}{z} \\ &= \frac{1}{z} \end{aligned} \quad (5.12)$$

i) 1-D Case

$$\begin{aligned} G(l, m; z) &= \frac{L}{N(2\pi)} \int_{-\pi/a}^{+\pi/a} dk \frac{e^{ika(l-m)}}{z - \varepsilon_0 - 2V \cos(ka)} \\ &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} d\phi \frac{e^{i\phi(l-m)}}{z - \varepsilon_0 - 2V \cos \phi} \end{aligned} \quad (5.13)$$

By symmetry the integral depends on the absolute value $|l - m|$. We transform it to an integral over the complex variable w along the unit circle

$$G(l, m; z) = \frac{-1}{2\pi i V} \oint dw \frac{w^{|l-m|}}{w^2 - 2xw + 1} \quad (5.14)$$

where

$$x = \frac{z - \varepsilon_0}{2V} \quad (5.15)$$

and the 2 roots of $w^2 - 2xw + 1 = 0$ are given by

$$\rho_{\pm} = x \mp \sqrt{x^2 - 1} \quad (5.16)$$

where $\sqrt{x^2 - 1}$ we denote the square root whose imaginary part has the same sign as $\text{Im}(x)$. Note that $\rho_+ \rho_- = 1$. Also $|\rho_+| < 1$ and $|\rho_-| > 1$ unless $-1 \leq x \leq 1$. Then both roots lie on the unit circle and the integral (5.14) is not well defined. This condition gives the continuous spectrum of \mathcal{H} which lies on the real axis between $\varepsilon_0 - 2V$ and $\varepsilon_0 + 2V$.

By the method of residues we have

$$\begin{aligned} G(l, m; z) &= \frac{-1}{V} \frac{\rho_+^{|l-m|}}{\rho_+ - \rho_-} \\ &= \frac{1}{\sqrt{(z - \varepsilon_0)^2 - (2V)^2}} \rho_+^{|l-m|} \end{aligned} \quad (5.17)$$

For z coinciding with the spectrum we have

$$G^{\pm}(l, m; E) = \frac{\mp i}{\sqrt{(2V)^2 - (E - \varepsilon_0)^2}} \left(x \mp i\sqrt{1 - x^2} \right)^{|l-m|} \quad (5.18)$$

The density of states per site is given by

$$\begin{aligned}\rho(E) &= \mp \frac{1}{\pi} \text{Im} G^\pm(l, l; E) \\ &= \frac{\Theta(ZV - |E - \epsilon_0|)}{\pi \sqrt{(ZV)^2 - (E - \epsilon_0)^2}}\end{aligned}\quad (5.19)$$

Note the square root singularities at the band edges $E = \pm ZV$. Note also that G decays exponentially with $|l - m|$ when z does not coincide with the band, but does not decay when z is a band energy.

ii) 2-D and 3-D cases

In 2-D and 3-D there is no closed analytical solution. The integral corresponding to (5.13) above can be reduced to a form containing elliptic integrals. However there is an important feature which does not appear in 1-D, namely singularities within the band, so-called *van Hove singularities*.

In 2-D the DOS has step-like singularities at the band edges and a logarithmic singularity in the middle of the band.

In 3-D the DOS has square root singularities at the band edges and 2 step-like singularities within the band.

A common approximate form for a 3-D Green's function is the *Hubbard Green's function* with the following form

$$G(\mathbf{l}, \mathbf{l}; z) = \frac{2}{z - \epsilon_0 + \sqrt{(z - \epsilon_0)^2 - (ZV)^2}} \quad (5.20a)$$

$$\rho(E) = \frac{2\Theta(ZV - |E - \epsilon_0|)}{\pi(ZV)^2} \sqrt{(ZV)^2 - (E - \epsilon_0)^2} \quad (5.20b)$$

which has the correct band edge singularities but no internal features.

iii) Bethe-Lattices and Cayley Trees

A Bethe lattice or Cayley tree is a branching structure containing no rings. Strictly speaking the Cayley tree can have a variable coordination number, but we shall ignore this possibility. The method of solving for the Green's function on such a lattice is a useful introduction to a more general method. We characterise the tree by its branching index $K = Z - 1$. $K = 1$ corresponds to a 1-D lattice.

Consider the tree to have been cut at some branch. Then the root node is connected to K branches and every other node is connected to $K + 1$. We denote by $G'(z)$ the diagonal element of the Green's function on the root node. If we join K branches together with a new atom to form a new root node then the Green's function of the new node is related to those of the old nodes by Dyson's equation where \mathcal{H}_0 is the Hamiltonian for K trees plus a single atom and \mathcal{H}_1 contains a matrix element V between the new atom and the old roots. Hence

$$G'(n, n; z) = G_0(n, n; z) + G_0(n, n; z) \sum_{i=1}^K V G'(i, n; z) \quad (5.21a)$$

$$= G_0(n, n; z) + G_0(n, n; z) V \sum_{i=1}^K G_0(i, i; z) V G'(n, n; z) \quad (5.21b)$$

$$= \left[1 - G_0(n, n; z) V^2 \sum_{i=1}^K G_0(i, i; z) \right]^{-1} G_0(n, n; z) \quad (5.21c)$$

where i runs over the K root nodes of the old trees and G_0 refers to the Green's function before the perturbation V is switched on, and $G_0(n, n; z)$ refers to a single isolated atom with $G_0 = [z - \epsilon_0]^{-1}$, where we can set $\epsilon_0 = 0$ without loss of generality. When the trees are infinitely large we have $G'(n, n; z) = G_0(i, i; z)$, as the end of an infinite tree must be invariant. Substituting in (5.21c) gives

$$G'(n, n; z) = [z - KV^2 G'(n, n; z)]^{-1} \quad (5.22a)$$

$$KV^2 G'(n, n; z)^2 - z G'(n, n; z) + 1 = 0 \quad (5.22b)$$

$$G'(n, n; z) = \frac{z \pm \sqrt{z^2 - 4KV^2}}{2KV^2} \quad (5.22c)$$

where the sign of the square root is chosen to make the imaginary part of G' be the opposite of the imaginary part of z . In order to obtain the Green's function on a typical site of the lattice we must perform one more iteration which connects $K + 1$ rather than K trees together. Hence

$$G(n, n; z) = [z - (K + 1)V^2 G'(n, n; z)]^{-1} \quad (5.23a)$$

$$= \frac{1}{4K} \frac{(K - 1)z - \mp(K + 1)\sqrt{z^2 - 4KV^2}}{(K + 1)^2 V^2 - z^2} \quad (5.23b)$$

Note the peculiar property of the Bethe lattice: that the continuous part of the spectrum (where the square root is imaginary) is narrower than expected ($-2\sqrt{K}V \leq E \leq 2\sqrt{K}V$), but that there are discrete singularities at $z = \pm(K + 1)V$ where the band edges would be expected. Note that the case $K = 1$ reduces to the 1-D case discussed above.

The Bethe lattice is a useful model for amorphous semiconductors where it is possible to build in short range, chemical, order without an underlying crystal lattice. More recently it has been used as a boundary condition for cluster models of amorphous systems; the so-called *cluster Bethe method*. A more complex variation involves building a tree from rings of atoms such as rings of 6 4-fold coordinated atoms. This is termed a *Husimi Cactus*.

c) The Renormalised Perturbation Expansion

Consider again the tight-binding Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ where

$$\mathcal{H}_0 = \sum_l |l\rangle \varepsilon_l \langle l| \quad (5.24a)$$

$$\mathcal{H}_1 = V \sum_{lm} |l\rangle \langle m| \quad (5.24b)$$

where the sum in (5.24b) is over nearest-neighbour sites only. Then we can write

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \dots \quad (5.25a)$$

$$\begin{aligned} G(\mathbf{l}, \mathbf{m}) &= G_0(\mathbf{l}, \mathbf{m}) + \sum_{\mathbf{n}_1 \mathbf{n}_2} G_0(\mathbf{l}, \mathbf{n}_1) \langle \mathbf{n}_1 | \mathcal{H}_1 | \mathbf{n}_1 \rangle G_0(\mathbf{n}_2, \mathbf{m}) \\ &+ \sum_{\mathbf{n}_1 \dots \mathbf{n}_2} G_0(\mathbf{l}, \mathbf{n}_1) \langle \mathbf{n}_1 | \mathcal{H}_1 | \mathbf{n}_2 \rangle G_0(\mathbf{n}_2, \mathbf{n}_3) \\ &\times \langle \mathbf{n}_3 | \mathcal{H}_1 | \mathbf{n}_4 \rangle G_0(\mathbf{n}_4, \mathbf{m}) + \dots \end{aligned} \quad (5.25b)$$

From (5.24) it is clear that $G_0(\mathbf{n}_1, \mathbf{n}_2) = \delta_{\mathbf{n}_1 \mathbf{n}_2} G_0(\mathbf{n}_1)$ where

$$G_0(\mathbf{n}) = \frac{1}{z - \varepsilon_{\mathbf{n}}} \quad (5.26)$$

and $\langle \mathbf{n}_1 | \mathcal{H}_1 | \mathbf{n}_2 \rangle$ is non-zero only when \mathbf{n}_1 and \mathbf{n}_2 are nearest neighbours. Hence (5.25) can be simplified to

$$G(\mathbf{l}, \mathbf{m}) = \delta_{\mathbf{l} \mathbf{m}} G_0(\mathbf{l}) + G_0(\mathbf{l}) V G_0(\mathbf{m}) \delta_{\mathbf{l}, \mathbf{m} \pm 1} + \sum_{\mathbf{n}_1} G_0(\mathbf{l}) V G_0(\mathbf{n}_1) V G_0(\mathbf{m}) + \dots \quad (5.27)$$

We can keep track of all the terms in (5.27) by noting that it consists of a sum over all possible paths from \mathbf{l} to \mathbf{m} . Thus for a particular path we include

- i) a factor $G_0(\mathbf{l})$ for each site visited and
- ii) a factor V for each step from one nearest neighbour to the next.

The most general path from \mathbf{l} to \mathbf{m} is found by *decorating* a skeleton path consisting of a *self-avoiding* path from \mathbf{l} to \mathbf{m} . For each site \mathbf{n}_1 we can replace $G_0(\mathbf{n}_1)$ by the sum over all possible paths beginning and ending at \mathbf{n}_1 , that is by $G(\mathbf{n}_1, \mathbf{n}_1)$. Unfortunately, when we come to consider a second site \mathbf{n}_2 we must be careful to avoid double counting. Some of the paths in the decoration of \mathbf{n}_2 have already been included in the decoration of \mathbf{n}_1 . Thus the decoration

of \mathbf{n}_2 consists of a sum over all paths from \mathbf{n}_2 to \mathbf{n}_2 which do not visit \mathbf{n}_1 . Let us write this sum as $G(\mathbf{n}_2, \mathbf{n}_2[\mathbf{n}_1])$. The exclusion is included automatically if we set $\varepsilon_{n_1} = \infty$ in the evaluation of $G(\mathbf{n}_2, \mathbf{n}_2[\mathbf{n}_1])$. Thus we can rewrite the summation in (5.27) as

$$G(\mathbf{l}, \mathbf{m}) = \sum G(\mathbf{l}, \mathbf{l})VG(\mathbf{n}_1, \mathbf{n}_1[\mathbf{l}])VG(\mathbf{n}_2, \mathbf{n}_2[\mathbf{l}, \mathbf{n}_1])V \dots VG(\mathbf{m}, \mathbf{m}[\mathbf{l}, \mathbf{n}_1, \mathbf{n}_2, \dots]) \quad (5.28)$$

where the summation is over all self-avoiding paths starting from \mathbf{l} and ending at \mathbf{m} , $\mathbf{l} \rightarrow \mathbf{n}_1 \rightarrow \mathbf{n}_2 \rightarrow \dots \rightarrow \mathbf{m}$. In particular for the diagonal matrix element we have

$$G(\mathbf{l}, \mathbf{l}) = G_0(\mathbf{l}) + \sum G(\mathbf{l}, \mathbf{l})VG(\mathbf{n}_1, \mathbf{n}_1[\mathbf{l}])V \dots G_0(\mathbf{l}) \quad (5.29)$$

Note that the last factor is $G_0(\mathbf{l})$ because all decorations of \mathbf{l} have already been included as decorations of the initial site.

It is worth noting at this point that in treating the Bethe Lattice we considered truncated trees. This is equivalent to the partial summations considered here.

Equation (5.29) can be rewritten as

$$G(\mathbf{l}, \mathbf{l}) = G_0(\mathbf{l}) + G(\mathbf{l}, \mathbf{l})\Sigma(\mathbf{l})G_0(\mathbf{l}) \quad (5.30a)$$

where $\Sigma(\mathbf{l})$ is called the *self-energy* and is given by

$$\Sigma(\mathbf{l}) = \sum VG(\mathbf{n}_1, \mathbf{n}_1[\mathbf{l}])V \dots V \quad (5.30b)$$

(5.30a) can be solved for $G(\mathbf{l}, \mathbf{l})$ to give

$$G(\mathbf{l}, \mathbf{l}; z) = \frac{G_0(\mathbf{l})}{1 - G_0(\mathbf{l})\Sigma(\mathbf{l}; z)} \quad (5.30c)$$

$$= \frac{1}{z - \varepsilon_{\mathbf{l}} - \Sigma(\mathbf{l}; z)} \quad (5.30d)$$

It is sometimes useful to write down an expansion for Σ in a similar form to (5.28) or (5.29)

$$\Sigma(\mathbf{l}) = V \sum \frac{V}{z - \varepsilon_{n_1} - \Sigma(\mathbf{n}_1[\mathbf{l}])} \quad (5.31)$$

In the case of the Bethe Lattice $\Sigma(\mathbf{n}_1[\mathbf{l}])$ is simple the self-energy at the end of a truncated tree ie

$$\Sigma(\mathbf{n}_2[\mathbf{l}, \mathbf{n}_1]) = \Sigma(\mathbf{n}_1[\mathbf{l}]) \quad (5.32)$$

which can easily be solved to yield the same result as before.

The self-energy has a number of useful properties which we may use later. Unlike the diagonal elements of the Green's function itself Σ is purely real when z is on the real axis close to a discrete eigenvalue of \mathcal{H} . Σ has an imaginary part when z is real but in a continuous region of the spectrum. This also applies to *localised* and *extended* states respectively. Thus $\text{Im } \Sigma$ provides a measure of whether the eigenstates can carry a current.

Also, since everything except Σ in (5.31) is real (when $\text{Im } z = 0$) Σ can only acquire an imaginary part when the sum contains an infinite number of significant terms such that the sum does not converge in a conventional sense when all the terms are real. Thus in principle we can write down the complete series for (5.31) where all terms are real. However, the solution, as for example is implicitly implied by the self-consistent condition used to solve the Bethe Lattice, has a complex Σ .

In a finite system the sum ends when all paths are exhausted and Σ remains real. In a localised system the terms involving very long and distant paths make negligibly small contributions. Again Σ remains real.

A more mathematically precise way of formulating this condition involves using a complex z and studying the limit $\text{Im } z \rightarrow 0$.

$$\lim_{\text{Im } z \rightarrow 0^\pm} \text{Im } \Sigma(\mathbf{l}; z) \begin{cases} = 0 & \text{for localised or discrete states} \\ < 0 & \text{for extended or continuous states} \end{cases} \quad (5.33)$$

6. Impurities and Disorder

a) Single Impurity Scattering

We now redivide our Hamiltonian into 2 parts where \mathcal{H}_0 describes an ordered system and \mathcal{H}_1 describes a single impurity at site l . Thus

$$\mathcal{H}_0 = \sum_m |m\rangle \varepsilon_0 \langle m| + V \sum_{nm} |n\rangle \langle m| \quad (6.1a)$$

$$\mathcal{H}_1 = |l\rangle \varepsilon \langle l| \quad (6.1b)$$

We can study either the Greens's function \mathcal{G} or the t-matrix \mathcal{T}

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 + \dots \quad (6.2a)$$

$$\mathcal{T} = \mathcal{H}_1 + \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 + \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 \mathcal{G}_0 \mathcal{H}_1 + \dots \quad (6.2b)$$

Substituting (6.1b) into (6.2b) gives

$$\begin{aligned} \mathcal{T} &= |l\rangle \varepsilon \langle l| + |l\rangle \varepsilon \langle l| \mathcal{G}_0 |l\rangle \varepsilon \langle l| + |l\rangle \varepsilon \langle l| \mathcal{G}_0 |l\rangle \varepsilon \langle l| \mathcal{G}_0 |l\rangle \varepsilon \langle l| + \dots \\ &= |l\rangle \varepsilon \left(1 + \varepsilon G_0(l, l) + (\varepsilon G_0(l, l))^2 + \dots \right) \langle l| \\ &= |l\rangle \frac{\varepsilon}{1 - \varepsilon G_0(l, l)} \langle l| \end{aligned} \quad (6.3a)$$

$$\begin{aligned} \mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0 \mathcal{T} \mathcal{G}_0 \\ &= \mathcal{G}_0 + \mathcal{G}_0 |l\rangle \frac{\varepsilon}{1 - \varepsilon G_0(l, l)} \langle l| \mathcal{G}_0 \end{aligned} \quad (6.3b)$$

Note that the poles of G (or T) coincide with those of \mathcal{G}_0 with the addition of a pole at

$$G_0(l, l; E_p) = \frac{1}{\varepsilon} \quad (6.4)$$

Note that this must be outside the band of \mathcal{H}_0 ; otherwise \mathcal{G}_0 has an imaginary part and (6.4) cannot be satisfied.

b) Two Impurities

Now let us consider the case where \mathcal{H}_1 consists of the potential due to 2 impurities. That is

$$\mathcal{H}_l = |l\rangle \varepsilon \langle l| \quad (6.5a)$$

$$\mathcal{H}_m = |m\rangle \varepsilon' \langle m| \quad (6.5b)$$

$$\mathcal{H}_{0l} = \mathcal{H}_0 + \mathcal{H}_l \quad (6.5c)$$

$$\mathcal{H}_{0m} = \mathcal{H}_0 + \mathcal{H}_m \quad (6.5d)$$

with corresponding Green's functions \mathcal{G}_0 , \mathcal{G}_{0l} , \mathcal{G}_{0m} , \mathcal{G} . Since we have already calculated $\mathcal{G}_{0l} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{T}_l \mathcal{G}_0$ we can consider \mathcal{H}_{0l} as the unperturbed part and \mathcal{H}_m as the perturbation. Thus

$$\begin{aligned} \mathcal{G} &= \mathcal{G}_{0l} + \mathcal{G}_{0l} \mathcal{H}_m \mathcal{G}_{0l} + \mathcal{G}_{0l} \mathcal{H}_m \mathcal{G}_{0l} \mathcal{H}_m \mathcal{G}_{0l} + \dots \\ &= \mathcal{G}_{0l} + \mathcal{G}_{0l} |m\rangle \frac{\varepsilon'}{1 - \varepsilon' G_{0l}(m, m)} \langle m| \mathcal{G}_{0l} \end{aligned} \quad (6.6)$$

By substituting now for \mathcal{G}_{0l} we can derive the final result. However a more symmetric formulation can be more revealing. Let \mathcal{G}' be the 2×2 submatrix of \mathcal{G}_0 for the 2 sites l and m . Note that \mathcal{H}_1 is effectively a 2×2 diagonal matrix already. Then

$$\begin{aligned} \mathcal{T} &= \mathcal{H}_1 + \mathcal{H}_1 \mathcal{G}' \mathcal{H}_1 + \mathcal{H}_1 \mathcal{G}' \mathcal{H}_1 \mathcal{G}' \mathcal{H}_1 + \dots \\ &= \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} + \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} \begin{pmatrix} G_0(l, l) & G_0(l, m) \\ G_0(m, l) & G_0(m, m) \end{pmatrix} \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} \\ &\quad + \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} \begin{pmatrix} G_0(l, l) & G_0(l, m) \\ G_0(m, l) & G_0(m, m) \end{pmatrix} \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} \\ &\quad \times \begin{pmatrix} G_0(l, l) & G_0(l, m) \\ G_0(m, l) & G_0(m, m) \end{pmatrix} \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon' \end{pmatrix} + \dots \end{aligned} \quad (6.7)$$

Note that the terms of (6.7) consist of a series of steps between l and m interspersed with any number of steps which remain on the same site. This latter can be summarised by t_l which is the t -matrix due to the single impurity at l . Thus each of the factors ε or ε' in (6.7) can be replaced by t_l or t_m and the \mathcal{G}' lose their diagonal terms. Thus

$$\begin{aligned} \mathcal{T} &= \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} + \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} \begin{pmatrix} 0 & G_0(l, m) \\ G_0(m, l) & 0 \end{pmatrix} \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} \\ &\quad + \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} \begin{pmatrix} 0 & G_0(l, m) \\ G_0(m, l) & 0 \end{pmatrix} \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} \\ &\quad \times \begin{pmatrix} 0 & G_0(l, m) \\ G_0(m, l) & 0 \end{pmatrix} \begin{pmatrix} t_l & 0 \\ 0 & t_m \end{pmatrix} + \dots \end{aligned} \quad (6.8)$$

We have thus separated the contributions to \mathcal{T} into those due to scattering from a single site and those associated with multiple scattering between sites.

The result can be written as

$$\mathcal{T} = f_{ml} (\mathcal{T}_l + \mathcal{T}_m + \mathcal{T}_l \mathcal{G}_0 \mathcal{T}_m + \mathcal{T}_m \mathcal{G}_0 \mathcal{T}_l) \quad (6.9a)$$

where the common factor f_{ml} is given by

$$f_{ml} = \frac{1}{1 - t_m t_l G_0(m, l) G_0(l, m)} \quad (6.9b)$$

where $t_m = \varepsilon' / (1 - \varepsilon' G_0(m, m))$ the value of the t -matrix for scattering from a single site.

The various terms derived above can be given a physical interpretation. The Green's function $G(l, m)$ represents propagation from site l to site m . Terms of the sort $G_0(l, n) t_n G_0(n, m)$ represent propagation from l to m with scattering from site n , etc. Thus it is customary to call the Green's function $G(l, m)$ a *propagator*. Sometimes the term *locator* is used for the diagonal elements, $G(l, l)$, whereas others use the term propagator for all the matrix elements of \mathcal{G} .

To first order in t_m we can write the t -matrix as

$$\mathcal{T} = \mathcal{T}_l + \mathcal{T}_m + O(\mathcal{T}_l^2, \mathcal{T}_m^2, \mathcal{T}_l \mathcal{T}_m) \quad (6.10)$$

and the multiple scattering terms can be ignored. In fact since they depend on $G_0(l, m)$ which decays as $|l - m| \rightarrow \infty$, the single scattering approximation is good when the impurities are dilute (i.e. far apart). Note that the one exception is a 1-D system where multiple scattering cannot be ignored as $G_0(l, m)$ does not decay.

c) Infinite Number of Impurities

In this section we consider the case where a finite percentage of the sites are occupied by impurities in a random way. An example would be a binary alloy A_xB_{1-x} , where a fraction x of the sites are occupied by atoms A with site energy $\epsilon_0 + \epsilon_A$, and the rest are occupied by atoms B with site energy $\epsilon_0 + \epsilon_B$. In general we don't know which sites are occupied by A or B , but only the probabilities. We are thus led to the concept of a *random* or *disordered* system, whose Hamiltonian is not known. If there are no correlations between the random variables $\{\epsilon'_n\}$, their probability distribution is given by

$$P(\{\epsilon'_n\}) = \prod_n p(\epsilon'_n) \quad (6.11a)$$

with

$$p(\epsilon'_n) = x\delta(\epsilon'_n - \epsilon_A) + (1-x)\delta(\epsilon'_n - \epsilon_B) \quad (6.11b)$$

In a random system we are usually interested in the average (over all configurations) of the physical quantities. More specifically we should like to know the average of the Green's function $\langle \mathcal{G} \rangle$ defined as

$$\langle \mathcal{G} \rangle = \int d\{\epsilon'_n\} P(\{\epsilon'_n\}) \mathcal{G}(\{\epsilon'_n\}) \quad (6.12)$$

In general $\langle \mathcal{G} \rangle$ cannot be calculated exactly. The *Lloyd model* constitutes one exception. When $p(\epsilon'_n)$ is a Lorentzian

$$p(\epsilon'_n) = \frac{1}{\pi} \frac{\Gamma}{\epsilon_n'^2 + \Gamma^2} \quad (6.13)$$

Then, because $p(\epsilon'_n)$ has 2 poles $\epsilon'_n = \pm i\Gamma$, each integration over ϵ'_n in (6.12) replaces ϵ'_n by $\pm i\Gamma$; thus finally $\langle \mathcal{G}^\pm(E) \rangle = G_0(E \pm i\Gamma)$.

Other commonly used distributions are the rectangular

$$p(\epsilon'_n) \begin{cases} = \frac{1}{W} & \text{for } |\epsilon'_n| < \frac{1}{2}W \\ 0 & \text{otherwise} \end{cases} \quad (6.14a)$$

and the Gaussian

$$p(\epsilon'_n) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\epsilon_n'^2}{2\sigma^2}\right) \quad (6.14b)$$

This Hamiltonian (often called the *Anderson Hamiltonian*) is the simplest one to model a random system. Even within the tight-binding approximation there are physically important aspects which it ignores.

- i) the off-diagonal matrix elements V_{ij} may also be random variables (*off-diagonal disorder*).
- ii) the quantity ϵ'_n may depend on other sites in its vicinity of n .
- iii) the random variables $\{\epsilon'_n\}$ may be statistically correlated (*short-range order*).
- iv) in amorphous systems such as glasses the disorder is associated with the absence of a lattice rather than the values of the matrix elements (*topological disorder*). Such disorder is much more difficult to treat. N.B. Some authors (e.g. N.Rivier) reserve the term topological disorder for systems containing odd numbered rings of atoms. This is often, but not always, the case in real glasses.

In spite of the approximations built into the models it is still necessary to make further approximations to solve these models for $\langle \mathcal{G} \rangle$.

d) Virtual Crystal Approximation (VCA)

We use again $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ where \mathcal{H}_0 is periodic and \mathcal{H}_1 contains the random part. Then

$$\langle \mathcal{G} \rangle = \mathcal{G}_0 + \mathcal{G}_0 \langle \mathcal{H}_1 \mathcal{G} \rangle \quad (6.15)$$

since \mathcal{G}_0 does not depend on the random variables. We assume

$$\langle \mathcal{H}_1 \mathcal{G} \rangle \approx \langle \mathcal{H}_1 \rangle \langle \mathcal{G} \rangle \quad (6.16)$$

Taking into account that

$$\langle \mathcal{H}_1 \rangle = \sum_m |\mathbf{m}\rangle \langle \varepsilon'_m | \langle \mathbf{m} | = \langle \varepsilon'_m \rangle \equiv \varepsilon \quad (6.17)$$

since $\langle \varepsilon'_n \rangle$ is independent of \mathbf{m} .

Substituting in (6.15) we have

$$\begin{aligned} \langle \mathcal{G}(E) \rangle &= \mathcal{G}_0 + \mathcal{G}_0 \varepsilon \langle \mathcal{G}(E) \rangle \\ &= \frac{1}{E - \mathcal{H}_0 - \varepsilon} \\ &= \frac{1}{E - \langle \mathcal{H} \rangle} \end{aligned} \quad (6.18)$$

This approximation for $\langle \mathcal{G} \rangle$ consists in calculating $\langle \mathcal{G}(\mathcal{H}) \rangle$ as $\mathcal{G}(\langle \mathcal{H} \rangle)$ and simply shifts the energy levels by $\varepsilon = \langle \varepsilon'_n \rangle$. This shift can always be made equal to zero by $\mathcal{H}_0 = \langle \mathcal{H} \rangle$ and $\mathcal{H}_1 = \mathcal{H} - \langle \mathcal{H} \rangle$. From now on we adopt this convention.

The VCA fails completely for large values of $\langle \varepsilon_m'^2 \rangle$. However it seems to work surprisingly well for some alloys (e.g. $Al_xGa_{1-x}As$).

e) Average t-Matrix Approximation (ATA)

If T is the t-matrix associated with \mathcal{H}_0 and \mathcal{H}_1 we have

$$\langle \mathcal{G} \rangle = \mathcal{G}_0 + \mathcal{G}_0 \langle T \rangle \mathcal{G}_0 \quad (6.19)$$

where T is a complicated function of the individual t_m 's

$$T = f(\{t_m\}) \quad (6.20a)$$

$$t_m = \frac{\varepsilon'_m}{1 - \varepsilon'_m G_0(\mathbf{m}, \mathbf{m})} \quad (6.20b)$$

The basic approximation of the ATA is to put

$$\langle T \rangle \approx f(\{\langle t_m \rangle\}) \quad (6.21)$$

Because (6.21) has the same form as (6.20a) with an \mathbf{m} -independent $\langle t_m \rangle$, it follows that $\langle T \rangle$ is the same as the t-matrix associated with \mathcal{H}_0 and a periodic $\mathcal{H}_1 = \Sigma$, where Σ is chosen to satisfy

$$\langle t_m \rangle = \frac{\Sigma}{1 - \Sigma G_0(\mathbf{m}, \mathbf{m})} \quad (6.22)$$

Thus the energy is shifted by the complex self-energy Σ to give

$$\langle \mathcal{G}(E) \rangle = \mathcal{G}_0(E - \Sigma) \quad (6.23a)$$

where

$$\Sigma = \frac{\langle t_m \rangle}{1 + \langle t_m \rangle G_0(\mathbf{m}, \mathbf{m})} \quad (6.23b)$$

In the limit of weak scattering $\varepsilon'_m \rightarrow 0$, we obtain, in lowest order that

$$\Sigma \rightarrow \langle \varepsilon_m'^2 \rangle G_0(\mathbf{m}, \mathbf{m}) \quad (6.24)$$

which is the correct limit. The ATA is also successful in the very dilute limit, where the concentration of impurities is $\ll 1$.

f) Coherent Potential Approximation (CPA)

As in the ATA case, the CPA calculates $\langle \mathcal{G} \rangle$ through an effective Hamiltonian \mathcal{H}_e , which in the simplest case is characterised by a single, complex, energy-dependent self-energy Σ . The CPA is based upon expanding \mathcal{G} in terms of $\mathcal{G}_e \equiv (E - \mathcal{H}_e)^{-1}$ and $\mathcal{H}'_1 \equiv \mathcal{H} - \mathcal{H}_e$. Thus

$$\mathcal{G} = \mathcal{G}_e + \mathcal{G}_e T' \mathcal{G}_e \quad (6.25a)$$

where the t-matrix T' is

$$T' = f(\{t'_m\}) \quad (6.25b)$$

with

$$t'_m = \frac{(\epsilon'_m - \Sigma)}{1 - (\epsilon'_m - \Sigma) G_e(\mathbf{m}, \mathbf{m})} \quad (6.25c)$$

As for the ATA the central approximation is

$$\langle T' \rangle \approx f(\langle \{t'_m\} \rangle) \quad (6.26)$$

Taking the average of (6.25a) and using $\langle \mathcal{G} \rangle = \mathcal{G}_e$ we obtain $\langle T' \rangle = 0$, which in view of (6.26) implies $\langle t'_m \rangle = 0$. From (6.25c) we can write an equation for the self energy in the form

$$\Sigma = \left\langle \frac{\epsilon'_m}{1 - (\epsilon'_m - \Sigma) G_e(\mathbf{m}, \mathbf{m})} \right\rangle \quad (6.27a)$$

$$1 = \left\langle \frac{1}{1 - (\epsilon'_m - \Sigma) G_e(\mathbf{m}, \mathbf{m})} \right\rangle \quad (6.27b)$$

In (6.27) the quantity $G_e(\mathbf{m}, \mathbf{m})$ depends on Σ through

$$G_e(\mathbf{m}, \mathbf{m}; E) = G_0(\mathbf{m}, \mathbf{m}; E - \Sigma) \quad (6.28)$$

The CPA has been impressively successful. In the weak scattering limit it reduces to (6.24). It behaves correctly in the strong scattering or dilute limit, and interpolates properly between them.

It does however have failures. The only approximation used is that $\langle t'_m \rangle = 0$ implies $\langle T' \rangle = 0$. The physical meaning of this can be found by expressing T' in terms of the T'_m 's as

$$T' = \sum_m T'_m + \sum_{n \neq m} T'_n \mathcal{G}'_0 T'_m + \sum_{n \neq m \neq r} T'_m \mathcal{G}'_0 T'_m \mathcal{G}'_0 T'_r + \dots \quad (6.29)$$

When the $\{\epsilon'_m\}$ are independent random variables the quantities $\{t'_m\}$ are also independent random variables. Thus the 1st 3 terms in (6.29) depend on $\langle t'_m \rangle$ alone, the 4th term contains contributions like

$$\begin{aligned} & \sum_{n \neq m} \langle T'_n \mathcal{G}'_0 T'_m \mathcal{G}'_0 T'_n \mathcal{G}'_0 T'_m \rangle \\ & = \sum_{n \neq m} |n\rangle \langle t'_n{}^2 \rangle \langle t'_m{}^2 \rangle G_0(\mathbf{n}, \mathbf{m}) G_0(\mathbf{m}, \mathbf{n}) G_0(\mathbf{n}, \mathbf{m}) \langle m| \end{aligned} \quad (6.30)$$

Similarly higher-order terms will involve terms in $\langle t'_m{}^n \rangle$ for any integer n , which correspond to multiple scattering from a fixed number of sites. We conclude then that CPA incorrectly treats such multiple scattering. Such scattering is of great importance for eigenstates which significantly enhanced in the vicinity of a particular cluster. The multiple scattering is what traps the electron in the region for a long time. Hence at energies where the DOS is dominated by resonance or localised states, the CPA is expected to fail. Since the tails of the band are composed of such states the CPA is a very bad approximation there, in that it predicts no tail at all. The CPA tends to eliminate the structure in the DOS associated with such states. If the probability of occurrence of a special cluster is small the CPA is good. Such special clusters will tend to be less likely in 3-d than in 1-d as the number of atoms involved will be larger. Thus the CPA is better the higher the dimensionality. In this it has much in common with a mean field theory of a phase transition.

g) Extensions of the CPA

In our derivation of the CPA we assumed that the random part \mathcal{H}_1 was a sum of local terms. This was a necessary assumption. It can however be easily generalised to the case where \mathcal{H}_1 involves a finite number of local orbitals. In this case we can write

$$\mathcal{H}_1 = \sum_{\mathbf{m}} \sum_{\mathbf{v}\mathbf{v}'} |\mathbf{m}, \mathbf{v}\rangle \varepsilon'_{\mathbf{m}, \mathbf{v}\mathbf{v}'} \langle \mathbf{v}', \mathbf{m}| \quad (6.31)$$

and the effective Hamiltonian takes the form

$$\mathcal{H}_{1e} = \sum_{\mathbf{m}} \sum_{\mathbf{v}\mathbf{v}'} |\mathbf{m}, \mathbf{v}\rangle \Sigma_{\mathbf{v}\mathbf{v}'} \langle \mathbf{m}, \mathbf{v}| \quad (6.32)$$

where the matrix $\Sigma_{\mathbf{v}\mathbf{v}'}$ is determined by a matrix equation of the form (6.23b) for the ATA and $\langle t'_m \rangle = 0$ for the CPA. Care must be taken with the order of the matrices.

Another example is a special case of off-diagonal disorder where

$$V_{mn} = V_m + V_n \quad (6.33)$$

then \mathcal{H}_1 is the sum of local terms of the form

$$|\mathbf{m}\rangle \sum_n (\varepsilon'_m \delta_{mn} + V_m) \langle \mathbf{n}| \quad (6.34)$$

where the summation is over the nearest neighbours of \mathbf{m} .

This is the case for the special binary alloy system where

$$V_{AB} = \frac{1}{2} (V_{AA} + V_{BB}) \quad (6.35)$$

and lattice vibrational systems with random spring constants where

$$\varepsilon'_m = - \sum_n V_{mn} \quad (6.36)$$

When (6.36) is satisfied, \mathcal{H}_1 can be decomposed into *bond* contributions of the form

$$|\mathbf{n}\rangle V_{nm} \langle \mathbf{m}| + |\mathbf{m}\rangle V_{mn} \langle \mathbf{n}| + |\mathbf{m}\rangle V_{mn} \langle \mathbf{m}| + |\mathbf{n}\rangle V_{nm} \langle \mathbf{n}| \quad (6.37)$$

The CPA can also be generalised to other representations than tight-binding. For example, the so-called *muffin-tin* CPA avoids the problems associated with off-diagonal randomness in the tight-binding case.

These generalisations of the simple CPA share with it its advantages and difficulties. The limiting cases are correctly reproduced and the resulting DOS has proper analytical behaviour, i.e. no negative DOS. However this was only achieved by assuming special forms for the Hamiltonian. There have been numerous attempts to develop cluster-CPA methods. These involve for example:

- a) Forcing the system to have the periodicity of a larger *supercell* rather than that of a single atom per unit cell.
- b) Embedding the disordered system in an ordered effective medium. This category includes certain versions of the *Recursion Method* and the *Method of Moments* as well as the *Cluster Bethe* method.

7. Electrical Conductivity

Disorder has a much more profound effect on transport properties than on the DOS. The DC electrical conductivity is no longer infinite (as $T \rightarrow \infty$), and we can even find a *metal-insulator transition*.

a) Definition and Basic Results

An electric field \mathbf{E} induces a current density \mathbf{j} . The conductivity is defined as the coefficient of the linear (in \mathbf{E}) part of \mathbf{j} .

$$j_\alpha(\mathbf{r}, t) = \int_0^\infty d\tau \int d\mathbf{r}' \sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \tau) E_\beta(\mathbf{r}', t - \tau) \quad (7.1)$$

where the subscripts α, β denote Cartesian coordinates and a summation is implied over the repeated index β . We shall assume that \mathbf{E} and \mathbf{j} are both along the x -axis, so that we only need to consider σ_{xx} ; for simplicity then we drop the subscripts.

Usually \mathbf{E} and \mathbf{j} vary slowly over distances of the order of l_0 , where l_0 is determined by the condition $\sigma \approx 0$ for $|\mathbf{r} - \mathbf{r}'| \gg l_0$. In this case we can perform the integration over \mathbf{r}' and the average over \mathbf{r} to obtain

$$j(t) = \int_0^\infty d\tau \sigma(\tau) E(t - \tau) \quad (7.2)$$

where

$$\sigma(\tau) = \frac{1}{\Omega} \int d\mathbf{r} d\mathbf{r}' \sigma(\mathbf{r}, \mathbf{r}'; \tau) \quad (7.3)$$

We now consider $\sigma(\tau)$ or its Fourier transform

$$\sigma(\omega) = \int_0^\infty d\tau \sigma(\tau) e^{i\omega\tau} \quad (7.4)$$

If $E(t)$ is given by

$$E(t) = F e^{-i\omega t} + F^* e^{i\omega t} \quad (7.5)$$

we have

$$j(t) = \sigma(\omega) F e^{-i\omega t} + \sigma(-\omega) F^* e^{i\omega t} \quad (7.6)$$

the reality of j requires that $\sigma(-\omega) = \sigma^*(\omega)$ from which it follows that the real (imaginary) part σ_1 (σ_2) of σ is an even (odd) function of ω . because of causality, $\sigma(\tau)$ is nonzero only for $\tau \geq 0$. Consequently, $\sigma(\omega)$ is analytic for $\text{Im } \omega \geq 0$ with the possible exception of $\omega = 0$. Taking this into account as well as the fact that $\sigma(\omega) \rightarrow 0$ as $\omega \rightarrow \infty$ (see later), we can see that

$$\int_{-\infty}^{+\infty} \frac{d\omega' \sigma(\omega')}{\omega' + i s - \omega} = 0 \quad (7.7)$$

To prove this consider a contour around the positive half plain. There are no poles. By taking the limit $s \rightarrow 0+$ and by considering the imaginary (real) part of (7.7) we obtain

$$\sigma_1(\omega) = \frac{1}{\pi} \text{P} \int \frac{d\omega' \sigma_2(\omega')}{\omega' - \omega} \quad (7.8a)$$

$$\sigma_2(\omega) = -\frac{1}{\pi} \text{P} \int \frac{d\omega' \sigma_1(\omega')}{\omega' - \omega} + \frac{A}{\omega} \quad (7.8b)$$

where iA is the residue (if any) of $\sigma(\omega)$ at $\omega = 0$. Thus, knowing $\sigma_1(\omega)$ for $\omega \neq 0$ one can calculate $\sigma_2(\omega)$ and consequently $\sigma(\omega)$. The constant A can be obtained from the behaviour of $\sigma(\omega)$ at infinity.

(7.8) are usually referred to as *Kramers–Kronig* relationships.

The simplest and crudest way to obtain $\sigma(\omega)$ is by using Newton's equations for the electronic drift velocity v in the presence of the field $F \exp(-i\omega t)$ and a friction force $-mv/\tau_{tr}$ (τ_{tr} is the transport relaxation time):

$$-i\omega m v = -\frac{mv}{\tau_{tr}} + eF \quad (7.9)$$

The current is given by $j = nev$ where n is the electronic density, we obtain for $\sigma(\omega)$

$$\sigma(\omega) \approx \frac{ne^2 \tau_{tr}}{m(1 - i\omega \tau_{tr})} \quad (7.10)$$

For $\omega \rightarrow \infty$ the electronic motion is classical, all scattering is negligible, and only the electronic inertia (as measured by its mass m) matters. Hence

$$\sigma(\omega) \xrightarrow{\omega \rightarrow \infty} i \frac{ne^2}{m\omega} \quad (7.11)$$

A slight generalisation of this approach, capable of treating non-spherical Fermi surfaces, consists in considering the whole equilibrium distribution transposed rigidly in \mathbf{k} -space by an amount $\delta\mathbf{k} = m\mathbf{v}/\hbar$, where \mathbf{v} is again given by (7.9). A more sophisticated approach is one given by Boltzmann's equation, which determines the electron distribution in \mathbf{k} -space in the presence of an applied electric field and scattering mechanism, which tends to restore equilibrium. The advantage of this approach is that the phenomenological parameter τ_{tr} is related to the scattering potential $V(\mathbf{r})$ by

$$\frac{1}{\tau_{tr}} = \frac{2\pi}{\hbar} \rho_F n_{imp} \frac{1}{4\pi} \int_F S d\mathbf{q} V^2(\mathbf{q})(1 - \cos \theta) \quad (7.12)$$

where ρ_F is the DOS per unit volume per spin direction, n_{imp} is the number of scatterers per unit volume, the integration is over all directions of \mathbf{q} ($E(\mathbf{q}) = E_F$) and $V(\mathbf{q})$ is the Fourier transform of $V(\mathbf{r})$. (7.12) follows from Fermi's golden rule for the transition rate from a given state on the Fermi-surface to all others. The extra factor $(1 - \cos \theta)$ accounts for the fact that what matters for transport is the momentum change along the direction of initial propagation. If $V^2(\mathbf{q})$ is isotropic (or more generally , if it does not contain a p -spherical harmonic) then the $\cos \theta$ term averages to zero, and $\tau_{tr} = \tau$, where τ is given by (7.12) without the $\cos \theta$ term.

b) General Formula for the Conductivity

i) Linear Response Theory

Consider the density matrix $\rho(\mathbf{r}, \mathbf{r}')$ which is defined as

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha_{occ}} \phi_{\alpha}(\mathbf{r}) \phi_{\alpha}^*(\mathbf{r}') \quad (7.13a)$$

$$= \sum_{\alpha_{occ}} \langle \mathbf{r} | \alpha \rangle \langle \alpha | \mathbf{r}' \rangle \quad (7.13b)$$

where the sum is over all occupied states. The density matrix is closely related to the Green's functions and shares many of their properties. A more general definition replaces $\sum_{\alpha_{occ}}$ by $\sum_{\alpha} f_{\alpha}$, where f_{α} represents the value of Fermi-Dirac distribution function for the state $|\alpha\rangle$.

We shall study the evolution of the density matrix using the equation

$$-i\hbar \dot{\rho} = [\mathcal{H}, \rho] \quad (7.14)$$

We write the unperturbed equilibrium \mathcal{H} and ρ as \mathcal{H}_0 and ρ_0 respectively, and the corresponding deviations as $\delta\mathcal{H}(t)$ and $\delta\rho$. We assume further that \mathcal{H}_0 and ρ_0 are time-independent, whereas $\delta\mathcal{H}(t)$ is explicitly time-dependent. Then to 1st order we can write

$$-i\hbar (\dot{\rho} + \dot{\delta\rho}) = [\mathcal{H}_0, \rho_0] + [\delta\mathcal{H}(t), \rho_0] + [\mathcal{H}_0, \delta\rho] \quad (7.15a)$$

$$-i\hbar \dot{\delta\rho} = [\delta\mathcal{H}(t), \rho_0] + [\mathcal{H}_0, \delta\rho] \quad (7.15b)$$

By taking the matrix element of both sides with eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of \mathcal{H}_0 we obtain

$$-i\hbar \langle \alpha | \dot{\delta\rho} | \beta \rangle = \langle \alpha | [\delta\mathcal{H}(t), \rho_0] | \beta \rangle + \langle \alpha | [\mathcal{H}_0, \delta\rho] | \beta \rangle \quad (7.16a)$$

$$= -(f_{\alpha} - f_{\beta}) \langle \alpha | \delta\mathcal{H}(t) | \beta \rangle + (\epsilon_{\alpha} - \epsilon_{\beta}) \langle \alpha | \delta\rho | \beta \rangle \quad (7.16b)$$

which can be rewritten in the form

$$\frac{\partial}{\partial t} \langle \alpha | \delta\rho | \beta \rangle - \frac{i}{\hbar} (\epsilon_{\alpha} - \epsilon_{\beta}) \langle \alpha | \delta\rho | \beta \rangle = -\frac{i}{\hbar} (f_{\alpha} - f_{\beta}) \langle \alpha | \delta\mathcal{H}(t) | \beta \rangle \quad (7.17)$$

Using the integrating factor method the solution of (7.17) can be written down

$$\langle \alpha | \delta \rho | \beta \rangle = -\frac{i}{\hbar} e^{i\delta\omega_{\alpha\beta}t} \int_{-\infty}^t dt' e^{-i\delta\omega_{\alpha\beta}t'} \delta f_{\alpha\beta} \langle \alpha | \delta \mathcal{H}(t') | \beta \rangle \quad (7.18)$$

where $\delta\omega_{\alpha\beta} = (\varepsilon_{\alpha} - \varepsilon_{\beta})/\hbar$ and $\delta f_{\alpha\beta} = f_{\alpha} - f_{\beta}$.

We now specialise to the case where $\delta \mathcal{H}(t) = \delta \mathcal{H} \exp(\eta t + i\omega t)$. The rationale behind this is that the perturbation should be switched on infinitesimally slowly at $t = -\infty$ and we are interested only in long term rather than transient behaviour. We shall later take the limit $\eta \rightarrow 0+$. Substituting this form into (7.18) and integrating gives

$$\langle \alpha | \delta \rho | \beta \rangle = -\frac{1}{\hbar} \delta f_{\alpha\beta} \frac{\langle \alpha | \delta \mathcal{H}(t) | \beta \rangle}{\omega - i\eta - \delta\omega_{\alpha\beta}} \quad (7.19)$$

This is the basic result of *linear response* theory.

In order to calculate the conductivity we require

$$\delta \mathcal{H}(t) = \frac{e}{m} \mathbf{E} \cdot \hat{\mathbf{p}} \frac{e^{(\eta+i\omega)t}}{\eta + i\omega} \quad (7.20a)$$

$$= e \mathbf{x} \cdot \mathbf{E} e^{(\eta+i\omega)t} \quad (7.20b)$$

$$\begin{aligned} \mathbf{j} &= \frac{1}{\Omega} \langle \hat{\mathbf{j}} \rho \rangle \\ &= \frac{1}{\Omega} \left\langle \frac{e}{m} \hat{\mathbf{p}} \delta \rho \right\rangle \end{aligned} \quad (7.20c)$$

$$= -\frac{e^2}{\Omega m^2 \hbar} \sum_{\alpha\beta} |\langle \alpha | \hat{\mathbf{p}} | \beta \rangle|^2 \frac{\delta f_{\alpha\beta}}{(\eta + i\omega)(\omega - i\eta - \delta\omega_{\alpha\beta})} \mathbf{E} e^{(\eta+i\omega)t} \quad (7.20d)$$

The real part of the conductivity σ is found by removing the time-dependent electric field factor from (7.20d), taking the limit $\eta \rightarrow 0+$, and expressing the result in terms of delta-functions to obtain

$$\sigma_1(\omega) = -\frac{\pi e^2}{\Omega m^2 \hbar} \sum_{\alpha\beta} |\langle \alpha | \hat{\mathbf{p}} | \beta \rangle|^2 \frac{\delta f_{\alpha\beta}}{\delta\omega_{\alpha\beta}} \delta(\omega - \delta\omega_{\alpha\beta}) \quad (7.21)$$

Note that this function is always positive: the ratio $\delta f/\delta\omega$ is always negative.

An alternative derivation of (7.21) is given by Economou.

This formula is usually referred to as the *Kubo–Greenwood* formula.

Using the Kramers–Kronig relations (7.8) we can now derive the expression for $\sigma_2(\omega)$. Combining these expressions we obtain finally

$$\begin{aligned} \sigma(\omega + is) &= \left(\frac{e^2 n}{m} + \frac{e^2}{\Omega m^2} \sum_{\alpha\beta} |\langle \alpha | \hat{p}_x | \beta \rangle|^2 \frac{\delta f_{\alpha\beta}}{\hbar \delta\omega_{\alpha\beta}} \right) \frac{i}{\omega + is} \\ &\quad - i \frac{e^2}{\Omega m^2} \sum_{\alpha\beta} |\langle \alpha | \hat{p}_x | \beta \rangle|^2 \frac{\delta f_{\alpha\beta}}{\hbar \delta\omega_{\alpha\beta}} \frac{1}{\omega + is + \delta\omega_{\alpha\beta}} \end{aligned} \quad (7.22)$$

The term $ie^2 n/m\omega \equiv \sigma_d(\omega)$ is the so-called *diamagnetic* contribution to $\sigma(\omega)$, and the rest, $\sigma_p(\omega)$, is the *paramagnetic* one, which can be recast as

$$\sigma_p(\omega) = +i \frac{e^2}{\Omega m^2 \hbar \omega} \sum_{\alpha\beta} |\langle \alpha | \hat{p}_x | \beta \rangle|^2 \frac{\delta f_{\alpha\beta}}{\omega + is + \delta\omega_{\alpha\beta}} \quad (7.23)$$

The local conductivity $\sigma(\mathbf{r}, \mathbf{r}'; \omega)$ can be obtained by replacing the velocity operator matrix elements, \hat{p}_x/m , by the current operator matrix elements:

$|\langle \alpha | \hat{p}_x | \beta \rangle|^2 / \Omega \mapsto \lambda_{\alpha\beta}(\mathbf{r}) \lambda_{\alpha\beta}^*(\mathbf{r}')$, where

$$\lambda_{\alpha\beta}(\mathbf{r}) = \frac{-i\hbar}{2} \left[\psi_{\alpha}^*(\mathbf{r}) \frac{\partial \psi_{\beta}(\mathbf{r})}{\partial x} - \psi_{\beta}(\mathbf{r}) \frac{\partial \psi_{\alpha}^*(\mathbf{r})}{\partial x} \right] \quad (7.24)$$

where $\psi_{\alpha}(\mathbf{r}) = \langle \mathbf{r} | \alpha \rangle$. To obtain $\sigma_{\mu\nu}$ we must replace $|\langle \alpha | \hat{p}_x | \beta \rangle|^2$ by $\langle \alpha | \hat{p}_{\mu} | \beta \rangle \langle \alpha | \hat{p}_{\nu} | \beta \rangle$.

A useful identity relates the position operator \hat{x} and the momentum operator \hat{p}_x :

$$\begin{aligned} \langle \alpha | \hat{p}_x | \beta \rangle &= \frac{im}{\hbar} \langle \alpha | [\mathcal{H}, \hat{x}] | \beta \rangle \\ &= im\delta\omega_{\alpha\beta} \langle \alpha | \hat{x} | \beta \rangle \end{aligned} \quad (7.25)$$

It should be noted that this relationship generally fails in the presence of periodic boundary conditions where the position operator is not well defined. Nevertheless when all states are localised in a region much smaller than the period (7.25) is often used.

Mott and Davis give an instructive way of deriving (7.10) (for $\omega = 0$) starting from (7.21). Their main assumption is that for weakly disordered systems the eigenfunctions have essentially constant amplitude (as in perfectly ordered systems) but phase coherence is maintained only over a distance of the order of the transport mean free path $l_{tr} = v_F \tau_{tr}$. If the total volume Ω is divided into cells, each of volume $v_i \approx l_{tr}^d$, then

$$\langle \alpha | \hat{p}_x | \beta \rangle = \sum_{v_i} \int_{v_i} d\mathbf{r} \psi_{\alpha}^* \hat{p}_x \psi_{\beta} \quad (7.26)$$

Multiplying (7.26) by its complex conjugate and cancelling the cross terms due to their random phases, one obtains

$$\begin{aligned} |\langle \alpha | \hat{p}_x | \beta \rangle|^2 &= \sum_i \left| \int_{v_i} d\mathbf{r} \psi_{\alpha}^* \hat{p}_x \psi_{\beta} \right|^2 \\ &= \frac{\Omega}{v} \left| \int_{v_i} d\mathbf{r} \psi_{\alpha}^* \hat{p}_x \psi_{\beta} \right|^2 \end{aligned} \quad (7.27)$$

Within the volume v , ψ_{α} and ψ_{β} are assumed to be plane waves so that the integral can be performed explicitly. Substituting the result in (7.21) one obtains

$$\sigma_1 \approx \frac{e^2 n l_{tr}}{2m v_F} \quad (7.28)$$

which coincides with (7.10) except for a factor of 2 (for $\omega = 0$).

Thouless has also obtained (7.10) starting from (7.21) by assuming that ψ_{α} and ψ_{β} are linear combinations of plane waves with coefficients which are uncorrelated Gaussian random variables whose variance is

$$\frac{\pi}{l_{tr} k^2 \Omega} \left[\frac{(k - k_{\alpha})^2 + l_{tr}^2}{4} \right] \quad (7.29)$$

c) The Conductivity in terms of Green's Functions

There are several different formulations of the conductivity in terms of Green's functions. Firstly we express $\sigma(\omega)$ in terms of the *causal* Green's function, $g(E)$, which is important in many-body theory. For the present purpose, non-interacting electrons, $g(E)$ can be defined as $G^-(E)$ for $E < E_F$ and $G^+(E)$ for $E > E_F$, i.e.

$$g(E) \equiv [E + is\bar{\epsilon}(E - E_F) - \mathcal{H}]^{-1} \quad (7.30)$$

At $T = 0$ we have

$$-\frac{\delta f_{\alpha\beta}}{\epsilon_{\alpha\beta} + \hbar\omega + is} = \frac{-1}{2\pi i} \int_{-\infty}^{+\infty} dE \langle \alpha | g(E) | \alpha \rangle \langle \beta | g(E + \hbar\omega) | \beta \rangle \quad (7.31)$$

Substituting in (7.23) leads to

$$\sigma(\omega) = \frac{ie^2 n}{m\omega} + \frac{e^2}{\Omega m^2 \omega} \int \frac{dE}{2\pi} \text{Tr} \{ \hat{p}_x g(E) \hat{p}_x g(E + \hbar\omega) \} \quad (7.32)$$

where the Tr operation includes a factor of 2 for the spin. By using standard many-body techniques (7.32) can be generalised to finite temperatures.

It is probably simpler to express $\sigma_1(\omega)$ in terms of $\tilde{\mathcal{G}} = \mathcal{G}^+ - \mathcal{G}^-$. for that purpose one notices first that

$$\frac{\delta f_{\alpha\beta}}{-\delta\omega_{\alpha\beta}} \delta(\hbar\omega + \delta\epsilon_{\alpha\beta}) = \int dE \delta(E - E_\alpha) \delta(E - E_\beta + \hbar\omega) \frac{f(E) - f(E + \hbar\omega)}{\omega} \quad (7.33)$$

Substituting (7.33) in (7.21) we have

$$\begin{aligned} \sigma_1(\omega) &= \frac{\pi e^2 \hbar}{\Omega m^2} \int_{-\infty}^{+\infty} dE \frac{f(E) - f(E + \hbar\omega)}{\hbar\omega} \\ &\quad \times \text{Tr} \{ \hat{p}_x \delta(E + \hbar\omega - \mathcal{H}) \hat{p}_x \delta(E - \mathcal{H}) \} \\ &= \frac{e^2 \hbar}{\pi \Omega m^2} \int_{-\infty}^{+\infty} dE \frac{f(E) - f(E + \hbar\omega)}{\hbar\omega} \\ &\quad \times \text{Tr} \{ \hat{p}_x \text{Im} \mathcal{G}^+(E + \hbar\omega) \hat{p}_x \text{Im} \mathcal{G}^+(E) \} \end{aligned} \quad (7.34)$$

where again the Tr includes a factor of 2 for spins. $\sigma_1(\omega)$ can be expressed in terms of \mathcal{G}^\pm by noticing that $\text{Im} \mathcal{G}^+ = i \frac{1}{2} (\mathcal{G}^- - \mathcal{G}^+)$.

Note that in the limit $\omega \rightarrow 0$ these equations can be simplified using

$$\lim_{\omega \rightarrow 0} \frac{f(E) - f(E + \hbar\omega)}{\hbar\omega} \mapsto -\frac{\partial f}{\partial E} \quad (7.35)$$

and that in the limit $T \rightarrow 0$ this further simplifies to

$$-\frac{\partial f}{\partial E} \mapsto \delta(E - E_F) \quad (7.36)$$

Another useful form is found by transforming the \hat{p}_x operators to \hat{x} operators using the relationship $i\hbar\hat{p}_x = m[H, \hat{x}]$. Substituting this in (7.34) and rearranging gives

$$\begin{aligned} \sigma_1(0) &= \frac{2e^2}{\hbar\Omega} \lim_{\eta \rightarrow 0^+} \text{Tr} \{ \eta^2 (\mathcal{G}(E + i\eta) \hat{x} \mathcal{G}(E - i\eta) \hat{x}) \\ &\quad - i \frac{1}{2} \eta (\mathcal{G}(E + i\eta) - \mathcal{G}(E - i\eta)) \hat{x}^2 \} \end{aligned} \quad (7.37)$$

This latter form has proven particularly useful as the starting point for the development of a numerical method for the calculation of the conductivity.

In all this it is necessary to average over the ensemble of disordered systems, usually employing the arithmetic mean of σ . There is much evidence that the distribution of $\ln \sigma$ is better behaved (approximately log-normal) and it is often argued that $\exp \langle \ln \sigma \rangle$ is more representative of the whole distribution of σ 's than $\langle \sigma \rangle$.

In order to calculate the arithmetic mean it is necessary to calculate the average of a product of 2 \mathcal{G} 's, which is not generally equal to the average of the product. However we shall consider the results of such a calculation. Working in the \mathbf{k} -representation where both \mathbf{p} and $\langle \mathcal{G} \rangle$ are diagonal and considering the d.c. conductivity at $T = 0$ we have

$$\sigma(0) = \frac{2e^2\hbar}{m\Omega} \sum_{\mathbf{k}} \left| \left\langle \mathbf{k} \left| \frac{\hat{p}_x}{m} \right| \mathbf{k} \right\rangle \right|^2 |\text{Im } \mathcal{G}^+(E, \mathbf{k})|^2 \quad (7.38)$$

Taking into account that $\langle \mathbf{k} | (\hat{p}_x/m) | \mathbf{k} \rangle = v_x(\mathbf{k})$, and that $\mathcal{G}^+(E, \mathbf{k}) = [E - \Sigma(E) - E(\mathbf{k})]^{-1}$, where $\Sigma = \Sigma_1 + i\Sigma_2$ is the self-energy we obtain

$$\sigma(0) = \frac{2e^2\hbar}{\pi\Omega} \sum_{\mathbf{k}} \frac{\Sigma_2^2}{\left([E_f - \Sigma_1 - E(\mathbf{k})]^2 + \Sigma_2^2 \right)^2} \quad (7.39)$$

The summation over \mathbf{k} is easier if we introduce an integration over $\delta(E' - E(\mathbf{k})) dE'$, so that

$$\begin{aligned} \sigma(0) &= \frac{2e^2\hbar}{\pi} \int dE' \left[\frac{1}{\Omega} \sum_{\mathbf{k}} v_x^2(\mathbf{k}) \delta(E' - E(\mathbf{k})) \right] \\ &\quad \times \frac{\Sigma_2^2}{\left([E_f - \Sigma_1 - E(\mathbf{k})]^2 + \Sigma_2^2 \right)^2} \end{aligned} \quad (7.40)$$

The quantity in brackets, $[\]$, only depends on the form of $E(\mathbf{k})$. For cubic symmetry lattices v_x^2 can be replaced by \mathbf{v}^2/d . Then the \mathbf{k} summation can be replaced by an integration over the Fermi-surface, so that

$$\begin{aligned} \frac{1}{d\Omega} \sum_{\mathbf{k}} |\mathbf{v}(\mathbf{k})|^2 \delta(E' - E(\mathbf{k})) &= \frac{1}{(2\pi)^d d} \int dS_{\mathbf{k}} \frac{1}{\hbar |\mathbf{v}(\mathbf{k})|} |\mathbf{v}(\mathbf{k})|^2 \\ &= \frac{1}{(2\pi)^d d \hbar} S(E') v(E') \end{aligned} \quad (7.41)$$

where S is the are of the surface of constant energy E' and $v(E')$ is the average of the magnitude of the velocity over this surface.

In the weak scattering limit, where Σ_2 is small, and Sv can be taken as a constant, the integration over E' can be performed explicitly to give

$$\sigma(0) = \frac{e^2 v_F}{|\Sigma_2|} \frac{S_F}{(2\pi)^d d} \quad (7.42)$$

For a spherical Fermi-surface this becomes

$$\sigma(0) = e^2 n \frac{v_F}{k_F} \frac{1}{2 |\Sigma_2|} \quad (7.42)$$

where n is the density of electrons at the Fermi-level. Comparing this result with the classical one (7.10) we can identify τ with $\hbar/2 |\Sigma_2|$.

Improved results can be obtained by including so-called *vertex corrections* for $\langle \mathcal{G}\mathcal{G} \rangle - \langle \mathcal{G} \rangle^2$. However we have already seen that the CPA omits much of the important physics of disordered systems.

d) CPA and Vertex Corrections

Consider a quantity of the form $\langle \mathcal{G} \hat{B} \mathcal{G} \rangle$. In the framework of the CPA this can be written as

$$\begin{aligned} \langle \mathcal{G} \hat{B} \mathcal{G} \rangle &= \mathcal{G}_e \hat{B} \mathcal{G}_e + \langle (\mathcal{G} - \mathcal{G}_e) \hat{B} (\mathcal{G} - \mathcal{G}_e) \rangle \\ &= \langle \mathcal{G}_e T' \mathcal{G}_e \hat{B} \mathcal{G}_e T' \mathcal{G}_e \rangle \\ &= \langle \mathcal{G}_e \Gamma \mathcal{G}_e \rangle \end{aligned} \quad (7.43)$$

where the residual t-matrix is non-diagonal in the site indices. We now use the property that

$$T'(\mathbf{m}, \mathbf{n}) = |\mathbf{m}\rangle t'_m \delta_{mn} \langle \mathbf{n}| + \sum_{\mathbf{m}' \neq \mathbf{m}} |\mathbf{m}\rangle t'_m \langle \mathbf{m}'| G_e(\mathbf{m}, \mathbf{m}') T'(\mathbf{m}', \mathbf{n}) \quad (7.44)$$

and substituting this in (7.43) to obtain

$$\begin{aligned} \Gamma_{mn} &= \left\langle t'_m \left(1 + \sum_{\mathbf{m}' \neq \mathbf{m}} G_e(\mathbf{m}, \mathbf{m}') T'(\mathbf{m}', \mathbf{m}'') \right) \mathcal{G}_e \hat{B} \mathcal{G}_e \right. \\ &\quad \left. \times \left(1 + \sum_{\mathbf{n}' \neq \mathbf{n}} T'(\mathbf{n}'', \mathbf{n}') G_e(\mathbf{n}', \mathbf{n}) \right) t'_n \right\rangle \end{aligned} \quad (7.45)$$

The CPA for the vertex part Γ_{mn} is to ignore the correlations between the t'_m 's and the $T'(\mathbf{m}, \mathbf{m}')$'s in (7.45). Thus we can write

$$\begin{aligned} \Gamma_{mn} &= \left\langle t'_m \left\langle \left(1 + \sum_{\mathbf{m}' \neq \mathbf{m}} G_e(\mathbf{m}, \mathbf{m}') T'(\mathbf{m}', \mathbf{m}'') \right) \mathcal{G}_e \hat{B} \mathcal{G}_e \right. \right. \\ &\quad \left. \left. \times \left(1 + \sum_{\mathbf{n}' \neq \mathbf{n}} T'(\mathbf{n}'', \mathbf{n}') G_e(\mathbf{n}', \mathbf{n}) \right) \right\rangle t'_n \right\rangle \end{aligned} \quad (7.46)$$

Since the t'_m are independent random variables with zero mean (due to the CPA condition) the RHS of (7.46) is non-zero only when $\mathbf{m} = \mathbf{n}$. Hence

$$\Gamma_{mn} = \delta_{mn} \Gamma_n = \delta_{mn} |\mathbf{n}\rangle \gamma_n \langle \mathbf{n}| \quad (7.47)$$

Of the 4 terms inside the average in (7.46) 2 are proportional to $\langle T \rangle$ and hence are zero within the CPA; the 3rd is simply $\mathcal{G}_e \hat{B} \mathcal{G}_e$, and the 4th is

$$\sum_{\mathbf{l}, \mathbf{n}' \neq \mathbf{n}} \mathcal{G}_e \langle T'(\mathbf{l}, \mathbf{l}') \mathcal{G}_e \hat{B} \mathcal{G}_e T'(\mathbf{n}', \mathbf{n}) \rangle \mathcal{G}_e = \sum_{\mathbf{n}' \neq \mathbf{n}} G_e(\mathbf{m}, \mathbf{n}) \Gamma_n G_e(\mathbf{n}, \mathbf{m}) \quad (7.48)$$

Using $\sum_{\mathbf{n}' \neq \mathbf{m}} \Gamma_n = \sum_{\mathbf{n}} \Gamma_n - \Gamma_m$ we can rewrite (7.46) as

$$\begin{aligned} &\gamma_n [1 + \langle t'_n t'_n \rangle G_e(\mathbf{n}, \mathbf{n}) G_e(\mathbf{n}, \mathbf{n})] \\ &= \sum_{\mathbf{l} \mathbf{m}} \langle t'_n t'_n \rangle G_e(\mathbf{n}, \mathbf{l}) [B_{\mathbf{l} \mathbf{m}} + \gamma_l \delta_{\mathbf{l} \mathbf{m}}] G_e(\mathbf{m}, \mathbf{n}) \end{aligned} \quad (7.49)$$

In order to simplify this expression we define the quantity $u(z, z')$ as

$$u(z, z') \equiv \langle t'_n(z) t'_n(z') \rangle [1 + \langle t'_n(z) t'_n(z') \rangle G_e(\mathbf{n}, \mathbf{n}; z) G_e(\mathbf{n}, \mathbf{n}; z')]^{-1} \quad (7.50)$$

so that (7.49) now becomes

$$\gamma_n(z, z') = \sum_{\mathbf{l} \mathbf{m}} u(z, z') G_e(\mathbf{n}, \mathbf{l}; z) [B_{\mathbf{l} \mathbf{m}} + \gamma_l(z, z') \delta_{\mathbf{l} \mathbf{m}}] G_e(\mathbf{m}, \mathbf{n}; z') \quad (7.51)$$

The solution of (7.51) can be found by making the substitution

$$\gamma_n = \sum_{mlk} \gamma_{nm} G_e(ml) B_{lk} G_e(km) \quad (7.52)$$

so that (7.51) can be rewritten in the form

$$\sum_m \left[\gamma_{nm} - u\delta_{nm} - \sum_l u G_e(n, l) G_e(l, n) \gamma_{lm} \right] \langle m | \mathcal{G}_e \hat{B} \mathcal{G}_e | m \rangle = 0 \quad (7.53)$$

The only B -independent solution is when the quantity in [] brackets is itself zero; that is

$$\gamma_{nm} = u\delta_{mn} + \sum_l u G_e(n, l) G_e(l, n) \gamma_{lm} \quad (7.54)$$

The quantity γ_{nm} corresponds to the *vertex-correction* in many-body theory. (7.54) can be solved in k space to yield

$$\gamma(\mathbf{q}; z, z') = u(z, z') [1 - u(z, z') A(\mathbf{q}; z, z')]^{-1} \quad (7.55a)$$

$$\begin{aligned} A(\mathbf{q}; z, z') &= \sum_m e^{iq \cdot m} G_e(\mathbf{0}, \mathbf{m}; z) G_e(\mathbf{m}, \mathbf{0}; z') \\ &= \frac{1}{N} \sum_k G_e(\mathbf{k}; z) G_e(\mathbf{k} - \mathbf{q}; z') \end{aligned} \quad (7.55b)$$

$$\gamma_{nm}(z, z') = \frac{1}{N} \sum_q e^{iq \cdot (n-m)} \gamma(\mathbf{q}; z, z') \quad (7.55c)$$

These results can also be written in a diagrammatic representation. Note that for weak scattering $u \mapsto \langle \epsilon_n^2 \rangle$ and $\gamma_{mn} \mapsto u\delta_{mn}$.

If we are interested in the conductivity tensor we first note that $\hat{B} = \hat{p}$ and that \hat{p} in the k -representation is an odd function of k due to time-reversal symmetry. Hence from (7.52) $\gamma_n = 0$ and the CPA vertex corrections vanish. Note however that for quantities like

$$\langle G(\mathbf{m}, \mathbf{n}; z) G(\mathbf{n}, \mathbf{m}; z') \rangle = \frac{1}{N} \sum_k e^{-ik \cdot (m-n)} \frac{A(\mathbf{k}; z, z')}{1 - u(z, z') A(\mathbf{k}; z, z')} \quad (7.56)$$

which is related to the transmission coefficient, they constitute a major contribution.

e) Vertex Corrections beyond the CPA

Clearly we have omitted some important terms from the CPA; (7.46) is an approximation. The most important of these form a group very similar to the CPA ones, and may, therefore, be equally important. They are best expressed diagrammatically using the so-called totally crossed diagrams. In conventional notation we have

$$\begin{aligned} &\text{Tr} \{ \hat{A} \langle \mathcal{G}(z) \hat{B} \mathcal{G}(z') \rangle \} - \text{Tr} \{ \hat{A} \langle \mathcal{G}(z) \rangle \hat{B} \langle \mathcal{G}(z') \rangle \} \\ &\approx \sum A_{ls} G_e(s, \mathbf{m}; z) \gamma_{mn} G_e(\mathbf{n}, \mathbf{i}; z) B_{ij} G_e(\mathbf{j}, \mathbf{m}; z') G_e(\mathbf{n}, \mathbf{l}; z') \end{aligned} \quad (7.57)$$

and the equation corresponding to (7.54) is expressed in expanded form as

$$\begin{aligned} \gamma_{nm} &= G_e(\mathbf{n}, \mathbf{m}) u \delta_{mm'} G_e(\mathbf{n}', \mathbf{m}') u \delta_{nn'} \\ &+ \sum_{l'l'} G_e(\mathbf{n}, \mathbf{l}) u \delta_{nn'} G_e(\mathbf{l}, \mathbf{m}) u \delta_{l'l'} G_e(\mathbf{n}', \mathbf{l}') u \delta_{mm'} G_e(\mathbf{l}', \mathbf{m}') + \dots \end{aligned} \quad (7.58)$$

This is really the same as before except that half the Green's functions have been turned round. That is $G_e(\mathbf{m}, \mathbf{n}) G_e(\mathbf{n}, \mathbf{m}) \mapsto G_e(\mathbf{m}, \mathbf{n}) G_e(\mathbf{n}, \mathbf{m})$. We note that in the presence of time-reversal symmetry $G_e(\mathbf{m}, \mathbf{n}) = G_e(\mathbf{n}, \mathbf{m})$ but that a magnetic field will destroy that symmetry. Hence $\gamma_{mn} = \gamma_{nm}$. The difference between the two cases lies in the way the vertex part γ_{mn} is connected to the rest of the system. In the CPA case the 2 G_e 's which connect γ_{mn} to \hat{A} and \hat{B} start and end on the same site, whereas in the case of the totally crossed diagrams the sites are different. The symmetry which made the CPA correction to the conductivity zero is no longer effective and a finite contribution results. This contribution plays a crucial role in localisation (see below).

8. Disorder and Localisation

Earlier we tried to calculate the conductivity of a disordered system by assuming that the amplitude of the wave function is constant and the phase is random. This is quite a common approximation in the metallic regime where the phase may be considered random on length scales larger than the mean free path. However there is no reason in principle why the amplitude should not be affected.

Consider the simple case of 2 coupled pendula. The transfer of motion from one to the other is facilitated by strong coupling and opposed by frequency mismatch. If we now consider an array of such pendula, then it is not difficult to imagine a region of strong frequency mismatch which a wave propagating in such a medium will find almost inaccessible. In fact one could imagine a wave surrounded by such regions which is confined to its own region, unable to escape.

Previously we considered a single or double impurity. These gave rise to discrete states outside the continuous spectrum of the rest of the system. What happens then when we go over to a finite density of impurities? We should expect the discrete spectrum to be smeared out to form a continuum which forms a tail of the main band. The question arises whether such states remain localised or become extended.

The answer to this can be found in the framework of the random tight-binding model often termed the *Anderson Model*. It contains in its simplest form the essential competition between the coupling V and the energy (or frequency) mismatch, which is characterised by a width $\delta\epsilon$ ($\delta\epsilon = |\epsilon_A - \epsilon_B|$, Γ , W for binary, Lorentzian and rectangular distributions respectively) of the probability distribution of the random variable ϵ_n . Thus the important parameter for localisation is

$$Q = \frac{V}{\delta\epsilon} \quad (8.1)$$

As we shall see an equally important parameter is the dimensionality d . Other aspects such as the shape of the probability distribution and the type of lattice are of secondary importance and are believed not to influence the alleged universal features of the problem.

We now summarise the main results in the field. These results have usually not been rigorously proven but are generally accepted.

i) There is a critical dimensionality $d = 2$. For $d \leq 2$ all eigenstates are localised, no matter how weak the disorder is. For $d > 2$ and for weak disorder the tails of the band consist of localised states whereas the interior corresponds to extended states. These regions are separated by critical energies, called *mobility edges*. As the disorder is increased the mobility edge tends towards the centre of the band until eventually, at the *Anderson Transition*, all states are localised. This can be represented on the $E - W$ plain, by a mobility edge trajectory which separates the regions of localised and extended states.

ii) For $d \leq 2$ the vertex correction to the conductivity, for *weak* disorder, is given by

$$\delta\sigma_1 \sim - \int_{1/L_M}^{1/L_m} \frac{dq}{q^2} \quad (8.2)$$

where L_M is dominated by the shortest of several upper cutoff lengths which may be present in the system, and L_m , the lower cutoff length, is believed to be very close to the mean free path l_{tr} ;

$$L_m \sim \sqrt{D\tau_{tr}} = l_{tr}/\sqrt{d} \quad (8.3)$$

where d is the dimensionality, D is the diffusion coefficient which is related to the conductivity by the Einstein relation

$$\sigma = 2e^2 \rho_F D \quad (8.4)$$

where ρ_F is the DOS at E_F per spin per unit volume (area or length).

Examples of upper cutoff lengths L_M , besides the geometrical dimension L , are; the diffusion length during the *inelastic* relaxation time τ_{in}

$$L_T = \sqrt{D\tau_{in}}; \quad (8.5)$$

the diffusion length during the time ω^{-1} , where ω is the frequency of an external AC field

$$L_\omega = \sqrt{D/\omega}. \quad (8.6)$$

The presence of an external magnetic field B introduces 2 characteristic lengths:

$$L'_B = \sqrt{D/\omega_0} \quad (8.7)$$

where $\omega_0 = eB/m$, the cyclotron frequency, and the cyclotron radius

$$L_H = \sqrt{\hbar/eB} \quad (8.8)$$

For weak disorder, $L'_B \gg L_H$, and hence L_H is the relevant length. If we assume that the various *rates* (i.e. $1/\tau$) are independent of one another, the effective upper cutoff length due to the combination of several is

$$L_M^{-2} = L^{-2} + L_T^{-2} + L_\omega^{-2} + \dots \quad (8.9)$$

For $d = 2$ (8.2) yields

$$\delta\sigma_1 = -\frac{e^2}{\pi^2\hbar} \ln \frac{L_M}{L_m} \quad (8.10)$$

while for $d = 1$ (where L_m can be taken as zero)

$$\delta\sigma_1 \sim -L_M \quad (8.11)$$

Equations (8.10,8.11) show that the corrections do not disappear as the upper cutoff length L_M becomes very large. In fact they increase with L_M until $\sigma \rightarrow 0$. Thus truly metallic behaviour is not possible for $d \leq 2$. This is, of course, consistent with the statement that all eigenstates are localised. This fact is often masked by the fact that at high enough temperatures L_T is quite short. Additionally the localisation length can be macroscopic for quite significant disorder and astronomical (literally) for weak disorder. $10^{10^{30}}$ has been published.

iii) The vertex correction (8.2) comes from the post-CPA terms discussed earlier. The CPA terms although quite similar produce no correction to the conductivity. The presence of electron-electron interactions eliminates this cancellation. In fact they produce a very similar result to (8.2). The cutoff L_M now depends on the frequency ω and the temperature T as

$$L_M^{-2} \approx k_B T / \hbar D + \omega / D \quad (8.12)$$

However in this case L_M does not depend significantly on the magnetic field. This is because the CPA terms involve $G_{nm}^+ G_{mn}^-$ which is unaffected by the field, while the post-CPA terms contain $G_{nm}^+ G_{nm}^-$ which acquires an extra phase factor in the presence of B .

iv) The theoretical results presented in (ii) and (iii) are in impressive agreement with experimental data, especially for 2-d.

v) It has been suggested that (8.2) can be used even for 3-d systems as we approach the mobility edge from the metallic side. For $d = 3$ (8.2) gives

$$\delta\sigma_1 \sim 1/L_M \quad (8.13)$$

When L_M is a magnetic length this predicts a negative magnetoresistance proportional to $B^{1/2}$.

a) One-Dimensional-Case

Mott & Twose were the first to propose that all eigenstates of a 1-d system are localised. If we assume that each back-scattered wave is lost due to destructive interference, then this picture suggests that the localisation length λ , defined by the relation

$$\lambda^{-1} = - \lim_{m \rightarrow \infty} \left(\langle \ln |\psi_m / \psi_0| \rangle / m \right) \quad (8.14)$$

is about the same as the mean free path l ; ψ_m is the amplitude of the eigenfunction at m .

Borland showed that for a random δ -function array the solution of the differential equation with fixed boundary conditions at one end grows exponentially on average with the distance. This exponential growth was seen to be the result of phase incoherence. The picture that emerges on the basis of this proof is that at every energy there are 2 independent solutions growing exponentially in opposite directions. At particular energies (the eigenvalues) the left growing solution matches up with the right growing solution to form a localised eigenstate. According to this picture the localisation length is the same as the rate of growth of the solution of the differential equation.

The exponential growth can be shown rigorously using the transfer matrix technique. The transfer matrix is a 2×2 matrix which connects e.g. $\psi, d\psi/dx$ at x with $\psi, d\psi/dx$ at x' . The concept of the transfer matrix transforms the propagation of the wave to a product of random matrices. There are exact theorem's which show under quite general conditions that the product of random matrices grows exponentially. (See e.g. various papers by J.B. Pendry and P.D.Kirkman).

The transfer matrix technique can be used for the calculation of the transmission ($|t|^2$) or reflection ($|r|^2$) coefficient associated with a disordered segment of length L . Using Fürstenberg's theorem it is easy to prove that

$$\frac{1}{L} \langle \ln |t|^2 \rangle = -\frac{2}{\lambda} \quad (8.15)$$

where $1/\lambda$ is the average rate of exponential growth of the solution. There is increased interest in $|t|^2$ because it is related to the conductance or resistance of the system. Landauer considered a disordered segment of length L connected to 2 semi-infinite leads. The leads are considered to be connected to reservoirs at $\pm\infty$ and all relaxation of energy takes place in these reservoirs. Then we can write equations for the right and left going contributions to the current on both sides of the system

$$\begin{aligned} i_{R+} &= |t|^2 i_{L+} + |r|^2 i_{R-} \\ i_{R-} &= |r|^2 i_{L+} + |t|^2 i_{R-} \end{aligned} \quad (8.16)$$

where the letters L and R refer to the left and right side of the disordered region respectively and the signs $+$ and $-$ to the direction of the current.

After relaxation to the ground state the change in potential energy is proportional to the total occupancy of the states which is proportional to the *scalar* sum of the 2 currents. The number of states associated with a change of potential energy $e\delta V$ is

$$N_s = e\delta V \frac{1}{2\pi} \frac{\partial k}{\partial E} \quad (8.17)$$

whereas the absolute current carried by each state is calculated using the group velocity

$$i_s = e \frac{1}{\hbar} \frac{\partial E}{\partial k} \quad (8.18)$$

Thus the total current associated with δV is the product of these

$$i = N_s i_s = 2 \frac{e^2}{h} \delta V \quad (8.19)$$

where the factor 2 is for spin.

We consider only right flowing total current (i.e. $i_{R-} = 0$) and combine (8.16) with (8.19) to obtain

$$G = 2 \frac{e^2}{h} \frac{|t|^2}{1 - |t|^2} \quad (8.20)$$

This formula has certain attractions. It does all the right things in the limits. At zero disorder $|t|^2 \rightarrow 1$ and G is infinite. However the formula is not uncontroversial. Other authors (e.g. J.B.Pendry) prefer the form

$$G = 2 \frac{e^2}{h} |t|^2 \quad (8.21)$$

which is obtained by ignoring the contribution of the reflected current to the voltage difference. The differences between these formulæ really lie in the description of the leads rather than the disordered region itself. For example consider the case of zero disorder. (8.21) would allow the potential to drop solely over the non-existent disordered region: clearly absurd. On the other hand in the case of a narrow channel between wide leads there is no difficulty.

The root cause of this controversy lies in a fundamental contradiction. Conductivity implies transport between 2 points at different electrochemical potentials. Hence transport and dissipation are inextricably linked. On the other hand there clearly is a relationship between transmission coefficient and conductance. Where does the dissipation come in?

In addition to the above uncertainties in defining properly the DC resistance of a finite one-dimensional system, it is found that the probability distribution of $|t|^2$ possesses long tails which are responsible for a peculiar behaviour of various averages. For example

$$\langle \ln |t|^2 \rangle = -2L/\lambda \quad (8.22a)$$

$$\langle |t|^{-2} \rangle = \frac{1}{2} [1 + \exp(4L/\lambda)] \quad (8.22b)$$

$$\langle |t|^{-4} \rangle = \frac{1}{3} + \frac{1}{2} \exp(4L/\lambda) + \frac{1}{6} \exp(12L/\lambda) \quad (8.22c)$$

$$\langle |t|^{2n} \rangle \xrightarrow{L \rightarrow \infty} D_n (\lambda/2L)^{3/2} \exp(-L/2\lambda) \quad (8.22d)$$

where the constant D_n depends only on n . The standard deviation of $\ln |t|^2$ is proportional to $(L/\lambda)^{1/2}$ for large L/λ , with a distribution that appears to be Gaussian.

The localisation length can be obtained from the Greens function as follows

$$\lambda^{-1} = -\frac{1}{|l-m|} \langle \ln |G(l, m)| \rangle \quad |l-m| \rightarrow \infty \quad (8.23)$$

Using the Renormalised Perturbation Expansion (see earlier) we have

$$G(l, m) = G(l, l) V G(l+1, l+1 [l]) V \dots G(m, m [m-1]) \quad (8.24)$$

Note that in 1-d $G(m, m [m-1])$ is independent of everything to the left of site m . It can be shown that products like (8.24) have the property that, if we define the submatrix G' to contain all the matrix elements $G(i, j)$ with i and j between l and m , then

$$G(l, m) = \det\{G'\} \quad (8.25)$$

Hence (8.23) becomes

$$\begin{aligned} \lambda^{-1} &= \lim_{|l-m| \rightarrow \infty} \frac{1}{|l-m|} \left\langle \sum_j \ln |E - E_j| \right\rangle \\ &= \lim_{|l-m| \rightarrow \infty} \int_{-\infty}^{+\infty} dE' \left\langle \frac{\sum_j \delta(E' - E_j)}{|l-m|} \right\rangle \ln |E - E'| \\ &= \int_{-\infty}^{+\infty} \langle \rho(E') \rangle \ln |E - E'| dE' \end{aligned} \quad (8.26)$$

This result was first obtained by Thouless.

b) Scaling Theory

The major breakthrough came in 1979 with the scaling theory of Abrahams, Anderson, Licciardello and Ramakrishnan (the *gang of four*). Many of the ideas go back to Thouless and to Wegner.

i) What's so special about the Conductance?

Consider a block of disordered material of dimensions L^d . The average difference in energy between neighbouring eigenstates is $\Delta E = L^d/\rho$ where ρ is the density of states. Another important energy scale is the effective uncertainty in the energy of each state, δE . When the disordered block is embedded in a solid we can define δE in terms of the average time a particle spends in the block. Thus

$$\delta E = \hbar/\tau \quad (8.27)$$

When L is larger than the mean free path the motion is effectively diffusive. Hence τ is related to the size of the block via the diffusion constant, D .

$$L^2 = D\tau \quad (8.28)$$

D however is related to the conductivity via the Einstein relation

$$\sigma = e^2 D\rho \quad (8.29)$$

Hence we can write

$$\delta E = \frac{\hbar}{e^2} \sigma \rho^{-1} L^{-2} = \frac{\hbar}{e^2} \sigma \Delta E L^{d-2} = g \Delta E. \quad (8.30)$$

The physical picture is that if $\delta E \ll \Delta E$ electrons from one block will not penetrate into the next block when several blocks are joined together, whereas if $\delta E \gg \Delta E$ there will be no barrier to transport. However (8.30) shows that $\delta E/\Delta E$ is essentially the conductance and this is the only quantity which controls the behaviour as blocks are joined together.

This result can be summarised in the form

$$g(2L) = f[g(L)] \quad (8.31)$$

or in differential form

$$\frac{dg}{d \ln L} = \beta(g) \quad \text{or} \quad \frac{d \ln g}{d \ln L} = \beta(\ln g) \quad (8.32)$$

This is the famous β function. Two important points should be borne in mind:

- a) (8.32) is simply a special case of a more general multi-dimensional relationship.
- b) A more general form would be to consider the whole distribution of values of g rather than an unspecified mean. So that we could write

$$\frac{d}{d \ln L} P(\ln g) = \beta [P(\ln g), \ln g] \quad (8.33)$$

We shall return to this case later.

ii) General Scaling Properties.

(8.32) looks like a non-linear equation of motion such as is studied in the theory of chaos, except that $t \rightarrow \ln L$. Most of the mathematical results from chaos can be applied to our problem. In particular if we consider a multi- or infinite-dimensional version of (8.32) it will in general be possible to identify various topological features of the phase space, such as

- a) Attractive and repulsive lines, surfaces, *etc.*, where the flow is always towards (away from) the feature.
- b) Fixed points. These are of 3 types.
 - 1) Stable fixed points or sinks. Everything flows towards the point.
 - 2) Unstable fixed points or sources. Everything flows away from the fixed point.
 - 3) Saddle points. Flow is towards the point in some directions, away in others.

It should be noted that it is always possible to write a general equation like (8.32) but it may have to be infinite dimensional. The one-parameter scaling theory contends that there exists an attractive line which may be parameterised by the conductance g . Thus we must be careful to make sure that the system is large enough that it is sufficiently close to that attractive line for the assumption that g is the only *relevant* variable to be valid. The other variables which control the deviation from the attractive line are often termed *irrelevant*. In reality this does not necessarily imply that they may be ignored.

iii) Fixed Points

Close to a fixed point an equation like (8.32) may be linearised to give

$$\frac{dg}{d \ln L} = B(g - g^*) \quad (8.34)$$

where B is the matrix of derivatives of β . (8.34) has solutions of the form

$$g_i = g_i^* + A_i L^{\beta'_i} \quad (8.35)$$

where the β'_i are the eigenvalues of B . The constant of integration A_i contains all the information about disorder, energy *etc.*. Consider for example one of the solutions (8.35). For any finite L we expect g to be a smooth function of disorder, $\delta\epsilon$, or energy, E . In this case we may Taylor expand A around the fixed point. Hence

$$g = g^* + A'(E - E^*)L^{\beta'} \quad (8.36)$$

where E^* is the fixed point energy, i.e. the energy at which g is independent of L . It is useful to write everything in terms of dimensionless variables. Thus

$$g = g^* + A''(L/\xi)^{\beta'} \quad (8.37)$$

Comparing (8.36,37,38) we obtain an expression for the length scale ξ

$$\xi \sim |E - E^*|^{-1/\beta'} \quad (8.38)$$

from which we can identify the critical exponent ν_i associated with the correlation length, ξ_i , as

$$\nu_i = -1/\beta'_i \quad (8.38)$$

iv) Crossed Diagrams

From the totally crossed diagrams (see beyond the CPA above) we can obtain an expression for the expansion of $\beta(\ln g)$ in terms of $1/g$. Suppose the leading terms (in 3-d) are

$$\frac{d \ln g}{d \ln L} = 1 - \left(\frac{g^*}{g}\right)^n \approx n(\ln g - \ln g^*) \quad (8.39)$$

which leads directly to the result that

$$\nu = 1/n \quad (8.40)$$

Thus if the leading term in the expansion is $1/g$ then $\nu = 1$, whereas if the leading term is $1/g^2$ then $\nu = \frac{1}{2}$. Note however that this is a very rash approximation. Recent results (Wegner) suggest that the next term in this expansion is at least as large as this. Nevertheless for ordinary disorder we have $\nu = 1$, but for random magnetic field or spin-orbit coupling $\nu = \frac{1}{2}$.

v) Conductivity

For large g we expect the scaling behaviour to be classical,

$$g = \frac{\hbar}{e^2} \sigma L^{d-2} \quad (8.41)$$

which gives directly the limiting behaviour $\beta = d - 2$. However, comparing (8.41) with (8.37) we obtain $\sigma \sim \xi^{-1}$ and hence the critical exponent s for the conductivity is related to ν by $s = (d - 2)\nu$. This result, originally derived by Wegner, was often misinterpreted to predict a minimum metallic conductivity in 2-d ($s = 0$). However it presupposes the existence of a fixed point, which is not necessarily valid in 2-d.

vi) Whole Distribution

Returning to the general (8.33) for a one-parameter scaling relationship for the whole distribution of g . If there exists a fixed point here it is represented by a scale invariant form of the distribution. In this case the linearisation takes the form

$$\frac{dP(g)}{d \ln L} = B [P(g) - P^*(g)] \quad (8.42)$$

which has the solution

$$P(g) = P^*(g) + A(g)L^B \quad (8.43)$$

where $A(g)$ depends on energy, disorder etc. and $\int_{-\infty}^{+\infty} A(g) dg = 0$. Note, in particular, that the value of the critical exponent is independent of which average is considered, $\langle g \rangle$, $\exp \langle \ln g \rangle$ or $1/\langle 1/g \rangle$, as long as the corresponding integral over $P(g)$ is well defined. It is by no means obvious that this last condition is fulfilled.

Another side effect of the existence of a fixed point distribution is that all the moments of $P^*(g)$ are also fixed. It may well appear that these moments are independent of the size of the system. There is considerable evidence for the existence of a universal value for the standard deviation of the conductance.

$$\delta g \approx 1 \quad \text{or} \quad \delta G \approx \frac{e^2}{\hbar} \quad (8.44)$$

These are often called *Universal Conductance Fluctuations*. The effect is observed at very low temperatures by varying Fermi level (gate voltage) or magnetic fields.

c) Field Theory Formulation

This section can only be the briefest of outlines of the field theoretical formulation of the problem.

Consider the integral form

$$\int_{-\infty}^{+\infty} D\phi^\dagger D\phi \exp \{ i (\phi^\dagger [E + i\gamma - \varepsilon] \phi) \} = \frac{i\pi}{[E + i\gamma - \varepsilon]} \quad (8.45)$$

Note that this is really a 2-dimensional integral, because we have integrated over the ϕ and ϕ^\dagger separately. The more general form of this is then

$$\int_{-\infty}^{+\infty} \prod_{ij} D\phi_i^\dagger D\phi_j \exp \{ i (\phi_i^\dagger [E + i\gamma - H_{ij}] \phi_j) \} = \frac{(i\pi)^N}{\det [E + i\gamma - H]} \quad (8.46)$$

From this form it is possible to calculate the Green's function using

$$\int_{-\infty}^{+\infty} \prod_{ij} D\phi_i^\dagger D\phi_j \phi_m^\dagger \phi_n \exp \{ \dots \} = G_{mn} \frac{(i\pi)^N}{\det [\dots]} \quad (8.47)$$

or even the 2-particle Green's function by including 4 ϕ 's in (8.47). However the presence of the determinant (8.47) makes it difficult to evaluate exactly. There are 2 ways to solve this problem:

- i) The *Replica Trick*. Consider n replicas of the system. Then the total system will include (8.46,47) raised to the power n . If we then take the limit $n \rightarrow 0$ we obtain $\det [\dots]^0 = 1$ and are left with the desired Green's function.
- ii) Supersymmetry. When the integral in (8.46,47) is evaluated using *Grassmann* or *anticommuting* variables, the result is the same except that the determinant appears in the numerator. By integrating over 2 normal (commuting) variables and 2 Grassmann variables the determinants cancel and again we are left with the Green's function as required.

In the case where the 2-particle Green's function is required (e.g. in order to calculate the conductivity), there is a further complication. The integral in (8.45,46,47) only converges when the real part of the exponent is negative. In (8.45) a factor i is introduced which combines with the imaginary part of the energy $i\gamma$ to give $-\gamma\phi^2$. For the conductivity, however, we require terms like G^+G^- . To enable us to calculate such quantities the integrand must take the form

$$\begin{aligned} & i \left\{ \phi_{1i}^\dagger [E + i\gamma - H_{ij}] \phi_{1j} - \phi_{2i}^\dagger [E - i\gamma - H_{ij}] \phi_{2j} \right\} \\ & = i \left\{ \phi_{1i}^\dagger \phi_{1j} - \phi_{2i}^\dagger \phi_{2j} \right\} [E - H_{ij}] + i\gamma \left\{ \phi_{1i}^\dagger \phi_{1j} + \phi_{2i}^\dagger \phi_{2j} \right\} \end{aligned} \quad (8.48)$$

The value of the exponent in the integrand in (8.48) is made up of a term which is invariant under transformations which preserve the value of $(\phi_{1i}^\dagger \phi_{1j} - \phi_{2i}^\dagger \phi_{2j})$, and a small perturbation, proportional to γ which breaks this symmetry. The group of allowed transformations is the *pseudo-unitary* group, $U(n, n)$. In the usual case where H is real and symmetric the real and imaginary parts of ϕ are independent of one another and the group is the *pseudo-orthogonal*, $O(2n, 2n)$. When the only source of scattering is the spin-orbit coupling there is an extra symmetry due to the spin exchange under time-reversal symmetry. The resulting group is pseudo-symplectic, $S(n, n)$.

These 3 cases form the *Universality Classes* for the localisation problem. In 3-d the orthogonal case, ordinary scattering, gives a critical exponent of 1, whereas the Unitary case gives $\nu = s = \frac{1}{2}$. There are no reliable predictions for the Symplectic case (the series doesn't converge). Experimentally this is still a matter of some controversy. In heavily doped semiconductors, for example, the exponent appears to be unity or $\frac{1}{2}$ for compensated and uncompensated systems respectively.

In 2-d the 3 cases differ in the way the β -function approaches zero, giving $\beta = -a/g$, $\beta = -a/g^2$ and $\beta = +a/g$ respectively. Note in particular the positive contribution from the symplectic (spin-orbit) case. This effect is sometimes termed, *weak antilocalisation*. Note that this implies the existence of extended states. It is not completely clear whether in fact there are any localised states in this case.

Note however that in real systems there will be a variety of scattering mechanisms, such that no single universality class need apply.

d) Numerical Approach.

A number of numerical approaches to the localisation problem have been developed. In the 1970's there was a remarkable degree of agreement on the details of the transition in 2-d. In retrospect the agreement was spurious, being due to the similar storage capacities of the various computers used.

More recently finite sized scaling methods have come to be accepted more generally. Using a numerical variant of the transfer matrix technique

$$\begin{aligned} \begin{pmatrix} \mathbf{y}_{n+1} \\ \mathbf{y}_n \end{pmatrix} &= \begin{pmatrix} E - H_n & -I \\ I & 0 \end{pmatrix} \begin{pmatrix} \mathbf{y}_n \\ \mathbf{y}_{n-1} \end{pmatrix} \\ &= \prod_{m=1}^n \begin{pmatrix} E - H_m & -I \\ I & 0 \end{pmatrix} \begin{pmatrix} \mathbf{y}_1 \\ \mathbf{y}_0 \end{pmatrix} \\ &= T_n \begin{pmatrix} \mathbf{y}_1 \\ \mathbf{y}_0 \end{pmatrix} \end{aligned} \quad (8.49)$$

we can calculate the Lyapunov exponents, essentially the logarithm of the eigenvalues of T . These are in pairs which are reciprocals of each other due to the symplectic symmetry of T . The smallest exponent may be identified with the localisation length λ_M of a strip or bar of width $M(\times M)$ for which the calculation is being carried out.

It is found (MacKinnon & Kramer) that $\Lambda = \lambda_M/M$ obeys a similar scaling relationship to the conductance. Thus many of the results discussed above can be transferred to Λ . In particular, by fitting

$$\Lambda = \Lambda^* + A(W - W^*)M^\alpha \quad (8.50)$$

to results for Λ as a function of strip width M and disorder W , it is possible to calculate the critical exponent. Most work has been done on the Rectangular distribution which seems to give $s = \nu \approx 1.5$ which is not compatible with the analytical approximations or with the experiment. However more recent work using other distributions is in better agreement with analytical work $s = \nu = 1$.

Clearly however the problem is not yet solved.