

QUANTUM THEORY OF SOLIDS

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SECOND QUANTIZATION

In this section we introduce the concept of second quantization. Historically, the first quantization is the quantization of particles due to the commutation relation between position and momentum, i.e.,

$$[x, p] = i\hbar. \quad (1)$$

Second quantization was introduced to describe cases, where the number of particles can vary. A quantum field such as the electromagnetic field is such an example, since the number of photons can vary. Here it is necessary to quantize a field $\Psi(r)$, which can also be expressed in terms of commutation relations

$$[\Psi(r), \Psi^+(r')] = \delta(r - r'). \quad (2)$$

However, there is only one quantum theory, hence nowadays first quantization refers to using eigenvalues and eigenfunctions to solve Schrödinger equation, whereas in second quantization one uses creation and annihilation operators to solve Schrödinger's equation. Both methods are consistent with each other and the choice of technique is dictated by the type of problems considered. In general, when considering many particles second quantization is the preferred technique and will be introduced next.

The Harmonic oscillator

The Hamiltonian of the harmonic oscillator is given by

$$H = \frac{p^2}{2m} + \frac{K}{2}x^2, \quad (3)$$

where $\omega = \sqrt{K/m}$. The eigenvalues of this Hamiltonian are then obtained by solving the Schrödinger eigenvalue equation $H\psi = E\psi$, where $p = -i\hbar\partial/\partial x$ is used and one obtains for the energy

$$E_n = \hbar\omega(n + 1/2), \quad (4)$$

where n is an integer. In the **second quantized** form we introduce the following operators:

$$\begin{aligned} a &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} (x + ip/m\omega) \text{ "annihilation operator"} \\ a^+ &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} (x - ip/m\omega) \text{ "creation operator"}. \end{aligned} \quad (5)$$

Here a^+ is simply the Hermitian conjugate of a . Using these definitions we can rewrite the Hamiltonian as:

$$H = \frac{\hbar\omega}{2} (aa^+ + a^+a). \quad (6)$$

We now calculate

$$\begin{aligned} (aa^+ - a^+a)f(x) &= [a, a^+]f(x), \quad f \text{ any function} \\ &= 1 \cdot f(x), \quad \text{since } p = -i\hbar\partial_x. \end{aligned} \quad (7)$$

Hence

$$[a, a^+] = 1, \quad (8)$$

which is the Boson commutation relation. In addition, $[a, a] = [a^+, a^+] = 0$. Using this commutation relation we can rewrite the Hamiltonian in second quantized form as

$$H = \hbar\omega(a^+a + 1/2). \quad (9)$$

In order to solve the Hamiltonian in this form we can write the wave function as

$$\psi_n = \frac{(a^+)^n}{\sqrt{n!}}|0\rangle, \quad (10)$$

and $a|0\rangle = 0$, where $|0\rangle$ is the vacuum level of the system. We now show that ψ_n defined in this way is indeed the solution to Schrödinger's equation $H\psi_n = E_n\psi_n$. To show this we first calculate

$$a^+\psi_n = \frac{(a^+)^{n+1}}{\sqrt{n!}}|0\rangle = \frac{\sqrt{n+1}}{\sqrt{(n+1)!}}(a^+)^{n+1}|0\rangle = \sqrt{n+1}\psi_{n+1} \quad (11)$$

and

$$\begin{aligned} a\psi_n &= \frac{a(a^+)^n}{\sqrt{n!}}|0\rangle = \frac{aa^+(a^+)^{n-1}}{\sqrt{n}\sqrt{(n-1)!}}|0\rangle \\ &= \frac{(a^+a + 1)(a^+)^{n-1}}{\sqrt{n}\sqrt{(n-1)!}}|0\rangle = \sqrt{n}\psi_{n-1}, \end{aligned} \quad (12)$$

where we used that $a^+a(a^+)^{n-1}|0\rangle = (n-1)(a^+)^{n-1}|0\rangle$ by using the commutation relation $(n-1)$ times. Coming back to the Hamiltonian we then have

$$\begin{aligned} H\psi_n &= \hbar\omega(a^+a + 1/2)\psi_n = \hbar\omega(a^+\sqrt{n}\psi_{n-1} + \psi_n/2) \\ &= \hbar\omega(n\psi_n + \psi_n/2) \\ &= \underbrace{\hbar\omega(n + 1/2)}_{E_n} \psi_n \end{aligned} \quad (13)$$

An important difference between the first quantization method and the second quantization method is that we don't need the expression for the wave functions in order to obtain the spectrum, which simply follows from the form (9). The form of the Hamiltonian in (9) is diagonal since the energy is simply given by counting the number of states, since a^+a is just the number operator. Indeed,

$a^+a(a^+)^n|0\rangle = n|0\rangle$, since we have n levels above vacuum. Hence, the whole task in solving problems with the second quantization method is to obtain an expression of the Hamiltonian in a diagonal form, like (9). The BCS theory of superconductivity in the next section is a nice example of this diagonalization procedure. However, before that we will see how we can transform any Hamiltonian in first quantized form into second quantized form.

General form

The general idea to second quantize a Hamiltonian or operator is to start by choosing a complete basis, $|\phi_\lambda(r)\rangle$ with $\sum_\lambda |\phi_\lambda(r)\rangle\langle\phi_\lambda(r)| = 1$. Here we are only interested in operators of the form $O(r)$ or $V(r_i - r_j)$. For example, $\sum_i O(r_i)$ can be a single particle potential like a confinement potential and $\sum_{i \neq j} V(r_i - r_j)$ can be a two-particle interaction potential, such as the Coulomb potential. For N particles we write O in our complete basis as:

$$\begin{aligned} O &= \sum_{i=1}^N O(r_i) \\ &= \sum_i \left(\sum_\alpha |\phi_\alpha(r_i)\rangle\langle\phi_\alpha(r_i)| \right) O(r_i) \sum_\beta |\phi_\beta(r_i)\rangle\langle\phi_\beta(r_i)| \\ &= \sum_{i,\alpha,\beta} |\phi_\alpha(r_i)\rangle \underbrace{\langle\phi_\alpha(r_i)|O(r_i)|\phi_\beta(r_i)\rangle}_{O_{\alpha\beta}} |\phi_\beta(r_i)\rangle \\ &= \sum_{\alpha,\beta} O_{\alpha\beta} \sum_i |\phi_\alpha(r_i)\rangle\langle\phi_\beta(r_i)|, \end{aligned} \quad (14)$$

where $\langle f(r) \rangle = \int f(r) dr$. Similarly, we can write:

$$\begin{aligned} V &= \frac{1}{2} \sum_{i \neq j}^N V(r_i - r_j) \\ &= \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} V_{\alpha\beta\gamma\delta} \sum_{i \neq j} |\phi_\alpha(r_i)\rangle\langle\phi_\beta(r_j)|\langle\phi_\gamma(r_i)|\langle\phi_\delta(r_j)| \end{aligned}$$

$$\text{and } V_{\alpha\beta\gamma\delta} = \langle\phi_\alpha(r_i)|\langle\phi_\beta(r_j)|V(r_i - r_j)|\phi_\gamma(r_i)\rangle|\phi_\delta(r_j)\rangle \quad (15)$$

This is all very general. Now the idea is to write (14,15) in second quantized form. If we had only one particle we could write the wave-function as

$$\begin{aligned} \psi &= \sum_\beta a_\beta |\phi_\beta(r)\rangle \text{ and} \\ \psi^* &= \sum_\alpha \langle\phi_\alpha(r)| a_\alpha^+. \end{aligned} \quad (16)$$

The expectation value of the operator O then becomes:

$$O_\psi = \langle\psi^* O \psi\rangle = \sum_{\alpha,\beta} O_{\alpha\beta} a_\alpha^+ a_\beta. \quad (17)$$

If a and a^+ are defined as the creation and annihilation operators we then have O written in second quantized form.

We now generalize this to more particles: In this case the wave-function is written as

$$\begin{aligned} \psi(\dots, r_i, \dots, r_j, \dots) &= \psi(\dots, r_j, \dots, r_i, \dots) \text{ bosons} \\ \psi(\dots, r_i, \dots, r_j, \dots) &= -\psi(\dots, r_j, \dots, r_i, \dots) \text{ fermions} \\ \psi(\dots, r_i, \dots, r_j, \dots) &= e^{-i\theta} \psi(\dots, r_j, \dots, r_i, \dots) \text{ anyons} \\ &= \sum_{\alpha_1, \dots, \alpha_N} A_{\alpha_1, \dots, \alpha_N} \phi_{\alpha_1}(r_1) \dots \phi_{\alpha_N}(r_N). \end{aligned} \quad (18)$$

Here $A_{\alpha_1, \dots, \alpha_N}$ are simply the coefficients. A simple product like $\phi_{\alpha_1}(r_1) \dots \phi_{\alpha_N}(r_N)$ has the correct symmetry for Bosons but not for Fermions, hence it is useful to introduce an antisymmetrization operator for Fermions, defined as

$$S_- \prod_i \phi_{\alpha_i}(r_i) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\alpha_1}(r_1) & \dots & \phi_{\alpha_N}(r_1) \\ \vdots & \dots & \vdots \\ \phi_{\alpha_1}(r_N) & \dots & \phi_{\alpha_N}(r_N) \end{vmatrix}, \quad (19)$$

which is the Slater determinant. Then we can write for Fermions

$$\psi(\dots, r_i, \dots, r_j, \dots) = \sum_{\alpha_1, \dots, \alpha_N} A_{\alpha_1, \dots, \alpha_N} S_- \prod_i \phi_{\alpha_i}(r_i). \quad (20)$$

Now we don't have to worry about symmetry anymore.

The next step is to introduce the occupation number so that we can rewrite the wave function as

$$\psi = |n_{\alpha_1}, \dots, n_{\alpha_N}\rangle \text{ with } N = \sum_i n_{\alpha_i}, \quad (21)$$

where n_{α_i} is the number of particles in state α_i . The occupation number operator is then defined as

$$\underbrace{n_{\alpha_i}}_{\text{operator}} |n_{\alpha_i}\rangle = \underbrace{n_{\alpha_i}}_{\text{number}} |n_{\alpha_i}\rangle \quad (22)$$

The number of states for fermions is limited to 0 and 1, whereas for bosons, n_{α_i} can take any integer value ≥ 0 .

In similarity with the harmonic oscillator described in the previous section, the Boson creation and annihilation operators are then defined as

$$\begin{aligned} b_{\alpha_i}^+ |\dots, n_{\alpha_i}, \dots\rangle &= \sqrt{n_{\alpha_i} + 1} |\dots, n_{\alpha_i} + 1, \dots\rangle \\ b_{\alpha_i} |\dots, n_{\alpha_i}, \dots\rangle &= \sqrt{n_{\alpha_i}} |\dots, n_{\alpha_i} - 1, \dots\rangle \end{aligned} \quad (23)$$

and

$$[b_{\alpha_i}, b_{\alpha_j}^+] = \delta_{\alpha_i, \alpha_j}. \quad (24)$$

All other commutators ($[b_i, b_j]$ and $[b_i^+, b_j^+]$) are zero.

For fermions we have

$$\begin{aligned} c_{\alpha_i}^+ |\cdots, n_{\alpha_i}, \cdots\rangle &= |\cdots, n_{\alpha_i} + 1, \cdots\rangle \text{ if } n_{\alpha_i} = 0 \\ &= 0 \text{ otherwise} \\ c_{\alpha_i} |\cdots, n_{\alpha_i}, \cdots\rangle &= |\cdots, n_{\alpha_i} - 1, \cdots\rangle \text{ if } n_{\alpha_i} = 1 \\ &= 0 \text{ otherwise.} \end{aligned} \quad (25)$$

Hence, $c_{\alpha_i}^+$ creates an electron in state α_i if state α_i is empty and c_{α_i} annihilates an electron from state α_i if α_i was occupied. It is quite straightforward to check that for symmetry reasons the Fermion creation and annihilation operators have to obey the following commutation relations:

$$\{c_{\alpha_i}, c_{\alpha_j}^+\} = c_{\alpha_i} c_{\alpha_j}^+ + c_{\alpha_j}^+ c_{\alpha_i} = \delta_{\alpha_i, \alpha_j} \quad (26)$$

and all others ($\{c_i, c_j\}$ and $\{c_i^+, c_j^+\}$) are zero. Also, $c_{\alpha_i}|0\rangle = 0$. The N -particle fermionic wave-function is now written as

$$\psi = S_- \prod_i |\phi_{\alpha_i}(r_i)\rangle = \prod_i c_{\alpha_i}^+ |0\rangle, \quad (27)$$

where the product of creation operators is antisymmetric by construction of the $\{, \}$. Similarly, we have for bosons:

$$\psi = \prod_i |\phi_{\alpha_i}(r_i)\rangle = \prod_i b_{\alpha_i}^+ |0\rangle. \quad (28)$$

Hence, with these definitions we obtain

$$O \prod_i a_{\alpha_i}^+ |0\rangle = \sum_{\alpha, \beta} O_{\alpha\beta} a_{\alpha}^+ a_{\beta} \prod_i a_{\alpha_i}^+ |0\rangle \quad (29)$$

or

$$O = \sum_{\alpha, \beta} O_{\alpha\beta} a_{\alpha}^+ a_{\beta} \quad (30)$$

and

$$V = \frac{1}{2} V_{\alpha\beta\gamma\delta} a_{\alpha}^+ a_{\beta}^+ a_{\gamma} a_{\delta}, \quad (31)$$

where a^+ and a are either bosonic or fermionic creation and annihilation operators.

We now show that (29) indeed follows from (14). For bosons, we have

$$\begin{aligned} O \prod_j |\phi_{\alpha_j}(r_j)\rangle &= \sum_{\alpha, \beta} O_{\alpha\beta} \sum_i |\phi_{\alpha}(r_i)\rangle \langle \phi_{\beta}(r_i) | \prod_j |\phi_{\alpha_j}(r_j)\rangle \\ &= \sum_{\alpha, \beta} O_{\alpha\beta} \sum_i \delta_{\beta, \alpha_i} \underbrace{|\phi_{\alpha_1}(r_1)\rangle \cdots |\phi_{\alpha_i}(r_i)\rangle \cdots}_{b_{\alpha_1}^+ \cdots b_{\alpha_i}^+ \cdots b_{\alpha_N}^+ |0\rangle} \end{aligned} \quad (32)$$

if there are p bosons in state β , one of them is replaced by state α , so that we have terms of the form:

$$\begin{aligned} b_{\alpha}^+ (b_{\beta}^+)^{p-1} |0\rangle &= b_{\alpha}^+ \left(\frac{1}{p} b_{\beta} b_{\beta}^+ \right) (b_{\beta}^+)^{p-1} |0\rangle \\ &= \frac{1}{p} b_{\alpha}^+ b_{\beta} (b_{\beta}^+)^p |0\rangle, \end{aligned} \quad (33)$$

where we used $[b, b^+] = 1$ and $b^+ b (b^+)^n |0\rangle = n (b^+)^n |0\rangle$ (the occupation number operator). The last term in (33) is obtained p times from the \sum_i , hence $\sum_i \delta_{\beta, \alpha_i} = p$. Therefore, (33) leads to

$$O = \sum_{\alpha, \beta} O_{\alpha\beta} b_{\alpha}^+ b_{\beta} \quad (34)$$

for bosons. For fermions the derivation is quite similar as well as for V .

Typical Hamiltonian

In first quantization we consider

$$H = \underbrace{\sum_i -\frac{\hbar^2 \partial_i^2}{2m} + U(r_i)}_{H^0} + \underbrace{\frac{1}{2} \sum_{i \neq j} V(r_i - r_j)}_V. \quad (35)$$

In order to write this Hamiltonian in second quantization we first need a basis. We chose as basis the free particle basis:

$$\phi_{\alpha}(r) = \frac{1}{\sqrt{V}} e^{ik_{\alpha} r}, \quad (36)$$

which is a complete orthogonal basis with $\int \phi_{\beta}^*(r) \phi_{\alpha}(r) dr = \delta_{\alpha, \beta}$.

Hence using the orthogonality relations we have,

$$H_{\alpha\beta}^0 = \delta_{\alpha, \beta} \underbrace{\frac{\hbar^2 k_{\beta}^2}{2m}}_{\epsilon_{k_{\beta}}} + U(\underbrace{k_{\beta} - k_{\alpha}}_q), \quad (37)$$

where $U(q)$ is the Fourier transform of $U(r)$. Similarly for the Coulomb potential $V(r_i - r_j) = \frac{e^2}{|r_i - r_j|}$ we obtain,

$$\begin{aligned} V_{\alpha\beta\gamma\delta} &= \int dr_i dr_j e^{ir_j(k_{\delta} + k_{\gamma} - k_{\alpha} - k_{\beta})} e^{i(r_i - r_j)(k_{\gamma} - k_{\alpha})} \frac{e^2}{|r_i - r_j|} \\ &= \delta_{\underbrace{k_{\delta} + k_{\gamma} - k_{\alpha} - k_{\beta}}_q, 0} \underbrace{\int e^{iqr} \frac{e^2}{r} dr}_{\frac{4\pi e^2}{q^2}} \\ &= \delta_{k_{\beta} - k_{\delta}, q} \frac{4\pi e^2}{q^2}. \end{aligned} \quad (38)$$

Finally, this Hamiltonian in second quantized form becomes

$$H = \sum_k \epsilon_k a_k^+ a_k + \sum_{k, q} U(q) a_{k-q}^+ a_k + \frac{1}{2} \sum_{k, k', q} \frac{4\pi e^2}{q^2} a_{k-q}^+ a_{k'+q}^+ a_k a_{k'}. \quad (39)$$

What is interesting in this formulation is that we got rid of the dependence in the number of particles.

TRANSPORT: THE QUANTUM APPROACH

One dimensional conductance

Suppose that we have a perfect one-dimensional conductor (quantum wire) connected by two large electron reservoirs. In real life they would be electrical contacts. The left reservoir is fixed at chemical potential $\mu_L = \mu_R + eV$ and the right one at μ_R for a potential difference of V . At zero temperature the current is then given as

$$\begin{aligned} I = -env &= -e \int_{E_F^L = E_F^R + eV}^{E_F^R} \underbrace{D(E)}_{\frac{1}{\pi} \left| \frac{\partial E}{\partial k} \right|^{-1}} \cdot \underbrace{V(E)}_{\frac{\partial E}{\hbar \partial k}} dE \\ &= \frac{2e^2}{h} V, \end{aligned} \quad (40)$$

where $D(E)$ is the one dimensional density of states for states moving in one direction and $V(E)$ their group velocity. Experimentally this conductance quantization can be seen in quantum point contacts, in transport through single molecule or in break junctions.

We now want to generalize this result to other configurations including non-ideal ones. Using Schrödinger's equation:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi &= H\psi \\ -i\hbar \frac{\partial}{\partial t} \psi^+ &= H\psi^+ \end{aligned} \quad (41)$$

we obtain for the density operator $\rho = \psi^+ \psi$

$$\begin{aligned} \frac{\partial}{\partial t} \rho &= \frac{1}{i\hbar} (\psi^+ H\psi - (H\psi^+) \psi) \\ &= \frac{i\hbar}{2m} (\psi^+ \nabla^2 \psi - \psi \nabla^2 \psi^+) \\ &= \frac{i\hbar}{2m} \nabla (\psi^+ \nabla \psi - \psi \nabla \psi^+) \\ &= -\nabla j, \end{aligned} \quad (42)$$

where the probability current density is given by

$$j = \frac{i\hbar}{2m} (\psi \nabla \psi^+ - \psi^+ \nabla \psi). \quad (43)$$

This expression is only valid in a zero magnetic field but for any potential $V(r)$ since $V(r)$ commutes with ψ^+ .

For a perfect one dimensional system the solution of a transmitted wave is of the form $\psi(x) = te^{ikx}$, where t is the transmission amplitude. In this case the probability current density is given by

$$j_k = \frac{i\hbar}{2m} (\psi \nabla \psi^+ - \psi^+ \nabla \psi)$$

$$\begin{aligned} &= \frac{i\hbar}{2m} |t|^2 (-ik - ik) \\ &= \frac{\hbar}{2m} |t|^2 2k \end{aligned} \quad (44)$$

The total electrical current is then

$$I = e \sum_k j_k = e \int_{k_F^L}^{k_F^R} \frac{2}{2\pi} j_k dk = \frac{2e}{h} |t|^2 \Delta E_F = \frac{2e^2}{h} |t|^2 V, \quad (45)$$

where we used that $E_F = \frac{\hbar^2 k_F^2}{2m}$ and we obtain the same expression as (40) for a transmission probability of $T = |t|^2$.

A similar expression can also be obtained for a single particle Hamiltonian expressed in second quantized form. Indeed, for $H = \sum_{ij} H_{ij} c_i^+ c_j$, where c_i is f.ex. expressed in a position basis, and using

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} c_i &= H c_i \\ -i\hbar \frac{\partial}{\partial t} c_i^+ &= c_i^+ H^+, \end{aligned} \quad (46)$$

we obtain for the local density operator $\rho_i = c_i^+ c_i$,

$$\begin{aligned} \frac{\partial}{\partial t} \rho_i &= \frac{1}{i\hbar} (c_i^+ H c_i - c_i^+ H^+ c_i) \\ &= \frac{1}{i\hbar} (c_i^+ \sum_j H_{ij} c_j - \sum_j c_j^+ H_{ji} c_i) \\ &= \frac{1}{i\hbar} \sum_j (c_i^+ H_{ij} c_j - c_j^+ H_{ji} c_i) \\ &= -\sum_j j_{ij}, \end{aligned} \quad (47)$$

with

$$j_{ij} = \frac{i}{\hbar} (c_i^+ H_{ij} c_j - c_j^+ H_{ji} c_i), \quad (48)$$

which is the probability current density flowing from i to j .

We can now calculate the current for a Hamiltonian in this representation by considering the expectation value of the probability current density operator for a given solution state $\psi = \sum_m \psi_m c_m^+ |0\rangle$. Hence,

$$\langle \psi | j_{ij} | \psi \rangle = \frac{i}{\hbar} (\psi_i^* H_{ij} \psi_j - \psi_j^* H_{ji} \psi_i). \quad (49)$$

For a plane wave solution $\psi_n = te^{ikn}$ of $H_{i,i\pm 1} = D$ and zero otherwise we obtain

$$\begin{aligned} j_k &= \langle \psi | j_{i,i+1} | \psi \rangle = \frac{i}{\hbar} D |t|^2 (2i \sin(k)) \\ &= -\frac{2}{\hbar} D |t|^2 \sin(k) \end{aligned} \quad (50)$$

This Hamiltonian corresponds to the free particle on a discrete one dimensional lattice, where

$$H\psi = E\psi \quad (51)$$

leads to

$$D(\psi_{n+1} + \psi_{n-1}) = E\psi_n, \quad (52)$$

which gives $\psi_n \sim e^{ikn}$ and $E = 2D \cos(k)$. Therefore the total electrical current can be expressed as

$$\begin{aligned} I &= e \sum_k j_k = -\frac{2e}{\hbar} |t|^2 D \int \frac{2}{2\pi} \sin(k) dk \\ &= \frac{2e}{\hbar} |t|^2 D \frac{2}{2\pi} (\cos(k_F^R) - \cos(k_F^L)) \\ &= \frac{2e}{\hbar} |t|^2 (E_F^R - E_F^L) = \frac{2e^2}{\hbar} |t|^2 V \end{aligned} \quad (53)$$

We now want to apply these expressions for the case of molecular transport in the tight binding approximation.

Tight binding approximation

The tight-binding approximation corresponds to the LCAO (Linear Combination of Atomic Orbitals) method. Suppose we have molecule consisting of a linear chain of N atoms, each at a specified position \vec{r}_m and having the corresponding potential $V_0(\vec{r} - \vec{r}_m)$. The total Hamiltonian of an electron introduced to the system is

$$H = H_0 + \sum_{m=1}^N V_0(\vec{r} - \vec{r}_m) \quad (54)$$

where H_0 is the free-electron Hamiltonian. We will assume that, in the N atom case, the electronic wavefunction $\Psi(\vec{r})$ takes the form of a superposition of the solutions $\psi_0(\vec{r} - \vec{r}_m)$ for the single-atom case and write

$$\Psi(\vec{r}) = \sum_{m=1}^N \psi_m \psi_0(\vec{r} - \vec{r}_m) \quad (55)$$

where $\{\psi_m\}$ are the amplitudes. The Schrödinger equation therefore takes the form

$$H \sum_{m=1}^N \psi_m \psi_0(\vec{r} - \vec{r}_m) = E \sum_{m=1}^N \psi_m \psi_0(\vec{r} - \vec{r}_m) \quad (56)$$

where E is the energy of the electron. We can multiply on the left by $\psi_0^*(\vec{r} - \vec{r}_n)$ and integrate over all of space to simplify this equation. Approximating the overlap between the single-atom solutions to be zero; that is, supposing

$$\int \vec{d}r \psi_0^*(\vec{r} - \vec{r}_n) \psi_0(\vec{r} - \vec{r}_m) = \delta_{m,n} \quad (57)$$

and defining the coefficients

$$T_{m,n} \equiv \int \vec{d}r \psi_0^*(\vec{r} - \vec{r}_n) H \psi_0(\vec{r} - \vec{r}_m) \quad (58)$$

we obtain the LCAO equation

$$\sum_{m=1}^N T_{m,n} \psi_m = E \psi_n \quad (59)$$

involving only the amplitudes of the superposition Ψ and the coefficients $\{T_{m,n}\}$.

Nearest Neighbor Approximation

Next, we will invoke the nearest-neighbor approximation; that is, we will let

$$T_{m,n} = \begin{cases} 0 & ; |m - n| \neq 1 \\ \epsilon_n & ; m = n \end{cases} \quad (60)$$

where ϵ_n is the on-site energy of the atom at position \vec{r}_n . The coefficients $\{T_{m,n}\}$ are the "hopping terms" of the molecule and represent the electronic orbital overlap between neighboring atoms. We can therefore re-write eq. (59) in the form

$$\sum_{m \neq n} T_{m,n} \psi_m = (E - \epsilon_n) \psi_n \quad (61)$$

which defines a system of coupled algebraic equations.

Hence, the free particle in this description is expressed as $T_{m,n} = D$ for $|m - n| = 1$ and zero otherwise.

MOLECULAR TRANSPORT

Infinite Chain of atoms with only one s-electron per atom:

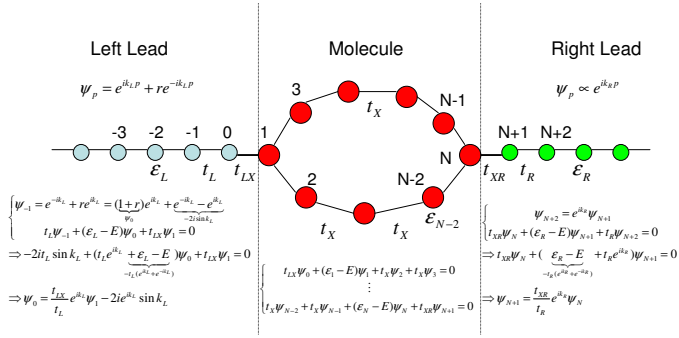
$\begin{cases} t_s \psi_{p-1} + (\epsilon_s - E) \psi_p + t_s \psi_{p+1} = 0 \\ \Rightarrow \psi_p \propto e^{ikp} \text{ and } E - \epsilon_s = t_s (e^{ik} + e^{-ik}) = 2t_s \cos k \end{cases} \quad \begin{cases} \epsilon_s = \int dr^3 \phi_s^*(r) H \phi_s(r) \\ t_s = \int dr^3 \phi_s^*(r) H \phi_s(r+a) \end{cases}$

(Onsite and overlap energies for s-orbitals: ϕ_s)

$I(\mu) = -e \int_{-\pi}^{\pi} \underbrace{D(k)}_{\text{Dens. of states}} \times \underbrace{v(k)}_{\text{velocity}} \times \underbrace{f_{FD}(k)}_{\text{Occ. Prob.}} dk = -2 \frac{e}{\hbar} \int_{\epsilon_{\min}}^{\epsilon_{\max}} f_{FD}(E - \mu) dE$

$I_{\text{tot}} = I_{\text{Left}} \left(\frac{\mu_L}{\mu + eV/2} \right) - I_{\text{Right}} \left(\frac{\mu_R}{\mu - eV/2} \right) = I(V) = \frac{2e}{\hbar} \int_{\epsilon_{\min}}^{\epsilon_{\max}} \left(\frac{1}{1 + e^{\frac{E - \mu + eV/2}{kT}}} - \frac{1}{1 + e^{\frac{E - \mu - eV/2}{kT}}} \right) dE$

Chemical potential
Fermi-Dirac distribution



$$T(E) = |\psi_{N+1}|^2 \times \left| \frac{t_R \sin k_R}{t_L \sin k_L} \right| = \left| \frac{t_{XR}^2 t_{LX}^2 4 \sin k_R \sin k_L [G(E)]_{(N,1)}^2}{t_R t_L} \right|$$

$$\begin{cases} \psi_{N+1} = \frac{t_{XR}}{t_R} e^{ik_R} \psi_N \\ \psi_N = [G(E)]_{(N,1)} (-2it_{LX} e^{ik_L} \sin k_L) \end{cases}$$

$$\Rightarrow I(V) = \frac{2e}{h} \int_{\epsilon_{\min}}^{\epsilon_{\max}} T(E) \left(\frac{1}{1 + e^{\frac{E - \mu + eV/2}{kT}}} - \frac{1}{1 + e^{\frac{E - \mu - eV/2}{kT}}} \right) dE$$

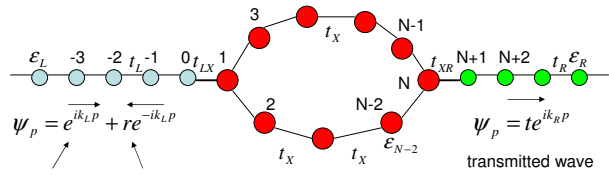
By introducing Γ_L and Γ_R it is possible to reexpress the transmission into the Fisher-Lee expression

$$\begin{pmatrix} t_{LX}^2 e^{ik_L} + \epsilon_1 - E & t_X & t_X & 0 & \dots & 0 \\ t_L & \epsilon_2 - E & 0 & t_X & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ 0 & \dots & \dots & \epsilon_N - E + \frac{t_{XR}^2}{t_R} e^{ik_R} & \dots & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} = \begin{pmatrix} 2it_{LX} e^{ik_L} \sin k_L \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} -J_L \\ \vdots \\ -J_L \end{pmatrix}$$

Hamiltonian of X Self-energy Energy Wavefunction Source function

$$H_X = \begin{pmatrix} \epsilon_1 & t_X & \dots & 0 \\ t_X & \epsilon_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon_N \end{pmatrix} \quad \Sigma = \begin{pmatrix} \frac{t_{LX}^2 e^{ik_L}}{t_L} & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{t_{XR}^2 e^{ik_R}}{t_R} \end{pmatrix} \quad E = \begin{pmatrix} E & 0 & \dots & 0 \\ 0 & E & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E \end{pmatrix}$$

$$\begin{cases} (H_X + \Sigma - E)\psi = -J_L \\ \Rightarrow \psi = \frac{(E - H_X - \Sigma)^{-1} J_L}{G(E)} \quad (\text{Green's function}) \end{cases} \Rightarrow \psi_n = [G(E)]_{(n,1)} (-2it_{LX} e^{ik_L} \sin k_L)$$



Incoming and reflected wave

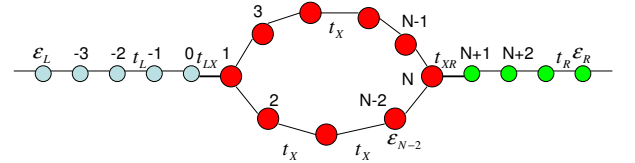
$$j_L = \frac{-2it_L \sin k_L}{h} \times (1 - r^2) \quad \leftarrow \text{Current probabilities} \quad \rightarrow \quad j_R = \frac{-2it_R \sin k_R}{h} \times (t^2)$$

$(j = \frac{i\hbar}{2m} \psi \nabla \psi' - \psi' \nabla \psi)$

But current probabilities are conserved: $\Rightarrow t^2 = \left| \frac{t_L \sin k_L}{t_R \sin k_R} \right| (1 - r^2) = |\psi_{N+1}|^2$

$$\Rightarrow T(E) = |\psi_{N+1}|^2 \times \left| \frac{t_R \sin k_R}{t_L \sin k_L} \right|$$

These expressions give us the solution for the Schrödinger equation and it was necessary to use the conservation of the current probabilities in order to match the left and right lead solutions.

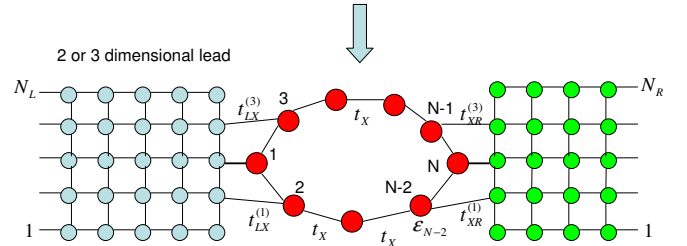
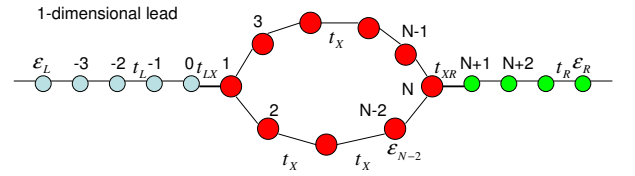


$$T(E) = |\psi_{N+1}|^2 \times \left| \frac{t_R \sin k_R}{t_L \sin k_L} \right| = \left| \frac{t_{XR}^2 t_{LX}^2 4 \sin k_R \sin k_L [G(E)]_{(N,1)}^2}{t_R t_L} \right|$$

$$= 4 \cdot \text{Tr}[\Gamma_L G \Gamma_R G^\dagger] \quad (\text{Fisher-Lee})$$

$$\Gamma_L = \text{Im}(\Sigma_L) \quad \Gamma_R = \text{Im}(\Sigma_R) \quad \Sigma = \Sigma_L + \Sigma_R; \Sigma_L = \begin{pmatrix} \frac{t_{LX}^2 e^{ik_L}}{t_L} & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 \end{pmatrix}; \Sigma_R = \begin{pmatrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{t_{XR}^2 e^{ik_R}}{t_R} \end{pmatrix}$$

Which allows us to extend our formulation for leads in more than one dimension.



The idea here is again to decompose the system in 3 parts, the periodic semi-infinite left lead, described by a Hamiltonian H_L the finite system under consideration, corresponding to H_X and the right semi-infinite lead H_R . The total Hamiltonian then becomes:

$$H = H_L + H_X + H_R + T_{LX} + T_{XR}, \quad (62)$$

where T_{LX} and T_{XR} describe the coupling between the different parts. In matrix form (for a tight binding hamiltonian) this corresponds to

$$H = \begin{pmatrix} H_L & T_{LX} & 0 \\ T_{LX}^+ & H_X & T_{XR} \\ 0 & T_{XR}^+ & H_R \end{pmatrix}, \quad (63)$$

which leads to the Green's function:

$$G = (E - H)^{-1} = \begin{pmatrix} E - H_L & -T_{LX} & 0 \\ -T_{LX}^+ & E - H_X & -T_{XR} \\ 0 & -T_{XR}^+ & E - H_R \end{pmatrix}^{-1}. \quad (64)$$

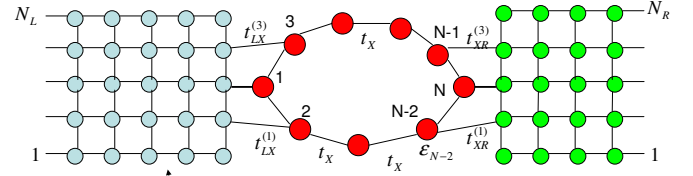
The center element of the Green's function G_X (element (2,2)) is then

$$\begin{aligned} G_X &= (E - H_X - \underbrace{T_{LX}^+(E - H_L)^{-1}T_{LX}}_{\Sigma_L} \\ &\quad - \underbrace{T_{XR}(E - H_R)^{-1}T_{XR}^+}_{\Sigma_R})^{-1} \\ &= (E - H_X - \Sigma_L - \Sigma_R)^{-1} \end{aligned} \quad (65)$$

Using again the Fisher-Lee formula, we have

$$T(E) = 4 \cdot \text{Tr}[\Gamma_L G_X \Gamma_R G_X^+], \quad (66)$$

where $\Gamma_\sigma = \Im(\Sigma_\sigma)$.



$$\begin{aligned} \psi_{p,q} &= \sum_{l=1}^{N_L} (a_l^{(L)} e^{ik_l^{(L,n)} p} + b_l^{(L)} e^{-ik_l^{(L,n)} p}) \sin(k_l^{(L,\perp)} q) \\ \psi_{p,q} &= \sum_{r=1}^{N_R} (a_r^{(R)} e^{ik_r^{(R,m)} p} + b_r^{(R)} e^{-ik_r^{(R,m)} p}) \sin(k_r^{(R,\perp)} q) \end{aligned}$$

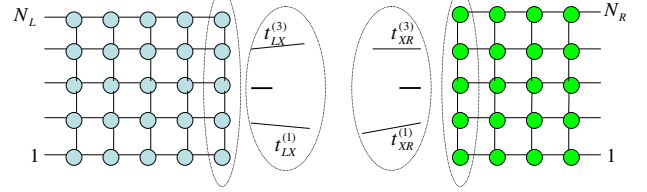
$$\begin{cases} t_L \psi_{p-1,q} + (\epsilon_L - E) \psi_{p,q} + t_L \psi_{p+1,q} + t_L \psi_{p,q-1} + t_L \psi_{p,q+1} = 0 \\ \Rightarrow \psi_{p,q} \propto e^{ik^{(L,\perp)} p} \sin(k^{(L,\perp)} q) \text{ and } E - \epsilon_L = 2t_L [\cos(k^{(L,\perp)}) + \cos(k^{(L,\perp)})] \\ k_l^{(L,\perp)} = l \frac{\pi}{N_L + 1}; k_r^{(R,\perp)} = r \frac{\pi}{N_R + 1} \end{cases}$$

$$T(E) = 4 \cdot \text{Tr}[\Gamma_L G \Gamma_R G^+]$$

$$\Gamma_L = \text{Im}(\Sigma_L)$$

$$\Gamma_R = \text{Im}(\Sigma_R)$$

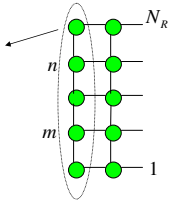
$$\Sigma_L = T_{XL} G_L^S T_{LX}; \Sigma_R = T_{XR} G_R^S T_{RX}$$



$$\begin{aligned} [G_L^S]_{n,m} &= \frac{2}{N_L + 1} \sum_{l=1}^{N_L} \frac{e^{ik_l^{(L,n)}}}{t_L} \sin(k_l^{(L,\perp)} n) \sin(k_l^{(L,\perp)} m) \\ \begin{cases} E - \epsilon_L = 2t_L [\cos(k_l^{(L,\perp)}) + \cos(k_l^{(L,\perp)})] \\ k_l^{(L,\perp)} = l \frac{\pi}{N_L + 1} \end{cases} \end{aligned}$$

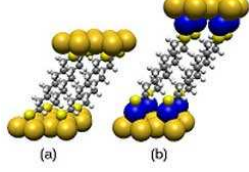
$$\frac{2}{N_R + 1} \sum_{r=1}^{N_R} \frac{e^{ik_r^{(R,m)}}}{t_R} \sin(k_r^{(R,\perp)} n) \sin(k_r^{(R,\perp)} m) = [G_R^S]_{n,m}$$

$$\begin{cases} E - \epsilon_R = 2t_R [\cos(k_r^{(R,\perp)}) + \cos(k_r^{(R,\perp)})] \\ k_r^{(R,\perp)} = r \frac{\pi}{N_R + 1} \end{cases}$$



$$\Rightarrow I(V) = \frac{2e}{h} \int_{\epsilon_{\min}}^{\epsilon_{\max}} T(E) \left(\frac{1}{1 + e^{-\frac{E - \mu + eV/2}{kT}}} - \frac{1}{1 + e^{-\frac{E - \mu - eV/2}{kT}}} \right) dE$$

$$(T(E) = 4 \cdot \text{Tr}[\Gamma_L G \Gamma_R G^+])$$



2D GREEN'S FUNCTION

The two-dimensional Green's function of an semi-infinite left lead, (semi-infinite in the \parallel direction and of finite width N in the \perp direction) can be expressed in terms of the plane eigenfunctions with the boundary conditions

$$\psi_{q,m=0} = \psi_{q=0,m} = \psi_{q=N+1,m} = 0. \quad (67)$$

These eigenfunctions can then be written as:

$$\langle \psi_{k_{\perp}, k_{\parallel}} | q, m \rangle = \underbrace{\sqrt{\frac{2}{N+1}} \sin(k_{\perp} q) \cdot K \sin(k_{\parallel} m)}_{\phi_q}, \quad (68)$$

where ϕ_q is normalized, i.e., $\sum_q \phi_q^* \phi_q = 1$ and K such that

$$\sum_{q,m} \langle \psi_{k_{\perp}, k_{\parallel}} | q, m \rangle \langle \psi_{k'_{\perp}, k'_{\parallel}} | q, m \rangle = \delta_{k'_{\perp}, k_{\perp}} \delta_{k'_{\parallel}, k_{\parallel}}. \quad (69)$$

The finite width forces the quantization of $k_{\perp} = n_{\perp} \frac{\pi}{N+1}$. Schrödinger's equation of the left semi-infinite lead is:

$$H_L \langle \psi_{k_{\perp}, k_{\parallel}} | q, m \rangle = 2t_L \cos(k_{\perp}) + 2t_L \cos(k_{\parallel}), \quad (70)$$

where t_L are the hopping elements of the left lead. The Green's function corresponding to H_L can then be written as

$$\begin{aligned} G_{(p,l),(q,m)} &= \langle p, l | \frac{1}{E - H_L} | q, m \rangle \\ &= \langle p, l | \sum_{k_{\perp}, k_{\parallel}} \frac{|\psi_{k_{\perp}, k_{\parallel}}\rangle \langle \psi_{k_{\perp}, k_{\parallel}}|}{E - H_L} | q, m \rangle \\ &= \sum_{k_{\perp}, k_{\parallel}} \frac{\langle p, l | \psi_{k_{\perp}, k_{\parallel}}\rangle \langle \psi_{k_{\perp}, k_{\parallel}} | q, m \rangle}{E - 2t_L \cos(k_{\perp}) - 2t_L \cos(k_{\parallel})} \\ &= \frac{2K^2}{N+1} \sum_{k_{\perp}, k_{\parallel}} \frac{\sin(k_{\perp} q) \sin(k_{\perp} p) \cdot \sin(k_{\parallel} m) \sin(k_{\parallel} l)}{\underbrace{E - 2t_L \cos(k_{\perp}) - 2t_L \cos(k_{\parallel})}_{E_{\perp}}} \\ &= \frac{2}{N+1} \sum_{k_{\perp}} \sin(k_{\perp} q) \sin(k_{\perp} p) \cdot \underbrace{K^2 \frac{\sin(k_{\parallel} m) \sin(k_{\parallel} l)}{E_{\perp} - 2t_L \cos(k_{\parallel})}}_{G_{m,l}^{1D}(E_{\perp})} \\ &= \frac{2}{N+1} \sum_{n_{\perp}} \sin(n_{\perp} \frac{\pi}{N+1} q) \sin(n_{\perp} \frac{\pi}{N+1} p) G_{m,l}^{1D} \left(E - 2t_L \cos(n_{\perp} \frac{\pi}{N+1}) \right), \end{aligned} \quad (71)$$

which is the expression used in page 7 for the edge of the two-dimensional lead for elements $m = 0, l = 0$, where $G_{0,0}^{1D}(E_{\perp}) = e^{ik_{\parallel}}/t_L$.

TRANSFER MATRIX APPROACH TO TIGHT-BINDING SYSTEMS

A simple method to solve discrete Schrödinger equations is the transfer matrix technique. We start with the

general one dimensional tight-binding equation:

$$t_{n+1}\psi_{n+1} + t_n\psi_{n-1} = (E - V_n)\psi_n, \quad (72)$$

which can be rewritten as

$$\begin{aligned} \begin{pmatrix} \psi_{n+1} \\ \psi_n \end{pmatrix} &= \underbrace{\begin{pmatrix} (E - V_n)/t_{n+1} & -t_n/t_{n+1} \\ 1 & 0 \end{pmatrix}}_{T_n} \begin{pmatrix} \psi_n \\ \psi_{n-1} \end{pmatrix} \\ &= \prod_{j=1}^n T_j \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix}, \end{aligned} \quad (73)$$

where T_j is the transfer matrix. Equation (73) allows us to express Schrödinger's equation in terms of the boundary condition ψ_1 and ψ_0 . This also shows the limitations of this technique, since it only works if the initial boundary conditions are either known or not important. For general geometries such as those discussed in the previous section this technique is often not adequate, because of the relevance of the initial conditions. However, a problem where the transfer matrix technique is very useful is in disordered systems. Indeed, in these systems the potential is typically random, hence each configuration of the potential is different, so that what becomes important are averaged quantities, such as the average transmission probability, where the transfer matrix technique can be used. If we start with eq. (73) and set $t_n = 1$ and leave only the potential to be n -dependent, it is interesting to distinguish the cases where V_n is periodic or random. In the simplest case, where $V_n = V_0$ the product of transfer matrices can be written as

$$\begin{aligned} \prod_{j=1}^n T_j &= T_0^n = S \begin{pmatrix} e^{ik} & 0 \\ 0 & e^{-ik} \end{pmatrix}^n S^+ \\ &= S \begin{pmatrix} e^{ikn} & 0 \\ 0 & e^{-ikn} \end{pmatrix} S^+, \end{aligned} \quad (74)$$

where $E - V_0 = 2\cos(k)$ and S the symmetric matrix, which diagonalizes T_0 . Interestingly, the eigenvalues e^{ik} and e^{-ik} are of norm 1 if $|E - V_0| \leq 2$ (k is real), which corresponds to the allowed band and supports plane wave solutions, whereas for $|E - V_0| > 2$, k is imaginary and $\prod_{j=1}^n T_j$ diverges, which corresponds to the exponentially vanishing modes (or evanescent waves). For any periodic potential V_n the situation is very similar, where

$$\prod_{j=1}^n T_j = \left(\prod_{j=1}^a T_j \right)^{n/a} \quad (75)$$

and a is the periodicity of V_n . Hence, the permitted bands correspond to the case where the eigenvalues of $\prod_{j=1}^a T_j$ are of norm one, since of $t_n = 1$ the determinant of T_j is one, which implies that the The product of the

two eigenvalues is always one. This gives us a simple way to obtain the bandstructure for a periodic potential.

It is then useful to define the Lyapounov exponent as

$$\lambda = - \lim_{n \rightarrow \infty} \frac{1}{n} \ln(\min |eig \left(\prod_{j=1}^n T_j \right)|) \quad (76)$$

in terms if the eigenvalue of the product of transfer matrices. For the periodic potential case $\lambda = 0$ inside the band and $\lambda > 0$ inside the gap, where transmission would be exponentially suppressed as shown in fig. 1, where we calculated the Lyapounov exponent (the dominant behavior of the product of transfer matrices) for a simple periodic potential.

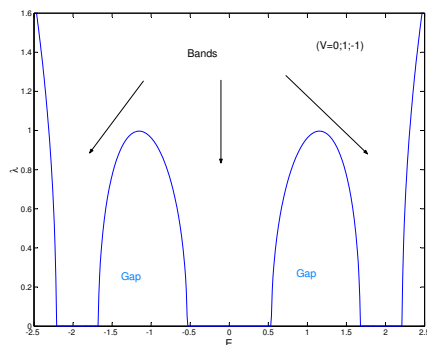


FIG. 1: Lyapounov exponent and corresponding bandstructure for the periodic potential ($t_n = 1$; $V_{3n} = 0$; $V_{3n+1} = 1$; $V_{3n+2} = -1$).

Moving towards disordered potentials

As a next step it is interesting to consider a periodic potential, where the periodicity extends over larger unit. This will lead to a much more complicated bandstructure with the appearance of many bands and gaps. This is illustrated in fig. 2, where we chose a potential of periodicity 40 in order to calculate the Lyapounov exponent.

When we now push this much further by considering a potential which is random the following structure of the Lyapounov is obtained (fig. 3).

Clearly the Lyapounov exponent is now strictly positive ($\lambda > 0$). This is known as Anderson localization, which tells us that in one dimension the transmission through a random potential tends exponentially to zero with the size of the system.

It turns out that the Lyapounov exponent defined in eq. (76) is self-averaging for a random potential if $n \rightarrow \infty$. This is known as the Oseledec theorem and tells us that λ is uniquely defined in that limit. Using (73) the wave function can be written as

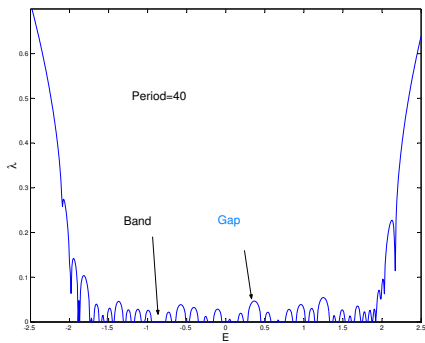


FIG. 2: Lyapounov exponent and corresponding bandstructure for a periodic potential of period 40.

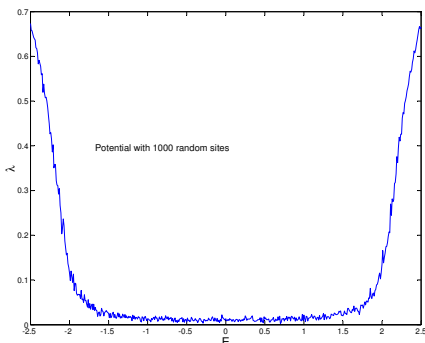


FIG. 3: Lyapounov exponent for a random potential of size 1000.

$$\psi_{n+1} = \left(\prod_{j=1}^n T_j \right)_{(1,1)} \psi_1 + \left(\prod_{j=1}^n T_j \right)_{(1,2)} \psi_0. \quad (77)$$

The envelope of the wavefunction is described by $e^{\pm\lambda n}$. Indeed, for a wavefunction of the form $e^{-\lambda n}$, the Lyapounov exponent is simply λ using

$$\lambda = - \lim_{n \rightarrow \infty} \frac{1}{n} \ln |\psi_n|, \quad (78)$$

which is equivalent to (76). The relationship between the Lyapounov exponent and the envelope of the wavefunction can be understood by realizing that the product of transfer matrices gives two eigenvalues $\{e^{-\lambda n}, e^{\lambda n}\}$ in the $n \rightarrow \infty$ limit, which means that in average

$$\langle T_j \rangle = \begin{pmatrix} e^{-\lambda} & 0 \\ 0 & e^{\lambda} \end{pmatrix}, \quad (79)$$

where $\langle \cdot \rangle$ is the average over the disorder. This average correctly gives us the expected dependence of the product of transfer matrices and also characterizes the typical envelope of the wavefunction. The fact that we have two

eigenvalues, one growing exponentially and the other decreasing exponentially reflects the role of the boundary condition. Indeed, the correct boundary condition would eliminate the diverging solution, hence $\psi \sim e^{-\lambda n}$ represents the correct typical envelope of a wavefunction in a disordered potential. Since this wavefunction decays exponentially it is called a localized wavefunction with a localization length $L_c = \lambda^{-1}$. Because of this exponential decay the propagation of an electron (or a wave) in a one-dimensional random potential is exponentially suppressed, which is commonly referred to as Anderson localization. In the next section we show this rigorously with the help of the Green's function using a perturbation calculation.

GREEN'S FUNCTION APPROACH TO DISORDERED SYSTEMS

The idea is to calculate the localization properties of the following nearest neighbor tight binding Hamiltonian:

$$H = \sum_i V_i c_i^\dagger c_i + c_{i+1}^\dagger c_i + c_{i-1}^\dagger c_i, \quad (80)$$

where V_i is a random variable. Writing the solution as $\psi = \sum_n \psi_n c_n^\dagger |0\rangle$, yields

$$\psi_{n+1} + \psi_{n-1} = (E - V_n)\psi_n. \quad (81)$$

In matrix form the Hamiltonian is written as

$$H = \begin{pmatrix} V_1 & 1 & 0 & \dots & 0 \\ 1 & V_2 & 1 & \dots & 0 \\ 0 & 1 & V_3 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & V_N \end{pmatrix}. \quad (82)$$

Since

$$E = \begin{pmatrix} E & 0 & 0 & \dots & 0 \\ 0 & E & 0 & \dots & 0 \\ 0 & 0 & E & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & E \end{pmatrix}, \quad (83)$$

the Green's function is simply the matrix inverse of $E - H$, i.e.,

$$G(E) = (E - H)^{-1} \Rightarrow (E - H)G(E) = \mathbf{1}. \quad (84)$$

From our calculation from the molecular wire, we have

$$\psi = \hat{G} \cdot J, \quad (85)$$

where J is the source function (with $J(1) \neq 0$ and $J(i > 1) = 0$), $\hat{G} = (E - H - \Sigma)^{-1}$ the total Green's function

including the leads, and Σ the self energy due to the leads. Hence,

$$\frac{\psi_N}{\psi_1} = \frac{\hat{G}_{1,N}}{\hat{G}_{1,1}}. \quad (86)$$

If we put the coupling to the leads to zero then $\hat{G} = G$ and the Lyapounov exponent (λ) becomes

$$\lambda = -\frac{1}{N-1} \ln \left| \frac{\psi_N}{\psi_1} \right| = -\frac{1}{N-1} \ln \left| \frac{G_{1,N}}{G_{1,1}} \right|. \quad (87)$$

From (85), we have that $G_{1,1}$ is proportional to ψ_1 , which we can set to one, without loss of generality. Hence to calculate (87) we are left with the evaluation of $G_{1,N}$. This can be done explicitly by inverting the matrix G using the expression for the matrix inverse: $(A_{ij})^{-1} = (-1)^{i+j} \text{cof}_{ij}(A) / \det(A)$ and applying it to $G(1, N)$. Hence,

$$G(1, N) = \frac{(-1)^{N+1} (-1)^{N-1}}{\det(E - H)}, \quad (88)$$

since the cofactor of $(E - H)_{1,N}$ is simply $(-1)^{N-1}$. The $\det(E - H)$ is also the product of the eigenvalues, i.e., $\det(E - H) = \prod_{\alpha} (E - \epsilon_{\alpha})$, where ϵ_{α} are the eigenvalues of H . Therefore,

$$\begin{aligned} G_{1,N} &= \frac{1}{\prod_{\alpha=1}^N (E - \epsilon_{\alpha})} \\ \Rightarrow \lambda &= \frac{1}{N-1} \sum_{\alpha=1}^N \ln |E - \epsilon_{\alpha}| \\ &= \int D(\epsilon) \ln |E - \epsilon| d\epsilon, \end{aligned} \quad (89)$$

which is known as the Herbert-Jones formula. Here $D(\epsilon)$ is the density of states $D(\epsilon) = \frac{1}{N-1} \sum_{\alpha} \delta(\epsilon - \epsilon_{\alpha})$, which clearly satisfies that $n = \int^{E_F} D(\epsilon) d\epsilon$, where n is the density. We can transform λ further by calculating the derivative, i.e.,

$$\begin{aligned} \partial_E \lambda &= \frac{1}{N-1} \sum_{\alpha=1}^N \frac{1}{E - \epsilon_{\alpha}} \\ &= \frac{1}{N-1} \sum_{\alpha=1}^N \frac{|\psi_{\alpha}|^2}{E - \epsilon_{\alpha}} \\ &= \frac{1}{N-1} \sum_{\alpha=1}^N \frac{\sum_{i=1}^N \langle i | \psi_{\alpha} \rangle \langle \psi_{\alpha} | i \rangle}{E - \epsilon_{\alpha}} \\ &= \frac{1}{N-1} \sum_{i=1}^N \langle i | \sum_{\alpha=1}^N \frac{|\psi_{\alpha} \rangle \langle \psi_{\alpha} |}{E - \epsilon_{\alpha}} | i \rangle \\ &= \frac{1}{N-1} \sum_{i=1}^N \langle i | \frac{1}{E - H} | i \rangle \end{aligned}$$

$$\begin{aligned} &= \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E) \\ \Rightarrow \lambda &= \int_{-\infty}^E dE' \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E'). \end{aligned} \quad (90)$$

Equation (89) is typically used to relate the density of states to the Lyapounov exponent and (90) will be used for the perturbative calculation of the Lyapounov exponent. Both expressions are exact and were obtained without any approximation. We will now calculate λ using perturbation theory.

Small disorder perturbation

In general we write the perturbation series for G as

$$\begin{aligned} G &= G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \dots \\ &= G^0 + G^0 V (G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \dots) \\ &= G^0 + G^0 V G \quad (\text{"Dyson eq."}) \\ \Rightarrow \mathbb{1} &= G^0 G^{-1} + G^0 V \\ \Rightarrow G^{-1} &= E - H^0 - V, \end{aligned} \quad (91)$$

where H^0 is the Hamiltonian without disorder and G^0 its corresponding Green's function. V is our small perturbation. Using indices the perturbation series reads:

$$G_{ij} = G_{ij}^0 + \sum_k G_{ik}^0 V_k G_{kj}^0 + \sum_{k,l} G_{ik}^0 V_k G_{kl}^0 V_l G_{lj}^0 + \dots \quad (92)$$

We now apply this perturbation series to our expression of the Lyapounov expression (90), which yields

$$\begin{aligned} \partial_E \lambda &= \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E) \\ &= \frac{1}{N-1} \left(\sum_{i=1}^N G_{ii}^0 + \sum_{ik} G_{ik}^0 V_k G_{ki}^0 + \sum_{ikl} G_{ik}^0 V_k G_{kl}^0 V_l G_{li}^0 + \dots \right) \end{aligned} \quad (93)$$

We now take the average $\langle \cdot \rangle_D$ over the disorder, where we assume the following properties for the disorder: $\langle V_k \rangle_D = 0$ and $\langle V_k V_l \rangle_D = \delta_{k,l} \sigma^2$, which corresponds to an uncorrelated disorder of standard deviation σ . Hence,

$$\begin{aligned} \langle \sum_{i=1}^N G_{i,i}(E) \rangle_D &= \sum_{i=1}^N G_{ii}^0 + 0 + \sum_{ikl} G_{ik}^0 G_{kl}^0 G_{li}^0 \langle V_k V_l \rangle_D + \dots \\ &= \sum_{i=1}^N G_{ii}^0 + \sigma^2 \sum_{ik} G_{ik}^0 G_{kk}^0 G_{ki}^0 + \dots \\ &= \sum_{i=1}^N G_{ii}^0 + \sigma^2 \sum_k G_{kk}^0 \sum_i G_{ki}^0 G_{ik}^0 + \dots \end{aligned}$$

$$\begin{aligned}
&= \sum_{i=1}^N G_{ii}^0 + \sigma^2 \sum_k G_{kk}^0 \langle k | \frac{1}{E - H^0} \frac{1}{E - H^0} | k \rangle + \dots \\
&= \sum_{i=1}^N G_{ii}^0 - \sigma^2 \sum_k G_{kk}^0 \partial_E \langle k | \frac{1}{E - H^0} | k \rangle + \dots \\
&= \sum_{i=1}^N G_{ii}^0 - \sigma^2 \sum_k G_{kk}^0 \partial_E G_{kk}^0 + \dots \\
&= \sum_{i=1}^N (G_{ii}^0(E) - \partial_E \frac{\sigma^2}{2} (G_{ii}^0(E))^2 + \dots)
\end{aligned}$$

Using expression (90) we obtain

$$\langle \lambda \rangle_D = \frac{1}{N-1} \sum_{i=1}^N \left(\int_{-\infty}^E G_{ii}^0(E') dE' - \frac{\sigma^2}{2} (G_{ii}^0(E))^2 + \dots \right) \quad (95)$$

Now we simply have to evaluate $G_{ii}^0(E)$. But since the eigenvalues of H^0 are $\epsilon_\alpha^0 = 2 \cos(k_\alpha)$ and $\langle \psi_\alpha^0 | n \rangle \sim e^{ik_\alpha n}$, we have

$$\begin{aligned}
G_{ii}^0(E) &= \sum_{\alpha} \frac{1}{E - \epsilon_\alpha^0} \\
&= \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{E - 2 \cos(k)} dk \\
&= \frac{1}{\sqrt{E^2 - 4}}.
\end{aligned} \quad (96)$$

For an energy inside the band, i.e., $|E| < 2$, $G_{ii}^0(E) = -i(4 - E^2)^{-1/2}$ and is imaginary, hence for $|E| < 2$ and using (95), we obtain

$$\Re \langle \lambda \rangle_D = \frac{\sigma^2}{2(4 - E^2)}, \quad (97)$$

which is the famous perturbative result obtained originally by Thouless. The real part is always strictly positive (for $V \neq 0$), which implies that *all* wavefunctions decay exponentially, which is the proof of Anderson localization in 1D, telling us that in the presence of any amount of disorder the transmission will always tend to zero when the system size tends to infinity. We can also define a localization length $L_c = (\Re \lambda)^{-1}$, which represents the spatial extent of the wavefunction and means that transmission can only occur for systems smaller than L_c . The imaginary part describes the density of state as we will discuss below.

To extract the imaginary part we use the definition of the retarded Green's function $G^+(E) = G(E + i\epsilon)$, where ϵ is an infinitesimal positive number. Using (90), the Lyapounov is now

$$\lambda = \int_{-\infty}^E dE \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E + i\epsilon)$$

$$\begin{aligned}
&= \int_{-\infty}^E dE \frac{1}{N-1} \sum_{i=1}^N \langle i | \sum_{\alpha} \frac{|\psi_{\alpha}\rangle \langle \psi_{\alpha}|}{(E - \epsilon_{\alpha} - i\epsilon)} | i \rangle \\
&= P\lambda - i\pi \int_{-\infty}^E dE \frac{1}{N-1} \sum_{i,\alpha} \langle i | \psi_{\alpha} \rangle \langle \psi_{\alpha} | i \rangle \delta(E - \epsilon_{\alpha}) \\
&= P\lambda - i\pi \int_{-\infty}^E dE \frac{1}{N-1} \sum_{\alpha} \delta(E - \epsilon_{\alpha}) \\
&= P\lambda - i\pi N(E)
\end{aligned} \quad (98)$$

where we used that $\frac{1}{x+i\epsilon} = P\frac{1}{x} - i\pi\delta(x)$, where P is the principle part and $N(E_F)$ is the density. In general, P corresponds to the real part of the integral, hence:

$$\begin{cases} \Re \lambda &= \Re \int_{-\infty}^E dE \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E + i\epsilon) \\ D(E) = \partial_E N(E) &= -\frac{1}{\pi} \Im \frac{1}{N-1} \sum_{i=1}^N G_{i,i}(E + i\epsilon) \end{cases} \Rightarrow \begin{cases} \Re \lambda &= \Re \int_{-\infty}^E \overline{G^+(E)} dE \\ D(E) &= -\frac{1}{\pi} \Im G^+(E) \end{cases}, \quad (99)$$

where $\overline{G} = \text{Tr}(G)/(N-1)$. Hence, in the case without disorder ($V = 0$) we have for $|E| < 2$ that $\Re \lambda = 0$ and $D(E) = \frac{1}{\pi}(4 - E^2)^{-1/2}$.

We can now verify, that the above expression for the density of states is the same as the standard expression: $D(E) = \frac{1}{\pi} |\partial_k E|^{-1}$, which indeed is equivalent to $D(E) = \frac{1}{\pi}(4 - E^2)^{-1/2}$, since $E = 2 \cos(k)$ for $V = 0$. It is also interesting to note that up to second order in perturbation theory the density of states does not depend on the disorder, only $\Re \lambda$ is affected by the disorder.

CONDUCTANCE QUANTIZATION

We can now apply this result to understand the experimentally observed conductance quantization seen in figs. 4 and 5.

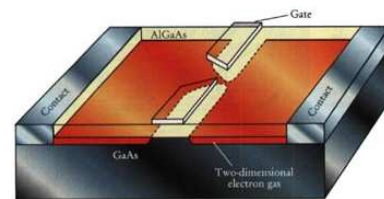


FIG. 4: Schematic cross-sectional view of a quantum point contact, defined in a high-mobility 2D electron gas at the interface of a GaAs-AlGaAs heterojunction. The point contact is formed when a negative voltage is applied to the gate electrodes on top of the AlGaAs layer. Transport measurements are made by employing contacts to the 2D electron gas at either side of the constriction.

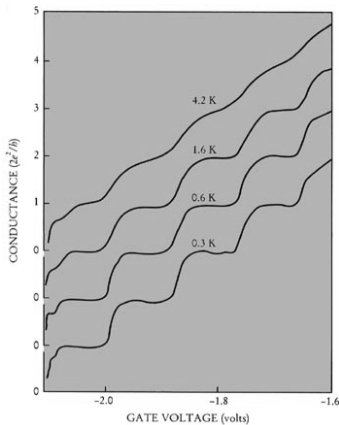


FIG. 5: Conductance quantization of a quantum point contact in units of $2e^2/h$. As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise. The resulting conductance steps are smeared out when the thermal energy becomes comparable to the energy separation of the modes.

In the ideal pure one dimensional case we had the conductance given by $2e^2/h$ (see eq. 40). When this is extended to a quasi 2-dimensional case the conductance increases by quantum steps (conductance quantization) of $2e^2/h$ as seen in the experiments. This can be understood simply in terms of number of channels, i.e., increasing the width of current channel increases the conductance by an integer multiple of $2e^2/h$. In this case the electron energy is given by

$$\epsilon = \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 (\pi n/W)^2}{2m^*} \quad (100)$$

if the boundary of our narrow wire is assumed to be sharp, since in this case the wave function has to vanish at the boundary (like for an electron in a box of width W). In general, if

$$\frac{\hbar^2 (\pi/W)^2}{2m^*} < E_F < \frac{\hbar^2 (2\pi/W)^2}{2m^*} \quad (101)$$

then we recover the ideal case of a one-dimensional quantum wire, or single channel. If, however,

$$\frac{\hbar^2 (N\pi/W)^2}{2m^*} < E_F < \frac{\hbar^2 ((N+1)\pi/W)^2}{2m^*} \quad (102)$$

we can have n channels, where each channel contributes equally to the total conductance. Hence in this case $G = N \cdot 2e^2/h$, where N is the number of channels. This implies that a system, where we reduce the width of the conductor will exhibit jumps in the conductance of step $2e^2/n$. Indeed, this is what is seen experimentally.

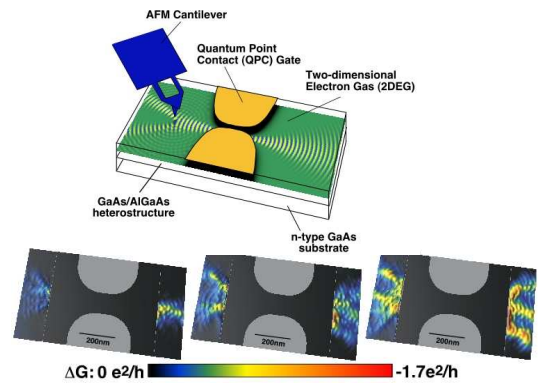


FIG. 6: Imaging of the channels using an AFM (1 to 3 channels from left to right). The images were obtained by applying a small negative potential on the AFM tip and then measuring the conductance as a function of the tip scan and then reconstruct the 2D image from the observed change in conductance.

We can also obtain this result directly using our tight binding approach and the Green's function approach described in the previous section. Taking for example a width of four sites we can calculate the total transmission using the Fisher-Lee formula () to obtain the energy dependence shown in fig. 7.

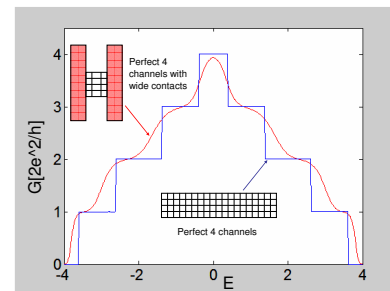


FIG. 7: The conductance of a 4 site wide conductor as a function of energy for the case with wide leads (smooth steps) or semi-infinite leads of width 4 (square steps).

The reason we obtain a curve which is symmetric in energy stems from the tight binding approximation. Indeed, the energy of the quasi two-dimensional system is given by $E = 2 \cos(k_{\perp}) + 2 \cos(k_{\parallel})$ (the hopping term is assumed to be 1). Hence, the maximum conductance is obtained when $E = 0$, since then $\cos(k_{\parallel}) = -2 \cos(k_{\perp})$, which is possible for any quantized value of $k_{\perp} = n\pi/(N+1)$, where N is the width. For energies closer to the band edges ($E = \pm 4$), the number of possible values for k_{\perp} are reduced, which leads to the observed decrease of the conductance close to the band edges.

INTRODUCING A MAGNETIC FIELD

When adding a magnetic field to the system the Hamiltonian transverse to the magnetic field ($\vec{B} = \nabla \times \vec{A}$) is written as

$$H = \frac{1}{2m}(-i\hbar\nabla - e\vec{A})^2. \quad (103)$$

For the symmetric gauge ($\vec{A} = (-By/2, Bx/2, 0)$) in coordinates (x, y, z) this becomes

$$H = \frac{\hbar^2}{2m} \left(-\partial_x^2 + \frac{ie}{\hbar}By\partial_x - \frac{ie}{\hbar}Bx\partial_y + \frac{e^2}{4\hbar^2}y^2B^2 + \frac{e^2}{4\hbar^2}x^2B^2 - \partial_y^2 \right) \quad (104)$$

It is now possible to discretize this equation by defining $x = la$, $y = ka$, $\alpha = \frac{eBa^2}{\hbar} = \frac{\phi}{\phi_0} = \frac{Ba^2}{\phi_0}$, $\phi_0 = h/e$ the flux quantum, a the lattice constant and ϕ the magnetic flux per unit cell. Using the following expressions of the derivatives:

$$\partial_x^2\psi = (\psi_{l+1,k} + \psi_{l-1,k} - 2\psi_{l,k})/a^2 \text{ and } \partial_x\psi = (\psi_{l+1,k} - \psi_{l-1,k})/2a \quad (105)$$

we obtain in the limit $\alpha \ll 1$

$$\begin{aligned} \frac{\hbar^2}{2ma^2} \left(-\psi_{l+1,k} - \psi_{l-1,k} + 2\psi_{l,k} + \frac{ia^2eBk}{\hbar}(\psi_{l+1,k} - \psi_{l-1,k})/2 + \underbrace{\frac{e^2a^4B^2k^2}{4\hbar^2}}_{\simeq 0} \psi_{l,k} + \dots \right) &= E\psi_{l,k} \\ \left(-\underbrace{e^{-i\pi\alpha k}}_{\simeq 1-i\pi\alpha k} \psi_{l+1,k} - e^{i\pi\alpha k} \psi_{l-1,k} - e^{i\pi\alpha l} \psi_{l,k+1} - e^{-i\pi\alpha l} \psi_{l,k-1} + 4\psi_{l,k} \right) &= E \frac{2ma^2}{\hbar^2} \psi_{l,k} \end{aligned} \quad (106)$$

The magnetic flux through a unit cell is then $\oint \vec{A} = Ba^2$, with $\vec{A} = (-Bk/2, Bl/2, 0)a$, which is consistent with $\vec{B} = \nabla \times \vec{A}$. In general, a Hamiltonian in second quantized form and in the presence of a magnetic field can therefore be written as

$$H = \sum_{\langle ij \rangle} e^{i\phi_{ij}} c_i^\dagger c_j + e^{-i\phi_{ij}} c_j^\dagger c_i, \quad (107)$$

where $\langle ij \rangle$ are the nearest neighbors and the sum of the phases over a lattice square is $\sum_{\square} \phi_{ij} = 2\pi\alpha$. Different Gauges will lead to different forms of the phase factors, but the sum over a unit cell is the flux per unit cell.

WEAK LOCALIZATION

An interesting consequence of the magnetic field in the presence of disorder is the weak localization effect, which is an increase in conductance at non-zero magnetic field. This effect arises from the destruction of the phase sym-

metry for two semiclassical trajectories in opposite directions in the presence of a magnetic field. The simplest way to understand this is when looking at a single return trajectory. Without a magnetic field the same trajectory exists in the opposing direction, hence when summing all possible trajectories one trajectory and its reverse add up, which leads to an enhance return probability. This effect is destroyed by the magnetic field since time reversal symmetry is then broken and two trajectories in opposite directions will then have different phases.

Using our Green's function technique to calculate the conductance for a square geometry it then possible to observe this effect when introducing some disorder as shown in fig. 8.

The analytical approach is obtained by a perturbative calculation on the disorder strength, which leads to the following expression due to Hikami valid in 2D (Ref: S. Hikami, A. I. Larkin, and Y. Nagaoka, Prog. Theor. Phys. **63**, 707 (1980)).

$$\Delta\sigma(B) = -\frac{e^2}{\pi h} \left[\Psi\left(\frac{1}{2} + \frac{B_0}{B}\right) - \Psi\left(\frac{1}{2} + \frac{B_\phi}{B}\right) \right] \quad (108)$$

where Ψ is the digamma function, $B_0 = h/(8\pi eD\tau)$, and $B_\phi = h/(8\pi eD\tau_\phi)$. The transport scattering time is τ with diffusion constant $D = v_F^2\tau/2$ (v_F the Fermi velocity) and τ_ϕ is the phase coherence time. This expression typically leads to a logarithmic increase of the resistance when lowering the temperature, following $\Delta\sigma = -\frac{e^2}{\pi h} \ln(\tau_\phi/\tau)$, where τ_ϕ is temperature dependent.

Weak localization (WL) also exists in 3D, where it was also observed experimentally. Moreover, this phenomenon is only observed when the conductance (or resistance) is averaged over many disorder configurations. For a given configuration, WL would not be observed since the conductance in this case is dominated by universal conductance fluctuations described in the next section. The averaging over disorder is equivalent to performing the experiment (numerical or physical) in a system, whose size is much larger than the quantum coherence length. Indeed, in this case the conductance of a system of size L is then simply the averaged conductance G_ϕ (multiplied by a dimensional factor) of the system of size L_ϕ , where L_ϕ is the coherence length of the system, i.e., $G = \langle G_\phi \rangle (L/L_\phi)^{D-2}$, where $\langle \cdot \rangle$ is the average of the disorder and D the dimension.

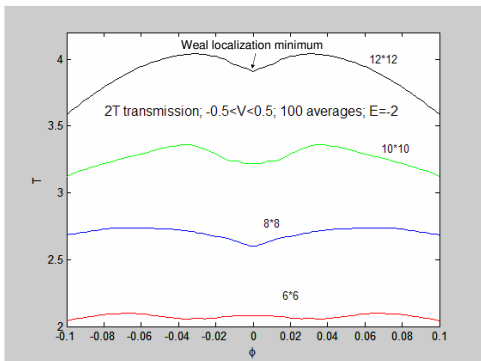


FIG. 8: Weak localization effect for different square sizes. The transmission probability is plotted as a function of the flux per unit cell ϕ for different square sizes. The dip is easily seen when averaging over different disorder configurations.

UNIVERSAL CONDUCTANCE FLUCTUATIONS

Universal conductance fluctuations (UCF) is a striking example of the importance of phase coherence. Indeed, if the phase coherence of the electron is maintained over the size of the system studied, the wavefunction describing the electron traveling through the system will

depend on the detailed shape and given impurity configuration. By changing slightly this configuration the wavefunction will change, which in turn affects the conductance through the system. This conductance is then characterized by fluctuations when any external parameter such as the Fermi energy or the magnetic field is changed. An example of this is shown in figure 9.

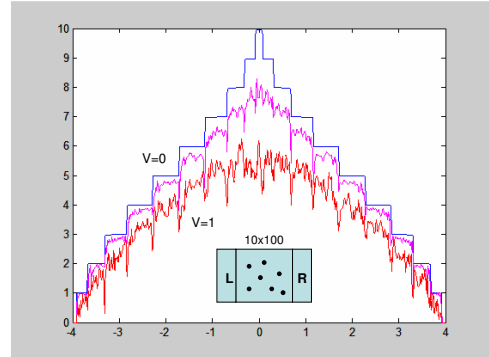


FIG. 9: Universal conductance fluctuations modeled in the tight binding approximation for a system of size 10×100 with increasing disorder.

In general, the conductance fluctuations are of the order of $\delta G \simeq e^2/h$ for a system where the coherence length L_ϕ exceeds the size of the system L . For a system, where $L \gg L_\phi$, these fluctuations will be averaged out, which leads to $\delta G \simeq e^2/h \cdot \sqrt{L_\phi/L}$. Hence, in the classical limit $L/L_\phi \rightarrow \infty$ no fluctuations survive.

AHARONOV AND BOHM OSCILLATIONS AND PERSISTENT CURRENTS

Aharonov and Bohm oscillations are another interesting manifestation of the quantum coherence of the system. When the system is composed of a ring with or without leads attached to it, when applying a magnetic field through the ring, the phase of the electrons in the ring will be affected by the magnetic field (even if there is no field in the conductor). This will lead to Aharonov and Bohm oscillations as a function of the number of quantum magnetic fluxes penetrating the ring. If leads are attached to the ring the current will oscillate as a function of the magnetic field, with an oscillation given by the quantization of the magnetic flux. This can be understood by describing the ring in the tight binding approximation as having two branches with opposite phases, $te^{i\pi\alpha}$ and $te^{-i\pi\alpha}$, where $\alpha = \phi/\phi_0$ is the magnetic flux through the ring in units of the quantum flux. The total overlap is then simply $te^{i\pi\alpha} + te^{-i\pi\alpha} = 2t \cos(\pi\alpha)$, which immediately shows that the transmission ($\sim |t^2|$) will oscillate with magnetic field with periodicity α .

Another interesting phenomena in a ring is the exist-

tence of **persistent currents**. In this case we consider a closed ring of N lattice sites. In the presence of a magnetic field the hopping elements are multiplied by a phase factor $te^{i2\pi\alpha/N}$. For an ordered ring (all hopping elements are equal and all onsite energies are zero) the wave functions are simply plane-wave with a phase factor, i.e., $\psi_n = e^{i(k-2\pi\alpha/N)n}$. These wave functions are indeed solutions to

$$te^{i2\pi\alpha/N}\psi_{n+1} + te^{-i2\pi\alpha/N}\psi_{n-1} = E\psi_n, \quad (109)$$

with $E = 2t \cos(k - 2\pi\alpha/N)$. A closed ring penetrated by a magnetic field implies the following boundary condition: $\psi_n = e^{i2\pi\alpha}\psi_{n+N}$, which leads to the quantization of $k = 2\pi l/N$, where l is an integer. This implies that each energy level (given by the quantum number l) will oscillate as a function of α ($E = 2t \cos[2\pi(l - \alpha)/N]$). From the associated normalized wavefunction $\psi_n^l = e^{i(2\pi/N)(l-\alpha)n}/\sqrt{N}$ it is possible to obtain the current probability expectation for state l . In the presence of a magnetic field the current operators have to be modified in order to include the phase factor. In the continuous case equ. (43) ∇ has to be replaced by $\nabla - eA$, where A is the vector potential and in the tight binding description the hopping term t_{ij} in equ. (48) has to be replaced by $t_{ij}e^{-i\phi_{ij}}$, where ϕ_{ij} is the associated gauge field induced phase factor. This leads to a current expectation $j_l = -(2/N\hbar)t \sin(2\pi(l - \alpha)/N)$, where the electrical current in this state is simple $e j_l$. Alternatively, the expression of the current can be simply obtained from

$$I_l = -(e/h)\partial_\alpha E_l = -(2e/N\hbar)t \sin(2\pi(l - \alpha)/N), \quad (110)$$

where E_l is the eigenvalue of state l . This last expression can be understood in terms of the analogy between the group velocity of Bloch waves ($v_g \sim \partial_k E$) in a periodic potential applied to the ring geometry, where α plays the role of the quantum number k .

QUANTUM HALL EFFECT

The quantum Hall effect is the quantization (due to the Landau levels) of the Hall resistance. This effect is observed in two dimensional systems as well as in quasi-1D systems. In order to observe a quantized Hall resistance in two dimensions only a magnetic and an edge a necessary. Hence, in order to understand its physics we need to solve the two dimensional Hamiltonian in a magnetic field and a confinement potential. Without confinement the spectrum in a magnetic field is simply given by the Landau levels:

$$E_n = \hbar\omega_c(n + 1/2). \quad (111)$$

A confinement potential changes this spectrum. In general, one can introduce a quantum number X describing the average position perpendicular to the long edge.

For a confinement potential where the potential is infinite at $x=0$ it is possible to show that the spectrum is given by the Landau levels far away enough from the edge and by $E_n = \hbar\omega_c(2n + 3/2)$ at the edge. Therefore, as a function of X , when approaching the edge the energy levels bend up as illustrated in fig. 10.

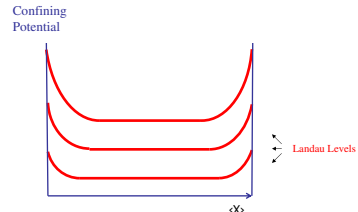


FIG. 10: Landau levels in a confined potential

It is possible to capture most of the physics of the quantum Hall effect by using the tight binding approximation, where the edge is naturally introduced when considering a finite size system. In this case the magnetic field has to be strong enough so that Landau levels develop in the system. On the other hand, when introducing the magnetic field in the tight binding approximation we assumed that amount of flux per flux quantum ($\alpha = \phi/\phi_0$) and per unit cell is small. It turns out that the description is still correct at large α in the case where a periodic potential is added to the system. In most physical systems this periodic potential does not exist or is irrelevant because the periodicity is so much smaller than the magnetic length. Hence we need to keep in mind to consider α small if we are probing Landau level physics.

In example of such a calculation for different fields is shown in figure 11 for a two terminal configuration.

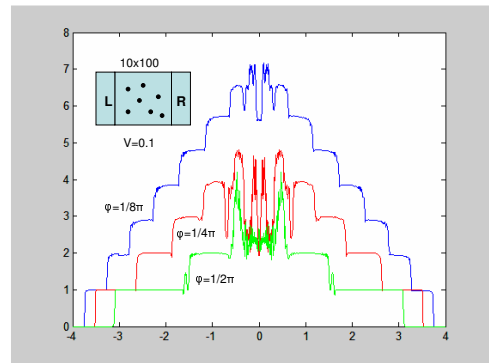


FIG. 11: Two-terminal transmission probability of a weakly disordered system in a strong magnetic field, showing quantum Hall plateaus.

In general, the quantum Hall effect is the most striking when looked at in a four probe geometry, where contact contributions are minimized. In order to describe a four probe device it is necessary to introduce additional leads

($i = 1, 2, 3, 4$). Each lead describes an electron reservoir at a given chemical potential μ_i . An example of such a configuration is given in figure 12. From Kirchhof's law it is then possible to write the current from lead i as

$$I_i = 2\frac{e}{h} \sum_j \int dE T_{ji}(E) f_i(E) - T_{ij}(E) f_j(E), \quad (112)$$

where $f_i(E)$ is the Fermi-Dirac distribution of lead i at the chemical potential μ_i and T_{ij} is the transmission probability between lead i and j . At zero temperature and assuming that $T_{ij}(E) = T_{ij}$, we then have

$$I_i = 2\frac{e}{h} \sum_j T_{ji} \mu_i - T_{ij} \mu_j = 2\frac{e^2}{h} \sum_j T_{ji} V_i - T_{ij} V_j, \quad (113)$$

where V_i are the voltages of the leads. If all voltages are equal this means that there cannot be any current, hence $I_i = 0$. This leads to the condition $\sum_j T_{ji} V_i - T_{ij} V_j = 0$, which implies

$$I_i = 2\frac{e}{h} \sum_j T_{ji} (V_i - V_j). \quad (114)$$

If we now assume without loss of generality that $V_4 = 0$ this implies that

$$\begin{pmatrix} I_1 \\ I_2 \\ I_3 \end{pmatrix} = \begin{pmatrix} T_{2,1} + T_{3,1} + T_{4,1} & -T_{1,2} & -T_{1,3} \\ -T_{2,1} & T_{1,2} + T_{3,2} + T_{4,2} & -T_{2,3} \\ -T_{3,1} & -T_{3,2} & T_{1,3} + T_{2,3} + T_{4,3} \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix}, \quad (115)$$

which can be written in short as

$$\vec{I} = \hat{T} \vec{V} \Rightarrow \vec{V} = \hat{T}^{-1} \vec{I}. \quad (116)$$

In a typical experimental configuration the Hall resistance would be obtained by applying a current between 1 and 4 and measuring the Hall voltage between 2 and 3, which we can define as $R_{14,23} = R_H$. In this case the expression for the Hall resistance reduces to

$$R_H = \frac{V_2 - V_3}{I_1} = (\hat{T}^{-1})_{2,1} - (\hat{T}^{-1})_{3,1}, \quad (117)$$

since $I_2 = I_3 = 0$ (shown in figure 12). Similarly, the diagonal resistance R_{xx} is obtained by flowing a current between 3 and 4 and measuring the voltage drop between 1 and 2. Hence,

$$R_{xx} = \frac{V_1 - V_2}{I_3} = (\hat{T}^{-1})_{1,3} - (\hat{T}^{-1})_{2,3}. \quad (118)$$

The transmission probabilities are simply obtained using the Green's function formalism, where

$$\begin{aligned} T_{ij} &= 4tr(\Gamma_i G \Gamma_j G^+) \\ G &= (E - H - \sum_i \Sigma_i)^{-1} \\ \Gamma_i &= \Im \Sigma_i, \end{aligned} \quad (119)$$

where Σ_i is the self-energy due to lead i and H is the Hamiltonian of the system without the leads.

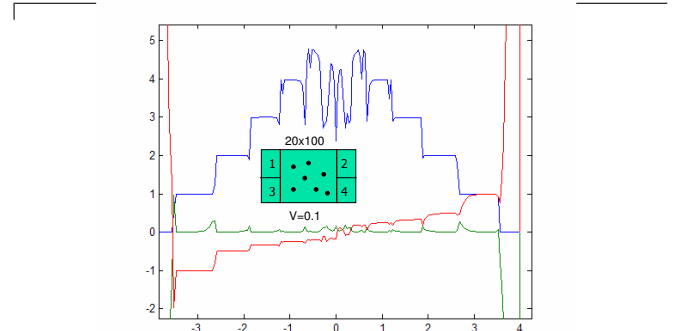


FIG. 12: Four-terminal resistance in units of $h/2e^2$ of a weakly disordered system in a strong magnetic field, showing quantum Hall plateaus. The red curve shows the Hall resistance, the green curve R_{xx} and the blue curve the two-terminal conductance in units of $2e^2/h$, similar to figure 11.

ITERATIVE GREEN'S FUNCTION CALCULATION

The main difficulty in the numerical implementation of the Green's function method is the size of the Hamiltonian for 2D or 3D systems (the inversion of a large matrix is the main difficulty). Realizing that the transmission probabilities only depend on the terms of the Green's function, which couple the leads it is then possible to use an iterative approach to obtaining only the relevant terms. For example, in a quasi 1 dimensional structure

it is possible to decompose the full Hamiltonian in slices H_l where the full hamiltonian is

$$H = \begin{pmatrix} \ddots & & & & & \\ & H_l & T_{l,l+1} & & & \\ & T_{l,l+1}^+ & H_{l+1} & & & \\ & & & \ddots & & \\ & & & & & \ddots \end{pmatrix}. \quad (120)$$

The idea then is to obtain the Green's function, which relates the elements of the two extremities H_1 and H_N , by starting with the pair of middle slices $H_{N/2}$ and $H_{N/2+1}$. Hence, we start by obtaining the Green's function of the middle slices ($l = N/2$), i.e.,

$$G_1 = \left[E - \begin{pmatrix} H_{l+1} & T_{l,l+1}^+ \\ T_{l,l+1} & H_l \end{pmatrix} \right]^{-1}. \quad (121)$$

The next Green's function relating H_{l-1} and H_{l+2} can then be obtained by using

$$G_2 = \left[E - \begin{pmatrix} H_{l+2} & 0 \\ 0 & H_{l-1} \end{pmatrix} - \Sigma_1 \right]^{-1}, \quad (122)$$

where Σ_1 is the self-energy due to the middle part given by H_l , H_{l+1} and $T_{l,l+1}$, which can be expressed as

$$\Sigma_1 = \begin{pmatrix} T_{l+1,l+2} & 0 \\ 0 & T_{l-1,l}^+ \end{pmatrix} G_1 \begin{pmatrix} T_{l+1,l+2}^+ & 0 \\ 0 & T_{l-1,l} \end{pmatrix}. \quad (123)$$

This iterative procedure can be continued until we hit the first and last slice H_1 and H_N . The last iteration then reads,

$$G_{N/2} = \left[E - \begin{pmatrix} H_N & 0 \\ 0 & H_1 \end{pmatrix} - \Sigma_{N/2} - \Sigma_L \right]^{-1}, \quad (124)$$

where

$$\Sigma_{N/2} = \begin{pmatrix} T_{N-1,N} & 0 \\ 0 & T_{1,2}^+ \end{pmatrix} G_1 \begin{pmatrix} T_{N-1,N}^+ & 0 \\ 0 & T_{1,2} \end{pmatrix} \quad (125)$$

and Σ_L is the total self energy due to the leads connecting H_1 and H_N . The number of leads is not limited to two. Indeed in the example of figure 12 a total of four leads were used.

QUANTUM DOTS

A simple quantum dot can be pictured like in fig. 13. In the tight binding approximation, the Green's function

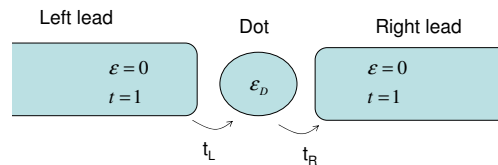


FIG. 13: A typical geometry of a quantum dot

of a quantum dot without interactions can be then written as

$$G = \begin{pmatrix} E - e^{ik} & t_L & 0 \\ t_L & E - \epsilon_D & t_R \\ 0 & t_R & E - e^{ik} \end{pmatrix}^{-1}, \quad (126)$$

where we used the self-energy e^{ik} due to the one-dimensional lead with dispersion $E = 2 \cos(k)$ ($t = 1$ hopping elements). In order to obtain the transmission probability we can use Fisher-Lee's relation (). Hence,

$$T(E) = |2 \sin(k)|^2 |G(1, 3)|^2 \underset{t_\sigma \ll 1}{\simeq} \frac{\Gamma_L \Gamma_R}{\left(\frac{\Gamma_L + \Gamma_R}{2}\right)^2 + (E - E_r)^2}, \quad (127)$$

where $\Gamma_\sigma = |t_\sigma^2 \sin(k)|$ and $\Gamma = (\Gamma_L + \Gamma_R)/2$ describes the average coupling strength and $E_r = \epsilon_D + (t_L^2 + t_R^2) \cos(k)$ is resonance energy. This Lorentzian resonance can also be obtained directly from a simple double barrier geometry.

An alternate approach to this quantum dot can be obtained by using the dot's Green's function directly. Indeed,

$$G_D = (E - (t_L^2 + t_R^2)e^{ik} - \epsilon_D)^{-1}, \quad (128)$$

since the self-energies due the leads evaluated directly on the dot are $t_\sigma^2 e^{ik}$. It is quite straightforward to show that indeed $G_D = G(2, 2)$. Separating the imaginary from the real part leads to

$$G_D = \frac{(E - E_r) + i\Gamma}{(E - E_r)^2 + \Gamma^2} \quad (129)$$

Twice the imaginary part defines the spectral function ($A(E) = 2\Im G_D(E)$). This spectral function describes the density probability as a function of energy and is normalized ($\int dEA(E) = 2\pi$). The imaginary part of the diagonal Green's function can also be related to the escape rate. Indeed, taking the Fourier transform of

$$\Im G_D(E) \xrightarrow{FT} e^{iE_r t} e^{-\Gamma t}, \quad (130)$$

leads to $|G_D(t)|^2 = e^{-2\Gamma t}$ which describes the probability of an electron to be on the dot. Hence, Γ is simply the escape rate due to the leads of an electron placed on the dot. It is further possible to relate this escape rate to the transmission through the dot by using an expression derived by Meir and Wingreen, which relates the transmission probability to the spectral function:

$$\begin{aligned} T(E) &\simeq \frac{|t_L|^2 |t_R|^2}{|t_L|^2 + |t_R|^2} A(E) \frac{\partial E}{\partial k} \\ &= \frac{\Gamma_L \Gamma_R}{\left(\frac{\Gamma_L + \Gamma_R}{2}\right)^2 + (E - E_r)^2}, \end{aligned} \quad (131)$$

which is the same expression as obtained earlier.

DEPHASING IN A QUANTUM DOT

The sharp resonance in a quantum dot is due to the multiple constructive interferences which occur between the tunneling barriers. Indeed, without phase coherence one would expect the transmission probability to be simply given by $T \sim |t_L|^2 \cdot |t_R|^2$. It is possible to model this incoherent process by introducing dephasing or decoherence into the quantum dot. A simple way to do this is to add an additional lead to the dot, which is equivalent to adding the self-energy due to the lead on the onsite energy of the dot $\rightarrow \epsilon_D + t_C^2 e^{ik}$, where t_C is the coupling strength to the additional lead.

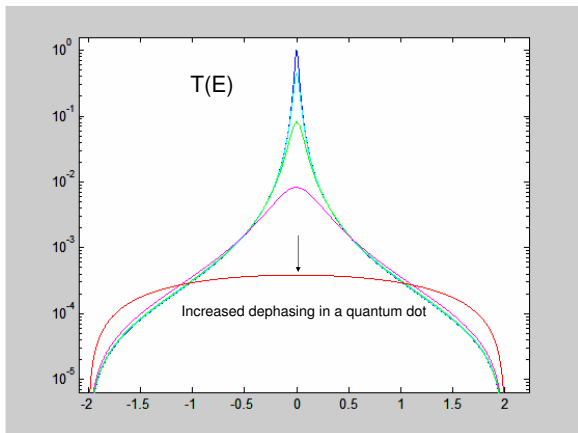


FIG. 14: The resonance transmission of a quantum dot for different values of dephasing obtained by coupling a lead directly to the dot. The dot energy was taken to be $\epsilon_D = 0$ with coupling $t_L = t_R = 0.1$ and t_C increasing from 0 to 1.

Similarly, when introducing a complex part to the onsite energy, one effectively introduces dissipation, which can mimic for example the effects due to electron-phonon coupling at non-zero temperatures. The results are very similar to introducing an additional lead and one would obtain a dependence similar to the one shown in fig. 14.

Dephasing due to the coupling to a two level system (TLS)

Quantum mechanical dephasing is in general present when our system under consideration is coupled to an environment. This environment can be a lead, coupling to phonons, coupling to spins or to some other defect or system, which has some internal degrees of freedom. The simplest example is a two level system, which is equivalent to a spin 1/2.

Here we will look at how to describe the coupling of a TLS to a quantum dot. Because of this additional degree of freedom we have to use the tensor product of the two systems in order to describe the larger Hilbert space. The Hamiltonian of a TLS is given by

$$H_{TLS} = \begin{pmatrix} E_u & t \\ t & E_d \end{pmatrix} \quad (132)$$

and the quantum dot Hamiltonian with two lead sites is

$$H_{QD} = \begin{pmatrix} 0 & t_L & 0 \\ t_L & \epsilon_D & t_R \\ 0 & t_R & 0 \end{pmatrix}. \quad (133)$$

The total Hamiltonian quantum dot plus TLS can then be written as

$$H = H_{QD} \otimes I_2 + I_3 \otimes H_{TLS} + H_U \quad (134)$$

where I_n is the $n \times n$ identity matrix and H_U the interaction between the TLS and the quantum dot, which could be of the form

$$H_U = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} U & t_I \\ t_I^* & 0 \end{pmatrix}, \quad (135)$$

which corresponds to the case where there is an additional energy U when the TLS is in the E_u state and the electron in the quantum dot. There is also a modified coupling $t \rightarrow t + t_I$ in the TLS if the electron is in the quantum dot. With this system it is then possible to obtain the Green's function of the total system with total energy E , which is given by

$$G = (E - H - \Sigma_L - \Sigma_R)^{-1}, \quad (136)$$

where

$$\Sigma_L = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} G_{1,1}^S & G_{1,2}^S \\ G_{2,1}^S & G_{2,2}^S \end{pmatrix} \quad (137)$$

and

$$\Sigma_R = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} G_{1,1}^S & G_{1,2}^S \\ G_{2,1}^S & G_{2,2}^S \end{pmatrix}. \quad (138)$$

G^S are the surface Green's functions of the semi-infinite leads, which by analogy to the two-dimensional leads can be expressed as

$$G_{n,m}^S = \sum_{E_{\perp}} \psi_n^{\perp,*}(E_{\perp}) \psi_m^{\perp}(E_{\perp}) G^{1D}(E - E_{\perp}), \quad (139)$$

where $\psi_m^{\perp}(E_{\perp})$ are the eigenfunctions of the TLS with energy E_{\perp} and G^{1D} the surface green's function of the 1D leads.

It is now possible to obtain the transmission probability of the quantum dot coupled to the TLS, by simply using Fisher-Lee's relation. An example is shown in fig. 15. An important point to remember is that the energy E is the total energy of the quantum dot plus the TLS. Hence, even when the two are not coupled the transmission probability curve has two peaks centered at the eigenvalues of the TLS (for $\epsilon_D = 0$ and the black curve in fig. 15).

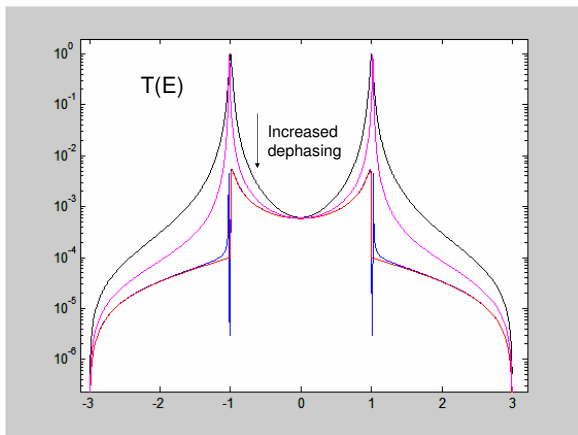


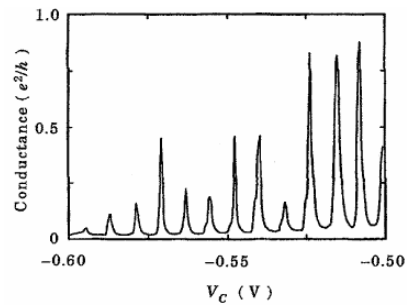
FIG. 15: The resonance transmission of a quantum dot for different values of dephasing obtained by coupling a TLS directly to the dot. The black curve corresponds to zero coupling between the quantum dot and the TLS.

Depending in the type of coupling and details of the TLS the dephasing effect can be non-existent or very strong.

CO-TUNNELING AND KONDO EFFECT IN QUANTUM DOTS

In most quantum dots, Coulomb interactions cannot be neglected and the single particle picture presented above breaks down. The most dramatic effect of Coulomb interactions is the presence of Coulomb blockade, which occurs when the Coulomb potential necessary to add one electron to the dot exceeds the Fermi energy, hence effectively suppressing the conductance. Experimentally this is seen as peaks in the conductance as a function of the

gate voltage applied to the dot. A typical example of these Coulomb blockade peaks is shown in fig. 16.



L. P. Kouwenhoven *et al.*, Z. Phys. B **85**, 367 (1991).

FIG. 16: The experimental conductance as a function of gate voltage in the Coulomb blockade regime.

The basic physics of this can be understood in terms of simple electrostatics, where the Coulomb potential due to an additional electron in the dot acts as a potential barrier, hence suppressing the current flow. This phenomenon is illustrated in fig. 17.

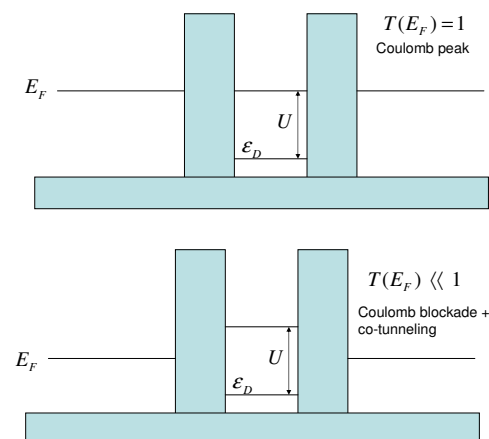


FIG. 17: The basic phenomena of Coulomb blockade, where U is the Coulomb energy and ϵ_D the dot energy.

Hence these basic features (existence of peaks in the conductance as a function of gate voltage) can be understood in terms of this single electron approach where the Coulomb interaction is simply treated as an electrostatic potential. However, there is a lot of additional physics happening when the electron interactions are treated in a quantum mechanical way. Co-tunneling and the Kondo resonance are prime examples, where these strong interactions in quantum systems lead to novel phenomena.

Co-tunneling occurs when the quantum dot is in the

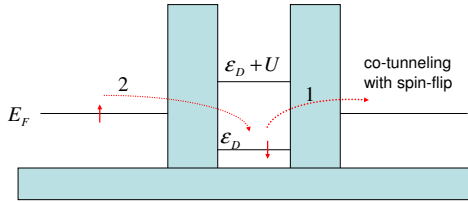


FIG. 18: A possible co-tunneling process, which involves a spin flip. This is a typical second order process

regime of Coulomb blockade, i.e., low transmission. Co-tunneling leads to an enhancement of the tunneling probability. While there exist many possible co-tunneling processes, the main idea is illustrated in fig. 18. Essentially, for an electron to get through the dot, the Coulomb blockade effect is circumvented by having one electron hopping out of the dot before the next one falls in again. This is only possible when these "events" occur simultaneously, i.e., co-tunneling, since otherwise energy conservation is violated. These co-tunneling paths can occur in many different ways and another possibility is illustrated in fig. 19, which is also a precursor for the Kondo effect.

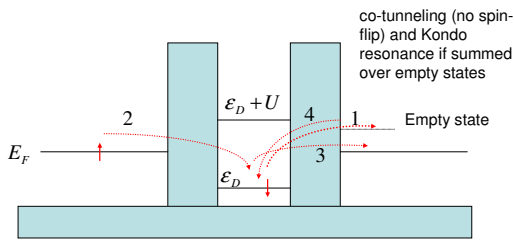


FIG. 19: Another co-tunneling process, which involves no spin-flip. This is a fourth order process, which can lead to the Kondo resonance. The numbers show the order of the virtual processes.

Tunneling matrix formalism

In order to describe quantitatively this co-tunneling process it is necessary to go beyond the single particle picture and it is important to include interactions directly. A powerful way to evaluate these processes is based on a generalization of Fermi's Golden rule. The starting point is to consider a quantum dot such as the one depicted in fig. 13 and to separate the couplings t_L and t_R . Hence, in quite general terms the total Hamiltonian can be written as

$$H = \underbrace{H_D + H_L + H_R}_{H_0} + \underbrace{H_{LD} + H_{DR}}_V, \quad (140)$$

where the coupling terms are treated as a perturbation. The idea is then to look at processes from some initial state: $|i\rangle$, which is an eigenstate of H_0 (f.ex. N electrons in the dot and one electron in the left lead) to a final state $|f\rangle$ also an eigenstate of H_0 (f. ex. N electron in the dot and one electron in the right lead). Then the generalization of Fermi's golden rule allows us to obtain the rate Γ_{fi} for going from state $|i\rangle$ to $|f\rangle$, which can then be related to the conductance through the quantum dot for that process. The generalized Fermi's golden rule is given by (see textbook)

$$\Gamma_{fi} = 2\pi |\langle f|T|i\rangle|^2 \delta(\epsilon_f - \epsilon_i), \quad (141)$$

where

$$T = V + VG_0V + VG_0VG_0V + \dots = V + VG_0T \quad (142)$$

and $G_0 = (E - H_0)^{-1}$ is the Green's function of H_0 . T is simply referred to the T -matrix and can be written as $T = \frac{V}{1 - G_0V}$. In principle the contribution of any possible process can now be evaluated in this formalism and it's usually done in a perturbative way using eq. (142). As an example we will evaluate the process depicted in fig. 18, which is a second order process since it involves the coupling elements twice. We can write the final state as

$$|f\rangle = c_{\epsilon_D}^{+\dagger} c_{\epsilon_L}^{\dagger} c_{\epsilon_R}^{+\dagger} c_{\epsilon_D}^{\dagger} |i\rangle \quad (143)$$

which represents the process of transferring one electron from the left lead to the right lead, effectively representing a tunneling process. We can now use the golden rule to second order, i.e.,

$$\Gamma_{fi} = 2\pi \sum_{\epsilon_R, \epsilon_L, i} |t_R|^2 |t_L|^2 \delta(\epsilon_R - \epsilon_L) \left| \langle f | c_{\epsilon_R}^{+\dagger} c_{\epsilon_D}^{\dagger} \frac{1}{\epsilon_L - 2\epsilon_D - U} c_{\epsilon_D}^{+\dagger} c_{\epsilon_L}^{\dagger} | i \rangle \right|^2 \quad (144)$$

Using (143) then leads to

$$\begin{aligned} \Gamma_{fi} &= 2\pi \sum_{\epsilon_R, \epsilon_L} |t_R|^2 |t_L|^2 \delta(\epsilon_R - \epsilon_L) \left(\frac{1}{\epsilon_L - 2\epsilon_D - U} \right)^2 \\ &\quad \times \sum_i |\langle i | c_{\epsilon_R}^{\dagger} c_{\epsilon_R}^{+\dagger} | i \rangle \langle i | c_{\epsilon_L}^{+\dagger} c_{\epsilon_L}^{\dagger} | i \rangle|^2 \\ &\sim \int |t_R|^2 |t_L|^2 d\epsilon_L D(\epsilon_L) \left(\frac{1}{\epsilon_L - 2\epsilon_D - U} \right)^2 \\ &\quad \times n_F(\epsilon_L - E_{F_L}) (1 - n_F(\epsilon_R - E_{F_R})), \end{aligned} \quad (145)$$

where $n_F(\epsilon)$ are the Fermi distributions of the leads and $D(\epsilon_L)$ the density of state of the lead. Hence, for a difference in Fermi energy between the left and right lead of eV we obtain

$$\Gamma_{fi} \sim V |t_R|^2 |t_L|^2, \quad (146)$$

which is a typical contribution for a co-tunneling process (linear in V and of order Γ^2).

This previous example was treated within a perturbative approach, where we used the second order T -matrix. Similarly one could look at different processes in that way, which is a very standard approach to co-tunneling in the perturbative regime (t small).

In the following, however, we will use a different approach, which doesn't use a perturbation on the T -matrix, but instead fixes the number of electrons in the system. The approach is similar to the one of the TLS coupled to a quantum dot described earlier. We will apply this formalism to the fourth order process depicted in fig. 19. The idea is to "rewrite" the process in fig. 19 as

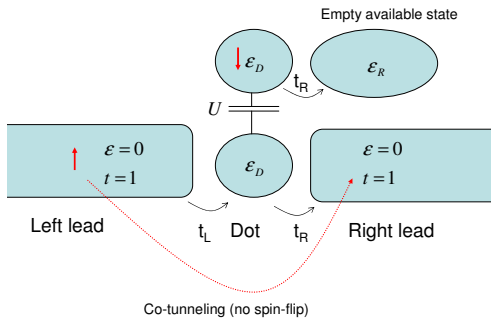


FIG. 20: The 2-particle equivalent of fig. 19, which grasps most of the physics.

This 2-particle version is equivalent to the TLS coupled to a quantum dot from eq. (134), i.e.,

$$H = H_{QD} \otimes I_2 + I_3 \otimes H_{TLS} + H_U, \quad (147)$$

with H_{TLS} given instead by:

$$H_{TLS} = \begin{pmatrix} \epsilon_D & t \\ t & \epsilon_R \end{pmatrix} \quad (148)$$

$$H_U = U \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (149)$$

$$H_{QD} = \begin{pmatrix} 0 & t_L & 0 \\ t_L & \epsilon_D & t_R \\ 0 & t_R & 0 \end{pmatrix} \quad (150)$$

and the Green's function is given by eq. (136). However, instead of using the Green's function we want to connect this formalism to the T -matrix. Hence we can define V as all the off-diagonal components of H , which represent the couplings to the dots: t_L and t_R . A reasonable initial state $|i\rangle$ is the down spin electron in the dot and the up spin electron in the left lead. The final state $|f\rangle$ is then

the down spin electron in the dot and the up spin electron in the right lead. In order to use this formalism we need the Green's function for H_0 which is simply

$$G_0 = (E - H_0 - \Sigma_L - \Sigma_R)^{-1}. \quad (151)$$

The self energies can be found in the same way as for the coupling to the TLS system. The transition rate $\Gamma_{fi} = T(E)$ can then be obtained by using a modified Fisher-Lee expression:

$$T(E) = 4 \cdot Tr[\Gamma_L T \Gamma_R T^+], \quad (152)$$

where

$$\begin{aligned} \Gamma_L &= \Im(L \cdot \Sigma_L \cdot L^+) \\ \Gamma_R &= \Im(R \cdot \Sigma_R \cdot R^+), \end{aligned} \quad (153)$$

and

$$\begin{aligned} L &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \\ R &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \end{aligned} \quad (154)$$

also T is the T -matrix given by:

$$T = \frac{V}{1 - G_0 V} = \frac{1}{V^{-1} - G_0}. \quad (155)$$

$T(E)$ is now the transmission probability corresponding to the co-tunneling of an up electron initially in the left lead, co-tunneling into the right lead in the presence of a down electron in the dot with a repulsion of strength U in the dot. Setting $\epsilon_R = 0$ allows the dot electron to virtually hop onto an empty lead state before returning. With this description we can now quantitatively obtain the transmission probability corresponding to the Coulomb peak as well as the co-tunneling process. The result is shown in fig. 21 for different values of the interaction parameter U .

The Kondo resonance can also be obtained within this frame-work, by summing over all available empty states. These empty states are described by ϵ_R , hence the Kondo resonance for this process contributes as:

$$\sim \sum_{\epsilon_R} T_{\epsilon_R}(E), \quad (156)$$

where $T_{\epsilon_R}(E)$ is obtained from (152) by using ϵ_R as summing parameter in H_{TLS} . Experimentally, the Kondo resonance is characterized by an increase in the conductance at low temperatures as seen in fig. 22.

The temperature dependence of the Kondo resonance arises from the temperature dependence of available states ϵ_R in the leads. Often the Kondo resonance is

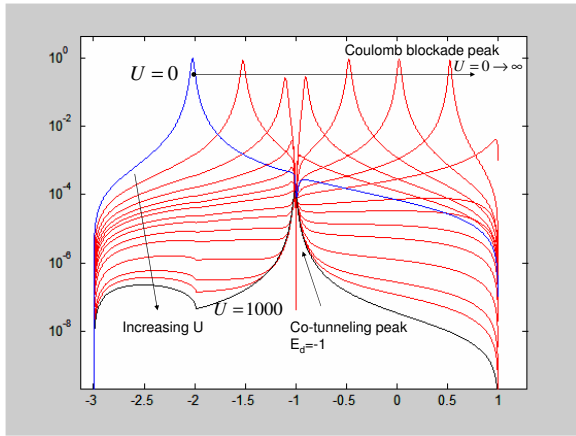


FIG. 21: The 2-particle co-tunneling process as function of the interaction parameter. One can observe the Coulomb blockade peak regime at low U and the emergence of a co-tunneling peak at $E = \epsilon_D + 0$ for large U

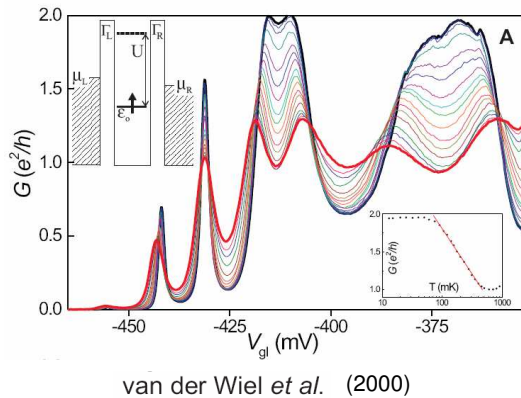


FIG. 22: Experimental Kondo resonance in a quantum dot, identified by the increase in conductance at low temperatures.

dominated by a process which involves a filled state in the leads instead of an empty state. A down electron form a filled state in the lead hops to the dot, the up electron from the dot hops to the right lead, then the up electron from the left lead hops onto the dot and the down electron on the dot hops back into the freed lead state. This process can then be described by a 3-particle T -matrix and the Kondo resonance is obtained by summing over the filled lead states.

SUPERCONDUCTIVITY

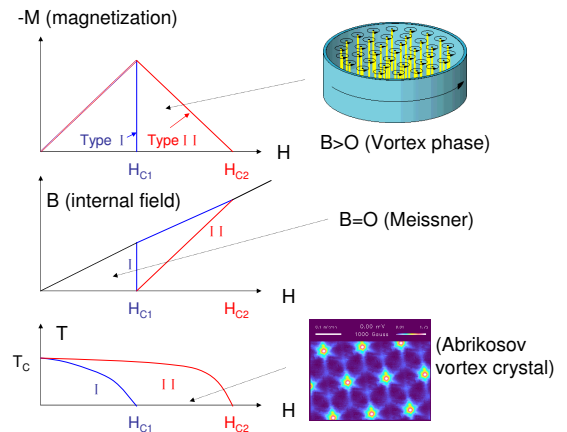


FIG. 23: Magnetic field dependence in a superconductor.

The main aspects of superconductivity are

- Zero resistance (Kammerlingh-Onnes, 1911) at $T < T_c$: The temperature T_c is called the critical temperature.
- Superconductivity can be destroyed by an external magnetic field H_c which is also called the critical field (Kammerlingh-Onnes, 1914). Empirically, $H_c(T) = H_c(0)(1 - (T/T_c)^2)$
- The Meissner-Ochsenfeld effect (1933). The magnetic field does not penetrate the sample, the magnetic induction is zero, $B = 0$. This effect distinguishes two types of superconductors, type I and type II. In Type I, no field penetrates the sample, whereas in type II the field penetrates in the form of vortices.
- Superconductors have a gap in the excitation spectrum.

The main mechanism behind superconductivity is the existence of an effective attractive force between electrons, which favors the pairing of two electrons of opposite momentum and spin. In conventional superconductors this effective attractive force is due to the interaction with phonons. This pair of electrons has now effectively zero total momentum and zero spin. In this sense this pair behaves like a boson and will Bose-Einstein condensate in a coherent quantum state with the lowest possible energy. This ground state is separated by a superconducting gap. Electrons have to jump over this gap in order to be excited. Hence when the thermal energy exceeds the gap energy the superconductor becomes normal.

The origin of the effective attraction between electrons can be understood in the following way:

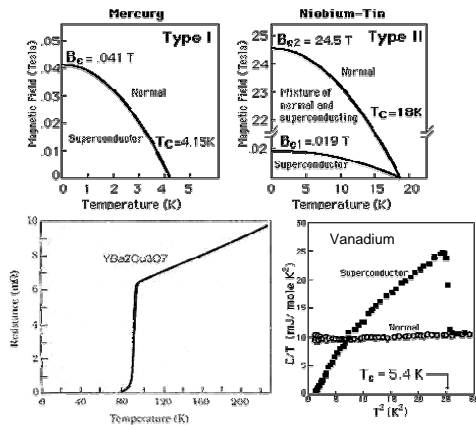


FIG. 24: The critical magnetic field, resistance and specific heat as a function of temperature.

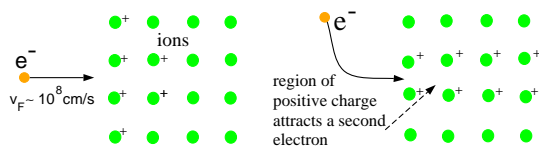


FIG. 25: Origin of the retarded attractive potential. Electrons at the Fermi surface travel with a high velocity v_F . As they pass through the lattice (left), the positive ions respond slowly. By the time they have reached their maximum excursion, the first electron is far away, leaving behind a region of positive charge which attracts a second electron.

When an electron flies through the lattice, the lattice deforms slowly with respect to the time scale of the electron. It reaches its maximum deformation at a time $\tau \simeq \frac{2\pi}{\omega_D} \simeq 10^{-13}$ s after the electron has passed. In this time the first electron has travelled $\simeq v_F \tau \simeq 10^8 \frac{\text{cm}}{\text{s}} \cdot 10^{-13}\text{s} \simeq 1000\text{\AA}$. The positive charge of the lattice deformation can then attract another electron without feeling the Coulomb repulsion of the first electron. Due to retardation, the electron-electron Coulomb repulsion may be neglected!

The net effect of the phonons is then to create an attractive interaction which tends to pair time-reversed quasiparticle states. They form an antisymmetric spin singlet so that the spatial part of the wave function can be symmetric and nodeless and so take advantage of the attractive interaction. Furthermore they tend to pair in a zero center of mass (cm) state so that the two electrons can chase each other around the lattice.

Using perturbation theory it is in fact possible to show that to second order (electron-phonon-electron) the effect of the phonons effectively leads to a potential of the form

$$V_{e-ph} \sim \frac{(\hbar\omega_q)^2}{(\epsilon(k) - \epsilon(k-q))^2 - (\hbar\omega(q))^2} \quad (157)$$

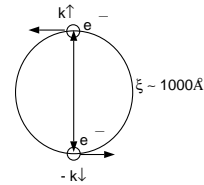


FIG. 26: To take full advantage of the attractive potential illustrated in Fig. 25, the spatial part of the electronic pair wave function is symmetric and hence nodeless. To obey the Pauli principle, the spin part must then be antisymmetric or a singlet.

This term can be negative, hence effectively produce an attraction between two electrons exceeding the Coulomb repulsion. This effect is the strongest for $k = k_F$ and $q = 2k_F$ since $\epsilon(k_F) = \epsilon(-k_F)$ and $\omega(2k_F) \simeq \omega_D$ (the Debye frequency). Hence electrons will want to form opposite momentum pairs $(k_F, -k_F)$. This will be our starting point for the microscopic theory of superconductivity à la BCS (Bardeen, Cooper and Schrieffer).

BCS theory

To describe our pair of electrons (the Cooper pair) we will use the formalism of second quantization, which is a convenient way to describe a system of more than one particle.

$$H_{1particle} = \frac{p^2}{2m} \Rightarrow H_{1p}\psi(x) = E\psi(x) \quad (158)$$

Let's define

$$c_1^\dagger(x) \underbrace{|0\rangle}_{\text{vacuum}} = \psi(x) \text{ and } \langle 0|c_1(x) = \psi^*(x) \quad (159)$$

With these definitions, $|0\rangle$ is the vacuum (or ground state), i.e., state without electrons. $c_1^\dagger(x)|0\rangle$ corresponds to one electron in state $\psi(x)$ which we call 1. c^\dagger is also called the creation operator, since it creates one electron from vacuum. c is then the annihilation operator, i.e., $c_1 c_1^\dagger |0\rangle = |0\rangle$, which corresponds to creating one electron from vacuum then annihilating it again. Other properties include

$$c_1|0\rangle = 0 \text{ and } c_1^\dagger c_1^\dagger |0\rangle = 0 \quad (160)$$

The first relation means that we cannot annihilate an electron from vacuum and the second relation is a consequence of the Pauli principle. We cannot have two electrons in the same state 1.

Hence,

$$\begin{aligned} c_1^\dagger c_1^\dagger = 0 &\Rightarrow (c_1^\dagger c_1^\dagger)^\dagger = 0 \Rightarrow c_1 c_1 = 0 \\ &\Rightarrow (c_1^\dagger c_1) c_1^\dagger |0\rangle = c_1^\dagger |0\rangle \end{aligned} \quad (161)$$

This shows that $c_1^\dagger c_1$ acts like a number operator. It counts the number of electrons in state 1. (Either 1 or 0).

We can now extend this algebra for two electrons in different states $c_1^\dagger|0\rangle$ corresponds to particle 1 in state 1 and $c_2^\dagger|0\rangle$ to particle 2 in state 2. The rule here is that $c_i^\dagger c_j + c_j c_i^\dagger = \delta_{i,j}$.

Finally we can write down the two particle hamiltonian as

$$H_{2p} = t_1 c_1^\dagger c_1 + t_2 c_2^\dagger c_2 - g c_1^\dagger c_1 c_2^\dagger c_2 \quad (162)$$

where t_i is the kinetic energy of particle i and g is the attraction between particle 1 and 2. We will also suppose that $t_1 = t_2$ for the Cooper pair. The job now is to find the ground state of this Hamiltonian. Without interactions ($g = 0$) we would simply have $E = t_1 + t_2$. The interaction term is what complicates the system since it leads to a quadratic term in the Hamiltonian. The idea is to simplify it by getting rid of the quadratic term. This is done in the following way. From eq. (162) we have

$$\begin{aligned} H &= t(c_1^\dagger c_1 + c_2^\dagger c_2) - g c_1^\dagger c_1 c_2^\dagger c_2 \\ &= t(c_1^\dagger c_1 + c_2^\dagger c_2) + g c_1^\dagger c_2^\dagger c_1 c_2 \\ &= t(c_1^\dagger c_1 + c_2^\dagger c_2) - g a (c_1 c_2 - c_1^\dagger c_2^\dagger) + g a^2 \\ &\quad + \underbrace{g(c_1^\dagger c_2^\dagger + a)(c_1 c_2 - a)}_{\simeq 0 \text{ (Mean field approx.)}} \end{aligned} \quad (163)$$

$$\Rightarrow H_{MF} = t(c_1^\dagger c_1 + c_2^\dagger c_2) - g a (c_1 c_2 - c_1^\dagger c_2^\dagger) + g a^2$$

We used the mean field approximation, which replaces $c_1 c_2$ by its expectation value $\langle a | c_1 c_2 | a \rangle = a \Rightarrow \langle a | c_1^\dagger c_2^\dagger | a \rangle = -a$, where $|a\rangle$ is the ground state of the Hamiltonian. The idea now is to diagonalize H_{MF} , i.e. a Hamiltonian in the form $H = \sum_i c_i^\dagger c_i$. The trick here is to use the Bogoliubov transformation:

$$\begin{aligned} &\begin{cases} c_1 = A_1 \cos(\theta) + A_2^\dagger \sin(\theta) \\ c_2^\dagger = -A_1 \sin(\theta) + A_2^\dagger \cos(\theta) \end{cases} \\ \Rightarrow &\begin{cases} A_1 = c_1 \cos(\theta) - c_2^\dagger \sin(\theta) \\ A_2^\dagger = c_1 \sin(\theta) + c_2^\dagger \cos(\theta) \end{cases} \end{aligned} \quad (164)$$

It is quite straightforward to see that $A_i^\dagger A_j + A_j A_i^\dagger = \delta_{ij}$, $A_i A_j + A_j A_i = 0$, and $A_i^\dagger A_j^\dagger + A_j^\dagger A_i^\dagger = 0$ using the properties of c_i . We can now rewrite H_{MF} in terms of our new operators A_i :

$$\begin{aligned} H_{MF} &= t(c_1^\dagger c_1 + c_2^\dagger c_2) - g a (c_1 c_2 - c_1^\dagger c_2^\dagger) + g a^2 \\ &= t(A_1^\dagger \cos(\theta) + A_2 \sin(\theta))(\cos(\theta) A_1 + \sin(\theta) A_2^\dagger) + \dots \\ &= (A_1^\dagger A_1 + A_2^\dagger A_2)(t \cos(2\theta) - g a \sin(2\theta)) \\ &\quad + t(1 - \cos(2\theta)) + g a \sin(2\theta) + g a^2 \\ &\quad + (A_1^\dagger A_2^\dagger - A_1 A_2) \underbrace{(t \sin(2\theta) + g a \cos(2\theta))}_{=0 \text{ to diagonalize } H_{MF}} \end{aligned}$$

Hence the diagonalization condition for H_{MF} fixes the angle θ of our Bogoliubov transformation:

$$\tan(2\theta) = -\frac{g a}{t} \Rightarrow \sin(2\theta) = \frac{-g a}{\sqrt{t^2 + (g a)^2}} \quad (166)$$

Hence H_{MF} now becomes

$$H_{MF} = (A_1^\dagger A_1 + A_2^\dagger A_2) \sqrt{t^2 + (g a)^2} + (t - \sqrt{t^2 + (g a)^2}) + g a^2 \quad (167)$$

It is now immediate to obtain the solutions of the Hamiltonian, since we have the ground state $|a\rangle$ and we have a diagonal Hamiltonian in terms of A_i hence the Ground state energy E_0 is simply given by $H_{MF}|a\rangle = E_0|a\rangle$ and $A_i|a\rangle = 0$. The first degenerate excited states are $A_i^\dagger|a\rangle$ with energy E_1 , where $H_{MF}A_i^\dagger|a\rangle = E_1A_i^\dagger|a\rangle$ and the next energy level and state is $A_1^\dagger A_2^\dagger|a\rangle$, with energy E_2 given by $H_{MF}A_1^\dagger A_2^\dagger|a\rangle = E_2A_1^\dagger A_2^\dagger|a\rangle$, hence

$$\begin{aligned} E_2 &= t + \sqrt{t^2 + (g a)^2} + g a^2 \\ E_1 &= t + g a^2 \\ E_0 &= t - \sqrt{t^2 + (g a)^2} + g a^2 \end{aligned} \quad (168)$$

If we take $t \rightarrow 0$ (this corresponds to considering zero temperature and the Fermi energy as the reference energy) and define $\Delta = g a$ we have

$$\begin{cases} E_2 = \Delta + g a^2 \\ E_1 = g a^2 \\ E_0 = -\Delta + g a^2 \end{cases} \quad (169)$$

We can now turn to what a is since,

$$\begin{aligned} a &= \langle a | c_1 c_2 | a \rangle \\ &= -\cos(\theta) \sin(\theta) \langle a | A_1 A_2^\dagger | a \rangle \\ &= -\cos(\theta) \sin(\theta) \underbrace{\langle a | a \rangle}_{=1} \\ \Rightarrow a &= -\sin(2\theta)/2 \end{aligned} \quad (170)$$

Combining (166) and (170) we obtain

$$2a = \frac{g a}{\sqrt{t^2 + (g a)^2}} \quad (171)$$

which is the famous BCS gap (Δ) equation. Indeed, it has two solutions,

$$\begin{aligned} a = 0 &\Rightarrow \langle a | c_1 c_2 | a \rangle = 0 \Rightarrow \text{Normal} \\ a \neq 0 &\Rightarrow \underbrace{t^2 + (g a)^2 = g^2/4}_{\Delta = g a = \sqrt{g^2/4 - t^2}} \Rightarrow \text{Superconducto} \end{aligned} \quad (172)$$

(165) This gives us the condition for superconductivity $g \geq 2t$. Hence the attraction between our two electrons has to be strong enough in order to form the superconducting

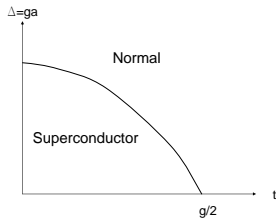


FIG. 27: The gap of a BCS superconductor as function of the kinetic energy.

gap Δ . For $t = 0$ (zero temperature and states at the Fermi energy, $E_F = 0$) and using (169) this leads to a ground state energy of $-\Delta/2$ and to the first excited state of $\Delta/2$. Hence the states at the Fermi energy have disappeared in order to form a lower energy ground state in the presence of an attractive interaction. Typically, t is proportional to the temperature, hence there is a superconducting transition as a function of temperature.

We now want to find the expression for our superconducting wavefunction $|a\rangle$. The most general possible form is

$$|a\rangle = \alpha|0\rangle + \beta_1 c_1^+|0\rangle + \beta_2 c_2^+|0\rangle + \gamma c_1^+ c_2^+|0\rangle \quad (173)$$

In addition the condition $A_i|a\rangle = 0$ has to be verified, which leads after some algebra to

$$|a\rangle = \alpha(1 + \tan(\theta)c_1^+ c_2^+)|0\rangle \quad (174)$$

This state clearly describes an electron pair, the Cooper pair and represents the superconducting ground state of the Hamiltonian. In our derivation we only considered two electrons, but this framework can be generalized to N electrons, where the generalized BCS Hamiltonian can be written as

$$H_{BCS} = \sum_{k,\sigma} t_k c_{k,\sigma}^+ \underbrace{c_{k,\sigma}}_{spin} - \sum_q g_q c_{k+q,\uparrow}^+ c_{-k-q,\downarrow}^+ c_{k,\uparrow} c_{-k,\downarrow} \quad (175)$$

Here V_q is positive and represents the effective phonon induced attraction between electrons at the Fermi level. It's maximum for $q = 0$. The second term describes the process of one electron with momentum k and another electron with momentum $-k$ which are annihilated in order to create one electron with momentum $k + q$ and another one with momentum $-k - q$, hence momentum is conserved in this scattering process and a phonon with momentum q is exchanged.

In mean field theory this BCS Hamiltonian become

$$H_{MF} = \sum_{k,\sigma} t_k c_{k,\sigma}^+ c_{k,\sigma} - \sum_k (\Delta_k c_{k,\uparrow}^+ c_{-k,\downarrow}^+ + h.c.), \quad (176)$$

with $\Delta_k = \sum_{k'} g_{kk'} \langle c_{-k',\downarrow} c_{k',\uparrow} \rangle$. Using the generalized Bogoliubov transformation

$$\begin{cases} A_{k,\uparrow} = \alpha c_{k,\uparrow} + \beta c_{-k,\downarrow}^+ \\ A_{-k,\downarrow} = -\beta^* c_{k,\uparrow} + \alpha c_{-k,\downarrow}^+ \end{cases} \quad (177)$$

leads to the following mean field hamiltonian:

$$H_{MF} = \sum_{k,\sigma} \underbrace{E_k}_{\sqrt{t_k^2 + |\Delta_k|^2}} (A_{k,\uparrow}^+ A_{k,\uparrow} + A_{k,\downarrow}^+ A_{k,\downarrow}) + K_0, \quad (178)$$

where Δ_k is the gap. Using $A_k|a\rangle = 0$, the BCS ground state can be written as

$$|a\rangle = \prod_k (u_k + v_k c_{k,\uparrow}^+ c_{-k,\downarrow} |0\rangle), \quad (179)$$

which leads to the famous BCS result

$$2\Delta(T=0) = 3.53 k_B T_c \quad (180)$$

and $|\Delta(0)| = 2\omega_D e^{-1/gd(E_F)}$, where ω_D is the phonon Debye frequency and $d(E_F)$ the density of states at the Fermi energy.

How can we relate BCS theory to the observed Meissner effect? Including the vector potential \vec{A} from the magnetic field $B = \nabla \times A$ into the Hamiltonian we have $p \rightarrow p - \frac{e}{c}A$. In second quantization the kinetic part of the Hamiltonian is then rewritten as

$$T = \frac{1}{2m} \int \Psi^+(r) (-i\hbar \nabla_r - \frac{e}{c}A)^2 \psi(r) dr \quad (181)$$

in the presence of a magnetic field. Free electrons are gauge invariant, which can be expressed by

$$\begin{cases} A \rightarrow A + \nabla\phi \\ \Psi(r) \rightarrow e^{-ie\phi} \Psi(r) \end{cases}, \quad (182)$$

which corresponds to $c_i \rightarrow c_i e^{-ie\phi}$ in our two particle example. Hence $\langle a|c_1 c_2|a\rangle \rightarrow e^{-2ie\phi} \langle a|c_1 c_2|a\rangle$ which is clearly not gauge invariant in the superconducting state since $\langle a|c_1 c_2|a\rangle = a \neq 0$. This clearly shows that the superconducting state breaks the gauge symmetry.

It is further possible to show that all solutions which break gauge invariance are solution of $p - \frac{e}{c}A = 0$. But the current density is given by $j = nev$, which leads to

$$\vec{j} = \frac{ne^2}{mc} \vec{A}. \quad (183)$$

The magnetic induction is $\vec{B} = \vec{\nabla} \times \vec{A}$ as usual. This is in fact London's equation for superconductivity. We can now take the rotational on both sides of (183), hence

$$\begin{aligned} \vec{\nabla} \times \underbrace{\vec{j}}_{\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}} &= \frac{ne^2}{mc} \vec{\nabla} \times \vec{A} \\ \Rightarrow \vec{\nabla} \times \vec{\nabla} \times \vec{B} &= -\frac{4\pi ne^2}{mc^2} \vec{B} \\ \Rightarrow B_x &\sim e^{-x/\lambda_L} \end{aligned} \quad (184)$$

with $\lambda_L = \sqrt{\frac{mc^2}{4\pi ne^2}}$ which is the London penetration length.

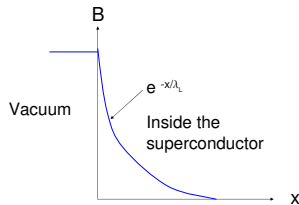


FIG. 28: The decay of the magnetic field inside the superconductor. The decay is characterized by the London penetration length λ_L .

If we had a perfect conductor, this would imply that the current would simply keep on increasing with an external field \vec{E} , hence

$$\begin{aligned} \frac{\partial \vec{j}}{\partial t} &= \frac{ne^2}{mc} \vec{E} \\ \Rightarrow \frac{\partial}{\partial t} \vec{\nabla} \times \vec{j} &= \frac{ne^2}{mc} \vec{\nabla} \times \vec{E} \\ \Rightarrow \frac{\partial}{\partial t} \vec{\nabla} \times \vec{\nabla} \times \vec{B} &= \frac{\partial}{\partial t} \frac{4\pi ne^2}{mc^2} \vec{B} \end{aligned} \quad (185)$$

This equation is automatically verified from (184). Hence, (184) implies both the Meissner effect and zero

resistance, which are the main ingredients of superconductivity. (Reminder: Maxwell gives $\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}$ and $\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$).

A remarkable aspect of superconductivity is that one of the most fundamental symmetries is broken. Indeed, Gauge invariance is broken because $\vec{j} \sim \vec{A}$. What happens is that below T_c we have a symmetry breaking, which leads to new particles, the Cooper pairs. Mathematically, we have

$$\underbrace{U(2)}_{\text{Normal state}} = \underbrace{SU(2)}_{\text{SC state}} \otimes \underbrace{U(1)}_{\text{Gauge invariance}}, \quad (186)$$

where $U(1) \Leftrightarrow c \rightarrow ce^{i\alpha}$ (Gauge invariance), $U(2) \Leftrightarrow c \rightarrow Ac$ ($A = e^{i\phi/2}a$) and $a^\dagger a = 1$, $SU(2) \Leftrightarrow \phi = 0$.

Another important theory in superconductivity is the Ginzburg-Landau (GL) theory. It stems from the general theory of phase transitions of which superconductivity is an important example. It is possible to connect BCS theory to the GL theory by realizing that the gap $\Delta \sim \Psi$ and the density of superconducting Cooper pairs (order parameter) $n_s \sim |\Psi|^2$ in the GL equation:

$$[\alpha + \beta|\Psi|^2 + \frac{1}{2m}(-i\hbar\nabla + \frac{2e}{c}A)^2]\Psi = 0 \quad (187)$$

Depending on the values of α and β we have either a type I or a type II superconductor.