We know that each eigenstate evolves in time like $\phi_n(x) e^{i\epsilon_n t/\hbar}$, and therefore the given state evolves as

$$\psi(x, t) = \sum_{n=1}^{\infty} a_n \phi_n(x) \exp\left(-\frac{i\epsilon_n t}{\hbar}\right).$$  \hspace{1cm} (1.81)

This is how we followed the evolution of the wave packet in Section 1.5.3.

### 1.7 Counting States

A complete description of a system requires the energies and wave functions of its states. Clearly this is an impossible task for anything but the simplest systems and most of the information would in any case be unwanted. For many applications the density of states $N(E)$ is adequate. The definition is that $N(E) \delta E$ is the number of states of the system whose energies lie in the range $E$ to $E + \delta E$. Clearly this tells us nothing about the wave functions at all, just the distribution of energies. We shall first calculate the density of states of a one-dimensional system before looking at more general results.

#### 1.7.1 ONE DIMENSION

An immediate problem, as we saw in the previous section, is that the wave function $\exp(ikx)$ cannot be normalized in the usual way if the particles travel through all space. The simplest way around this problem is to put the particles in a finite box of length $L$, and set $L \rightarrow \infty$ at the end of the calculation. Having put the particle in a box, we need to choose boundary conditions. Two are commonly used.

(i) **Fixed** or **box** boundary conditions, in which the wave function vanishes at the boundary:

$$\psi(0) = \psi(L) = 0.$$  \hspace{1cm} (1.82)

(ii) **Periodic** or **Born–von Karman** boundary conditions, in which we imagine repeating the system periodically with the same wave function in each system. The wave function at $x = L$ must match smoothly to that at $x = 0$ which requires

$$\psi(0) = \psi(L), \quad \frac{\partial \psi}{\partial x}\Big|_{x=0} = \frac{\partial \psi}{\partial x}\Big|_{x=L}. \hspace{1cm} (1.83)$$

Fixed boundary conditions are obviously the same as the particle in a box studied earlier. The energy levels are given by $\epsilon_0(k) = \hbar^2 k^2/2m$ and the allowed values of $k$ are

$$k_m = \frac{\pi m}{L}, \quad m = 1, 2, 3, \ldots.$$  \hspace{1cm} (1.84)
The wave functions are standing waves with this choice. They carry no current, and the allowed values of \( k \) are all positive.

Periodic boundary conditions require a different choice of \( k \). We can use travelling exponential waves rather than sine waves, and they must obey \( \exp(i k L) = \exp(i k 0) = 1 = \exp(2\pi n i) \). This also satisfies the condition on the gradient, and the normalized states are \( \phi_n(x) = L^{-1/2} \exp(i k_n x) \). The allowed values of \( k \) are

\[
k_n = \frac{2\pi n}{L}, \quad n = 0, \pm 1, \pm 2, \ldots \tag{1.85}
\]

These are twice as far apart as with fixed boundary conditions, but both signs of \( k \) are permitted and there are two degenerate states at each energy level (except for \( k = 0 \)), with opposite signs of \( k \) and velocity.

This raises the following crucial question: does the density of states, which we are trying to calculate, depend on which boundary conditions we choose to apply to our artificial box? Fortunately it can be shown that the result is insensitive to boundary conditions as \( L \to \infty \). It is usually more appropriate to treat free electrons as travelling rather than standing waves, so periodic boundary conditions are generally used.

To turn these allowed values of \( k \) into a density of states, plot the allowed values of \( k \) along a line as in Figure 1.6. This is a simple one-dimensional version of ‘\( k \)-space’. The values are regularly spaced, separated by \( 2\pi / L \). They become closer together as \( L \) increases and tend to blur into a continuum. In this case the number of allowed \( k \)-values in the range \( \delta k \) is just \( \delta k \) divided by the spacing of the points.

These points account for the different states that arise from motion in the box, but we must also consider the internal motion of the particle. Classically, free motion can be separated into translation and rotation about the centre of mass, and it is found that electrons carry an angular momentum that is known as spin. The treatment of angular momentum within quantum mechanics shows that the spin can take two states, which are conventionally labelled as up and down. Each spatial wave function can be associated with either spin, so the total number of states available to the electron should be doubled to take account of spin.

Spin enters only as a factor of 2 in the density of states for most of the topics considered in this book, but there are two areas where care must be taken. The first is the behaviour of electrons in a magnetic field \( \mathbf{B} \), because there is a magnetic moment associated with the spin which contributes an energy \( -\mu \cdot \mathbf{B} \). This will be discussed in Section 6.4.3. Second, the separation of velocity and spin holds only

![Figure 1.6](https://example.com/figure1.6)  
**Figure 1.6.** Allowed values of \( k \) for periodic boundary conditions in a system of length \( L \) plotted along a line, as a simple form of \( k \)-space.
within non-relativistic quantum mechanics. The conditions under which special relativity is important might seem far removed from ordinary semiconductors, but electrons move at a significant fraction of the speed of light when they pass close to a nucleus. This leads to an effect called spin–orbit coupling, which has a profound effect on the top of the valence band and therefore on the behaviour of holes. This will be described in Section 2.6.3.

Returning to the problem at hand, we can define a density of states in \( k \)-space such that \( N_{1D}(k) \delta k \) is the number of allowed states in the range \( k \) to \( k + \delta k \). It is given by

\[
N_{1D}(k) \delta k = \frac{L}{2\pi} \delta k.
\]  

(1.86)

The factor of 2 accounts for the spin, \( L/2\pi \) is the density of points, and the range \( \delta k \) cancels to leave \( N_{1D}(k) = L/\pi \). This is proportional to the volume (length) of the system, which makes sense: we would expect to double the number of states if we doubled the size of the system. Usually one takes this factor out to leave a density of states per unit length, which is \( n_{1D}(k) = N_{1D}(k)/L = 1/\pi \).

The next task is to turn this into a density of states in energy. Figure 1.7 shows how the allowed values of \( k \), which are evenly spaced, map to allowed values in energy through the dispersion relation \( E = \epsilon(k) \). These energies lie in a continuous band for \( E \geq 0 \) in a large system. The figure shows a parabola but the theory works for a more general dispersion relation. The resulting values of energy get further apart as \( k \) rises, so the density of states falls with increasing energy. A range \( \delta k \) in wave number corresponds to a range in energy of \( \delta E = (dE/dk)\delta k \). The number of states in this range can be written in terms of \( n_{1D}(k) \) or in terms of the density of states in energy per unit volume \( n_{1D}(E) \). The two expressions must give the same number of states, so

\[
n_{1D}(E) \delta E = n_{1D}(E) \frac{dE}{dk} \delta k = 2n_{1D}(k) \delta k.
\]  

(1.87)

**FIGURE 1.7.** Dispersion relation \( \epsilon_0(k) \) for free electrons, showing how the allowed values of \( k \) map onto \( E \).
The factor of 2 in front of $n_{1D}(k)$ arises because of the two directions of motion; there is one range $\delta k$ for $k > 0$ and another for $k < 0$. Note that the same symbol $n_{1D}$ is used to represent the density of states in $k$ and $E$; this is bad mathematics but typical usage in physics, where one rapidly tends to run out of variants of $n$ and $E$ to denote commonly used quantities. It shouldn’t lead to confusion provided that the argument $k$ or $E$ is always included. Thus $n_{1D}(E) = (2/\pi)/(d\omega/dk)$. This can be simplified using the group velocity $v = d\omega/dk = (1/\hbar)(dE/dk)$, giving

$$n_{1D}(E) = \frac{2}{\pi \hbar v(E)}.$$  \hspace{1cm} (1.88)

We shall see in Section 5.7.1 that the current depends on the product of the velocity and the density of states. Equation (1.88) shows that this is a constant in one dimension, which in turn leads to a quantized conductance.

Substituting the velocity for the special case of free electrons gives

$$n_{1D}(E) = \frac{1}{\pi \hbar} \sqrt{\frac{2m}{E}}.$$  \hspace{1cm} (1.89)

The density of states diverges as $E^{-1/2}$ as $E \to 0$, a characteristic feature of one dimension.

### 1.7.2 THREE DIMENSIONS

In three dimensions, put the electrons into a box of volume $\Omega = L_x \times L_y \times L_z$. The wave functions are travelling waves in each direction with periodic boundary conditions, just as in the one-dimensional case, and their product gives

$$\phi_{lmn}(\mathbf{R}) = \frac{1}{\sqrt{L_x L_y L_z}} \exp[i(k_x x + k_y y + k_z z)] = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{K} \cdot \mathbf{R}].$$  \hspace{1cm} (1.90)

Remember our convention that upper-case letters are used for three-dimensional positions and wave vectors. The product of three waves has been written as a three-dimensional plane wave using the scalar product. Similarly, the allowed values of $K$ in each of the three directions can be combined into three-dimensional wave vectors

$$\mathbf{K} = \left(\frac{2\pi l}{L_x}, \frac{2\pi m}{L_y}, \frac{2\pi n}{L_z}\right), \hspace{1cm} l, m, n = 0, \pm 1, \pm 2, \ldots$$  \hspace{1cm} (1.91)

These can be plotted as points in a three-dimensional $\mathbf{K}$-space with $(k_x, k_y, k_z)$ as axes, where they form an evenly spaced rectangular mesh. Each unit cell encloses volume $(2\pi/L_x)(2\pi/L_y)(2\pi/L_z) = (2\pi)^3/\Omega$. Thus the density of allowed states is $N_{3D}(\mathbf{K}) = 2\Omega/(2\pi)^3$, where the 2 accounts for spin. Dividing by the volume gives the density of states in $\mathbf{K}$-space per unit volume of the system in real space, $n_{3D}(\mathbf{K}) = 2/(2\pi)^3$. This is again a constant, and generalizes in an obvious way to $d$ dimensions as $n_d(\mathbf{K}) = 2/(2\pi)^d$. 
Now we need to derive the density of states as a function of energy. Consider free electrons only, because the calculation is more complicated for a general function $\varepsilon(\mathbf{K})$. Figure 1.8 shows two spheres about the origin in $\mathbf{K}$-space, one with radius $K$ and the other with radius $K + \delta K$. The volume of the shell between these two spheres is $4\pi K^2 \delta K$. The number of states in the shell is found from the product of this volume and the density of states $n_{3D}(\mathbf{K})$, giving $(K^2/\pi^2)\delta K$. The separation $\delta K$ corresponds to a difference in energy of

$$\delta E = \frac{dE}{dK} \delta K = \frac{\hbar^2 K}{m} \delta K.$$  \hspace{2cm} (1.92)

The number of states in the shell is given in terms of the density of states in energy by $n(E)\delta E$. Equating the two expressions yields $n_{3D}(E)\delta E = n_{3D}(E)(\hbar^2 K/m)\delta K = (K^2/\pi^2)\delta K$, whence

$$n_{3D}(E) = \frac{mK}{\pi^2 \hbar^2} = \frac{m}{\pi^2 \hbar^3} \sqrt{2mE}.$$ \hspace{2cm} (1.93)

The square root is characteristic of three dimensions. Its singularity at the bottom of the band is much weaker than the one-dimensional result of $E^{-1/2}$. In general the density of states shows a stronger feature at the bottom of the band in fewer dimensions. Optical properties such as absorption are strongly influenced by the density of states, and low-dimensional systems are preferred for optoelectronic devices because their density of states is larger at the bottom of the band. The density of states for free electrons in one, two, and three dimensions is plotted in Figure 1.9. In all cases a low mass is associated with a low density of states.

The density of states for a three-dimensional crystal is more complicated because the surfaces of constant energy in $\mathbf{K}$-space are not spheres. Further singularities of $n(E)$ appear inside bands, and provide fruitful material for optical spectroscopy. A simpler case arises if the energy depends on only the magnitude of $\mathbf{K}$ but not
1.7 COUNTING STATES

\[ n_{1D}(E) = \frac{1}{\pi \hbar} \sqrt{\frac{2m}{E}} \]

\[ n_{2D}(E) = \frac{m}{\pi \hbar^2} \]

\[ n_{3D}(E) = \frac{m \sqrt{2mE}}{\pi^2 \hbar^3} \]

FIGURE 1.9. Densities of states for free electrons in one, two, and three dimensions.

its direction. In this case the surfaces of constant energy remain spherical and the derivation of \( n(E) \) proceeds as before except for the form of \( \varepsilon(K) \). For example, the conduction band of GaAs is often modelled by the expression

\[ \varepsilon(K)[1 + \alpha \varepsilon(K)] = \frac{\hbar^2 K^2}{2m_0 m_e}. \]

(1.94)

This takes account of the fact that the band is not parabolic for high energies, with \( \alpha \approx 0.6 \text{eV}^{-1} \).

1.7.3 A GENERAL DEFINITION OF THE DENSITY OF STATES

A general definition of the density of states is often useful. Let the states of a system have energies \( \varepsilon_n \). Then the density of states in energy can be written as

\[ N(E) = \sum_n \delta(E - \varepsilon_n), \]

(1.95)

where \( \delta(E) \) is the Dirac \( \delta \)-function. This is the total density of states, not that per unit volume. We shall now justify this definition and see how it is related to our previous calculations.

First, it is clear that equation (1.95) makes sense only if we integrate over it, because of the \( \delta \)-functions. Consider

\[ \int_{E_1}^{E_2} N(E) \, dE = \int_{E_1}^{E_2} \sum_n \delta(E - \varepsilon_n) \, dE = \sum_n \int_{E_1}^{E_2} \delta(E - \varepsilon_n) \, dE. \]

(1.96)

This is illustrated in Figure 1.10. If the energy of a state \( n \) lies within the range of integration from \( E_1 \) to \( E_2 \), the integral over \( \delta(E - \varepsilon_n) \) gives unity by definition. If the energy \( \varepsilon_n \) lies outside the range of integration, on the other hand, there is no contribution because the weight of the \( \delta \)-function is concentrated entirely at \( E = \varepsilon_n \). Thus the integral gives 1 for all states in the range \( E_1 \leq \varepsilon_n \leq E_2 \) and zero for those...
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Conductance quantization at room temperature in magnetic and nonmagnetic metallic nanowires

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This paper shows that conductance quantization at room temperature is a physical and reliable observation. This is demonstrated by conductance histograms taking all (12 000) consecutive nanowire conductance experiments in Au at room temperature. On the other hand, conductance curves in Ni, a room-temperature ferromagnet, show staircase-quantized behavior, but the histograms do not show quantized peaks, most probably due to the lifting of the spin degeneracy. [S0163-1829(97)50108-1]

Recent experimental results using scanning tunneling microscopy (STM),1,2 mechanically controllable break junctions,3 and quantum table-top experiments using household macroscopic wires4,5 have shown conductance quantization (CQ) in metallic nanowires at room temperature (RT). Previous to these experiments, CQ was predicted theoretically.6,7 in these nanostructures. Metallic nanowires (NW) are obtained by breaking a contact between two metallic electrodes. The contact does not break cleanly but is stretched into many nanofilaments.8 At the last stages, one thread remains, and quantum-mechanical effects take over. This happens in all the experiments mentioned above.1–5 If, simultaneously to the formation, stretching, and breaking of the NW, its conductance is measured, a staircase dependence is found just before it breaks. Conductance histograms showing up to 100–200 such curves have been reported showing CQ peaks. However, some criteria have been always used to select the conductance curves with which the histogram is built. The metallic nanowire formation has been also predicted by molecular-dynamics simulations,8 and recent scanning electron microscopy and chemical analysis experiments have displayed it in real time as a macroscopic metallic contact breaks.9,10

In this work histograms built using all (up to 12 000), consecutive conductance curves are presented for Au, Pt, and Ni nanowires at RT. This is ~100 times more than any previously reported experiments and without histogram selection. The conductance histogram for Au at RT and in air shows clear CQ peaks. The histogram for Ni electrodes does not show CQ peaks, even though the conductance shows a stepped behavior, most probably due to the lifting of the spin degeneracy.

The experiments are performed in a home-built STM at RT in air. Two high-purity polycrystalline macroscopic electrodes with a few tens of mV potential difference between them, are brought in and out of contact. The current flowing through is measured with a current-voltage (I–V) converter working at 107 gain (100-mV/μA, 3-ps settling time). The position of one electrode is fixed, while the other is moved with a piezoelectric actuator driven with a triangular wave. The electrode speed is controlled by varying the amplitude and/or the frequency of this signal. The output of the I–V converter (the current signal) is measured with a LeCroy 9354AM oscilloscope, with a 500-MHz bandwidth and a 5-G sample/sampling rate. The current data acquisition is triggered when the current signal crosses a predetermined value with a predetermined slope; in the case of a breaking contact we are interested in signals with negative slope, i.e., the current decreases as the contact breaks. At least 25 k samples per conductance curve are acquired and used to build the histogram. This histogram is constructed and displayed in real time. The histogram parameters, center width and number of bins, are adjusted to cover the experimental current window. The raw histogram is tightly filtered, in real time too, in order to avoid fictitious peaks due to the difference between the vertical resolution of the current window (8 bits=256 levels) and the number of bins of the histogram, or to the digital electronics.

Typical conductance experiments for Au (a) and Ni (b) nanowires are shown in Fig. 1, where the stepped behavior of the conductance is quite apparent. The curves shown look very similar. However, conductance jumps of about e/2 are observed more often in nickel. These statements are based on the experience of seeing millions of curves for both metals. When reproducible conductance histograms corresponding to these elements are built, Au presents clear peaks [Fig. 2(a)], but Ni does not [Fig. 2(b)]. In all the elements studied with this technique in our group up to date (more than 10) we find steady and reproducible conductance histograms with a few thousand curves. Evidence of this statement is illustrated in Fig. 2(a) where it can be observed that the features of the Au histogram are not modified when the number of samples changes from 3000 to 12 000. In addition, the histograms obtained with our technique, using a few thousand conductance curves, are identical in different locations of the sample. The experimental conditions for both histograms presented in Fig. 2 are identical; the potential difference between electrodes is V=90.4 mV and the electrode separation speed is v=89 000 Å/s.

The gold histogram presented in Fig. 2(a) has been obtained by subtracting 490 Ω from the original data. This is due to backscattering of electrons.10 The value of the resistance quantifies the average disorder in the nanowire under the experimental conditions. Evidence for this statement is twofold: Tight-binding calculations demonstrate that as disorder grows the amplitude of the quantum conductance step decreases.10 This is displayed in Fig. 3, where histograms corresponding to conductance curves [Fig. 2(a) in Ref. 10] for nanowires of different degrees of disorder are shown. The parameter D in the figure is a disorder parameter. Notice
that for zero disorder the conductance follows a perfect $2e^2/h$ step staircase, while for increasing disorder the amplitude of the conductance step decreases.

In conductance terms, this means that the position of the peak for the $n$th channel departs from the value $nG_0 = n^2e^2/h$ following approximately a law $G_n = nG_0(1-\beta n)$ with $\beta$ small. Therefore, the effect of disorder, for low-$n$ values, can be quantified by a constant resistance value. This is basically the behavior experimentally found in gold nanowires as shown by the (490 Ω subtracted) histogram in Fig. 2(a). Additional evidence for a conductance that depends mostly on the disorder in the nanowire comes from the electrode separation speed effect on the histogram. This is shown in Fig. 4, where the position of the first peak of the conductance histogram, without subtracting any resistance, is displayed as a function of the electrode separation speed. Notice that as the electrodes separate more slowly, that is, the nanowire stretches more slowly, the position of the first conductance peak approaches the value $G_0 = 2e^2/h$, corresponding to a perfectly ordered nanowire. The peak position is determined from a Gaussian fit of the data between $0.8G_0$ and $1.2G_0$. The line in Fig. 4 is drawn as a guide to the eye. The experimental findings reported above can be theoretically justified in detail as follows: When considering experiments revealing conductance quantization at RT, it is necessary that the mean free path of the charge carriers, $l$, is larger than the length $L$ and the width $W$ of the construction, filament, or nanowire that carries the current. Then, using a Landauer formalism, the conductance for a given NW, $G(n)$, can be expressed as

$$ G(n) = \frac{e^2}{h} \sum_{i=1}^{N_1} T_{1i}(n) + \sum_{i=1}^{N_2} T_{1i}(n), $$

(1)

where the sums run over occupied states, $T_{1i}(n)$ is the transmittance for the $i$th channel with spin up, and $T_{1i}(n)$ is the transmittance for the $i$th channel for spin down for a given nanowire with a certain atomic configuration $n$. In a metal, the Fermi wavelength $\lambda_F$ is $\sim 0.5$ nm, and the level separation is $\sim 1$ eV, which means that at RT conductance quantization can be observed if $W$ and $L$ are smaller than $l \sim 10$ nm. For diamagnetic nanowires $T_{1i}(n) = T_{1i}(n)$. Then Eq. (1) becomes

$$ G(n) = \frac{2e^2}{h} \sum_{i=1}^{N} T_{1i}(n). $$

(2)

This function has a staircase behavior but the height of the quantum conductance step is $2T_{1i}(n)e^2/h$, not $2e^2/h$. To have a quantum step equal to this last value we should have $T_{1i}(n) = 1$. This happens when there is spin degeneration and the conductance is ballistic, i.e., there is no backscattering due to disorder and surface roughness in the NW. In a diamagnetic metal such as Au, there is spin degeneration in the nanowires formed at RT, as demonstrated by Fig. 2(a). For a
ferromagnetic metal such as Ni the situation on breaking a contact is considerably more complex. There is a spin-dependent density of states at both sides of the nanowire, and the transmittance should depend, besides topological factors, on the spin direction [Eq. (1)]. In addition, the number of occupied states with spin up ($N_1$) does not have to be equal to the number of occupied states with spin down ($N_2$) for any nanowire. Magnetic effects should then play an important role in the NW transport characteristics. In principle, $0 < T_{11}(n) < 1$; in fact, the experiment shown in Fig. 2(b) suggests that $T_{11}(n)$ is a random number between 0 and 1 due to the lack of spin degeneracy and a transmittance that depends very much on the particular topology of the $n$th state in the $n$-NW. This implies that Au histograms show well-defined peaks because $T_1(n) = T(n) = 1$, but for Ni the histogram is flat because there is no spin degeneracy of the electronic states in the nanowire and their transmittance depend strongly on the actual topology of the nanowire, as shown in Fig. 2(b). However, the individual conductance curves present well-defined steps.

It could be argued that the flat histogram measured for Ni is just a consequence of a flat distribution of transmittance values due to a different plastic behavior at the nanoscale when compared with Au. In other words, while in Au there is a peaked distribution of $T(n)$ for the different $n$ nanowires under the experimental conditions obtained, this distribution is broader for Ni, rendering the conductance histogram flat.

We have performed additional conductance experiments with Ag, Pt, Co, Fe, and Cu electrodes, and, while Ag, Pt, and Cu show peaks (better defined for Ag and Cu, softer materials) in their conductance histograms, Co and Fe, RT ferromagnets show a flat histogram. There is certainly some effect due to the nanomechanical behavior of the different metals when brought in and out of contact; however, Pt and Ni are very similar metals from the mechanical point of view, but Ni shows a flat conductance histogram and Pt does not (Fig. 5). Relevant data for the polycrystalline materials used in the conductance experiments is shown in Table I. As shown in Fig. 5, Pt shows a broad peak at $2e^2/h$ and another, almost unnoticeable, at $4e^2/h$. Due to the large half-width of the observed peak, it is not difficult to see that a material with the same mechanical properties as Pt, but with a conductance quantum of half the value for spin degeneracy, will produce a flat histogram.

Finally we would like to mention that it is well known that purely geometrical effects (the shape of the nanowire) can produce a widening of the conductance histogram peaks. This effect cannot account for the large peak dis-

![Fig. 3. Histograms corresponding to conductance curves [Fig. 2(a) in Ref. 10] obtained by tight-binding calculations, showing the conductance of a 30x30 nanowire with different degrees of disorder. The parameter D quantifies the degree of disorder.](image-url)

![Fig. 4. Dependence of the position of the first conductance peak for gold nanowires on the electrode separation speed. The line is drawn as a guide to the eye.](image-url)

![Fig. 5. Conductance histogram for platinum nanowires built with 6000 consecutive curves. The applied potential difference between the electrodes is 90.4 mV. The electrodes separate at 89000 A/s. No resistance has been subtracted from the original data.](image-url)

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<th>Bulk modulus (GPa)</th>
<th>Tensile modulus (GPa)</th>
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placement observed experimentally. A combination of this effect with the lifting of the spin degeneracy and the shift of the conductance due to disorder in the nanowire is, in our opinion, what produces a flat conductance histogram for Ni.

Summarizing, conductance histograms taking all (12,000) consecutive nanowire conductance experiments in Au at room temperature show the quantized nature of the transport through nanowires at room temperature. The measured histograms are totally reproducible. Departures from a perfect $2e^2/h$ quantization can be explained in terms of the effect of disorder. On the other hand, conductance curves in Ni, a RT ferromagnet, show staircase quantized behavior, but the histograms do not show quantized peaks most probably due to the lifting of the spin degeneracy combined with the effect of disorder, and, a widening of the peaks due to purely geometrical effects.

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Evidence of shell structures in Au nanowires at room temperature

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Abstract
Statistical conductance properties of gold elongating nanowires at room temperature are studied experimentally. The measured conductance histogram, built with thousands of consecutive nanocontact breakage experiments, exhibits a rich structure of low-intensity peaks at high-conductance quanta values. Their position as a function of a peak index number suggests two markedly different regimes for electronic and atomic shell structures in these nanowires, as observed previously for alkali metal nanowires.

1. Introduction

Recently it has been observed that the stability of atomic-sized alkali metal nanowires is influenced by electronic shell filling effects [1]. However, at larger diameters there is a crossover to crystalline wires with shell closings corresponding to the completion of additional atomic layers [2, 3]. The same effects have been previously observed for metallic clusters [4, 5]. The shell effects in nanowires manifest as stability peaks in the conductance histograms, as the conductance depends on the wire minimum cross-section. This arises from the number of conduction electron modes in the nanowire dictated by the confinement in the lateral dimensions, and the number of atoms. In [1–3] the conductance is measured at about 1/3 of the metal melting temperature as all the shell effect oscillations were observed at elevated temperatures.

The study of the presence of shell structures in gold nanowires has been a topic of increasing interest during the last few years, both from experimental [6–11] and theoretical [12–16] points of view. The experiments with transmission electron microscopy (TEM) have shown the formation of suspended gold nanowires at room temperature (full the Au melting point ~1340 K) and evidence of preferred configurations (magic numbers) in these quasi-one-dimensional systems. This work presents conductance measurements of Au nanocontacts formed at room temperature and under ambient conditions. Instead of analysing stable configurations by direct observation (as in TEM), a statistical analysis is performed using conductance histograms covering a wide range of conductance (i.e. nanowire radii) values. This method allows us to resolve nanowire configurations with higher stability with improved statistics.

2. Experiments
A custom-made scanning tunnelling microscope (STM) is used to form and break the contact between two Au polycrystalline electrodes (99.999% purity) at room temperature. This is achieved by a voltage ramp, typically ±100 V at 1 Hz, fed to a piezoelectric actuator with an elongation constant of ~18 nm V⁻¹. The current between tip and sample at constant bias voltage (~80 mV) is measured at the last stages of the contact rupture using a current–voltage (I–V) converter with 9 × 10⁻⁵ gain and 3 μs rise time. The current signal, triggered properly, is digitized and acquired with a Tektronix TDS220 digital oscilloscope and transferred to a personal computer through a general-purpose interface bus (GPIB) where the conductance is calculated, displayed and the cumulative histogram of hundreds/thousands of consecutive experiments is built. This is done by counting occurrences of the digitized signal, which is sampled at 400 ns. The experiments are performed in air using paraffin oil on the electrodes to prevent contamination effects, as demonstrated for Au [17] and Al [18] nanowires. Preliminary unpublished results on Au at 300 K in UHV confirm the results presented in this work.
3. Results and discussion

Figure 1 shows typical conductance curves for the last stages of the Au nanowires breakage. The conductance is displayed in terms of the reduced conductance $g = G/G_0$, where $G_0 = 2e^2/h \sim 1/12.907 \Omega$ is the quantum of conductance. Due to the inherent irreproducibility of the conductance of a breaking nanowire, one must invoke statistical concepts to obtain quantitative information. This analysis is performed in figure 2(a), where the histogram of conductance values, built with 6000 consecutive curves, is shown. This histogram has been only corrected for the non-ideal differential linearity (NIDL) of the oscilloscope [19, 20]. For the Au case, it is known that about 2000 curves are enough to obtain reproducible histograms at low conductance values. This is also the case for large $g$ values.

Sharp conductance plateaus are observed in figure 1 at all ranges of conductance ($0 < g < 70$). However, in the conductance histogram (see figure 2(a)) a series of intense peaks at low conductance ($g < 16$) is observed, while beyond this point there is a rich structure of low-intensity peaks. This could be indicative of two different behaviours for the conductance of the nanowire. In addition, the rich peak structure observed at high conductance has very low intensity, possibly because the temperature is low compared with the Au bulk melting point ($\sim 1340$ K). In fact, for high conductance, peaks grow at this conductance range on raising temperatures owing to the increased mobility of atoms [3, 16, 21].

In order to resolve the high-conductance structure, the second-derivative smoothing of the histogram is calculated (see figure 2(b)), its minima corresponding to the more stable configurations of the nanococontact. The use of the second derivative avoids the need of subtracting a background that could introduce a slight shift of the peaks, especially at high conductance where the peak intensities are low. We emphasize that 2000 curves are enough to obtain reproducible histograms. In fact, the results are the same for each one of the three histograms built with 2000 of the 6000 total curves. This discards any noise influence in our results at high conductance due to the low intensity of the peaks. The positions of observed main minima for all the histograms remained unchanged, indicating that peak positions are well determined. The positions of the main peaks, labelled by sequential numbers $m$, are linearly related to $g^{1/2}$ as observed in figure 3 (or equivalently, linearly related to the wire’s radius $R$ since $g \sim (k_F R/2)^2$ using the semiclassical expression for a ballistic nanowire at first order [22, 23]). In this figure two markedly different slopes are evident, for $g < 16$ a $0.46 \pm 0.01$ slope is found while for $g > 16$ the slope is $0.21 \pm 0.02$. The different slope indicates a transition in the mechanism governing the stability of the wires.

The $0.46 \pm 0.01$ slope is smaller that those previously reported in alkali metals (between 0.54 for K and 0.62 for Li experimentally and about 0.59 according to jellium theories) [2, 3] that have been associated with atomic arrangements that produce the closing of electronic shells. This slope seems to follow in part from the successive occupation of individual quantum modes leading to regular
conductance quantization (first three points in figure 3). This
behaviour at very low conductance is expected at room
temperature in Au [17, 24], while a gradual disappearance
of these peaks is expected when the temperature is raised
[3, 21]. Therefore, the experimentally obtained value of 0.46
could be indicative of a combination of effects: conductance
quantization and electronic shell filling effects.

The value of the second slope, 0.21 ± 0.02, is well
explained by optimal sections of a fcc crystal. Accordingly,
the lattice structure of the wire is that of the bulk metal
(fcc for Au), at large wire radius, a stable configuration is
obtained each time a single facet of the wire cross-section
is completely covered with atoms, as suggested by Yanson
et al. [2, 3]. Then, the peaks on the histogram result from
fluctuations in the atomic energy for this case. In figure 4,
two geometries for the fcc wires cross-section are depicted.
In order to calculate the slope of $g^{1/2}$ versus $m$, the
semiclassical expression for a ballistic nanowire at first order
is used. Under this approximation, the calculated values of the
slope are in close agreement with the experimentally observed values.

In figure 4(a) the hexagonal cross-section proposed by
Yanson et al. [2] is sketched with the axis along [011] and six
facets perpendicular to [100], [111], [111], [100], [111], and
[111]. This arrangement maximizes the number of [111] facets
exposed by the fcc nanowire surface. For this arrangement
the slope $d(g^{1/2})/dm$ is 1.427 and divided by the facet number, 6,
the slope obtained is 0.24. This slope is slightly higher than
the experimental one. On the other hand, in figure 4(b) we
plot the octagonal cross-section proposed by Gilsener et al.
[2, 6, 25, 26]. Although this arrangement was proposed to
study Pb and Al nanowires (fcc metals), we believe that it
also is suitable to describe Au nanowires. This octagonal
configuration is characterized by different fractions ($\beta_{ijk}$)
of exposed area relative to $(ijk)$ facets, where $\beta_{111} = 0.55$,
$\beta_{100} = 0.25$, and $\beta_{110} = 0.20$. For this arrangement the slope
is $d(g^{1/2})/dm = 1.882$ and divided by the facets number,
8 in this case, the slope is 0.23. The slopes obtained for
both geometries are very close and can explain reasonably
well the experimental results, but this last value is slightly
closer to the measured value within the error bars. However,
experimentally, nanowires are generated from polycrystalline
electrodes; so it is also expected that structures with axis along
directions different to [110] can contribute to this experimental
value. From our results we cannot exclude other atomic
wire arrangements that have been observed experimentally
or found with computer simulations [8, 12–15]. Nevertheless,
we observe a good agreement between our experimental values
and the expected values for the proposed structures.

The results shown in figure 3 clearly indicate that there
are two regimes when analysing the presence of stable
configurations in gold nanowires: on the one hand a region
of high conductance values ($g > 16$) where a octagonal geometry
(figure 4(b)) gives a better description than the hexagonal
one (figure 4(a)); on the other hand, a region ($g < 16$
where experimental results are slightly different from those
expected from a pure electronic shell structure [1–3]. This
difference could be due to the development of exotic non-
crystalline structures as was demonstrated for Al and Pb [26]
for wire diameter below a critical size, or as has been recently
demonstrated for Au where helical multi-shell gold nanowires
have been observed [8] and theoretically studied [12–14].

4. Conclusions

Our results suggest evidence of shell structure in the
conductance histogram for Au nanowires at room temperature;
at low conductance there is a combination of effects, regular
conductance quantization and electronic shell filling effects
($g^{1/2} \sim 0.46 \text{ m}$); at high conductance, atomic shell effects
($g^{1/2} \sim 0.21 \text{ m}$). These results are expected to be affected
by the temperature, that in the case presented here (RT) is
low compared with the Au bulk melting point (~1340 K).

Preliminary unpublished results on Au at 600°C in UHV
confirm this point. These results confirm conductance
histograms as a powerful tool to study stable configurations,
and the corresponding magic numbers, of nanostructures.

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LETTER TO THE EDITOR

$e^2/h$ quantization of the conduction in Cu nanowires

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Abstract

We have investigated the quantum transport behaviour of Cu nanowires created by moving two macroscopic Cu wires into and out of contact. We have observed quantum conductance with steps of both $e^2/h$ and $2e^2/h$. We conclude that the spin degeneracy can be broken in non-magnetic Cu nanowires.

In the past couple of decades the subjects of nanowires and point contacts have been investigated [1]. Quantum conduction has been seen in metallic nanowires [2] and in two-dimensional electron gas devices [3]. The study of metallic nanowires has received more attention recently because of the technological potential for creating nanoscale electronic devices. There are a variety of methods which can be used to make nanowires; for example: retracting a STM tip after it has hit a metallic surface [4], growth via an electrochemical process [5] and tapping plain wires together [6].

The general structure of a nanowire can be seen in figure 1: that is, a narrow constriction between two reservoirs. Most studies have reported that the conductance is quantized in units of $2e^2/h$ as expected from the Landauer formula [7–9] for non-magnetic materials:

$$G = G_0 \sum_i T_i$$

(1)

where $G$ is the conductance, $G_0 = 2e^2/h$ and $T_i$ is the transmission coefficient for the $i$th conduction channel which will be either open or closed (1 or 0). So if there are $n$ conduction channels open, $G = 2ne^2/h$. The factor of 2 appears due to the spin degeneracy expected for non-magnetic materials. Recent studies however [5, 10–12] have reported that in ferromagnetic Fe and Ni nanocontacts this spin degeneracy is lifted, as expected.

In a low-dimensional structure such as a nanowire the spin-polarized electronic structure and spin order can be different from the corresponding bulk quantities, depending on the physical structure of the contact. It is therefore of interest to search for possible spin-dependent effects in non-magnetic nanocontacts. In the present work we carried out an investigation into quantum transport in Cu nanowires. The nanowires were made by tapping Cu wires together in air at room temperature. The Cu wires were vibrated by mounting the wires in a light metallic...
box on top of a speaker driven by a sinusoidal signal at about 10 Hz. The circuit used can be seen in figure 2. A voltage source supplying in the region of 10 mV was connected to the wires and the current flowing through the wires was measured via a current-to-voltage converter. Both the current and the voltage were measured by a Tektronix TDS430A digital oscilloscope. Nanowires were not created every time a contact was broken, so the data sets had to be filtered to separate out those which demonstrated quantum conduction.

How the nanowires are formed is important in this case. Thin filaments extend from each Cu wire because the wire is not smooth on an atomic scale. When the wires separate, these filaments may remain in contact with the other wire and be stretched [13]. As the wires are being stretched the filaments get thinner and quantum conductance can arise. As the wire gets still thinner the various conduction channels will become closed, so the conductance will fall in the familiar staircase curve. Towards the end of the process we will have a very small number of atoms remaining in contact with the wires.

Figure 3 shows conductance against time curves; these are representative of the data that we have obtained. The nanowires are made and broken on the millisecond timescale. Quantum conduction is seen in making (e.g. figure 3(a)) and breaking contacts (e.g. figure 3(b)). Figure 3(a) shows the $G_0$ quantization of the conduction; this is as expected from equation (1). Figure 3(b) reveals a different story: it also shows quantization, but in this case in units of $G_0/2$. Both behaviours of the quantization can be seen in making and breaking contacts. Usually the contacts are quantized in steps of $G_0$, but in 5–10% of the contacts which show quantization the $G_0/2$ quantization are seen. The quantization in units of $G_0/2$ can also be seen in figure 4; this is a conduction histogram built up from many different conduction curves. Above $2G_0$ the peaks are shifted away from integer and half-integer values of $G_0$, due to changes in the topography of the nanowire [14, 15].

The importance of these measurements is that the observation of $G_0/2$ steps is not consistent with equation (1) for a non-magnetic material. This is because in the derivation of equation (1) we have assumed spin degeneracy which gives rise to the factor of 2 in $G_0$. 

Figure 1. An outline of the nanowire: a narrow metallic constriction (B) between two metallic reservoirs (A and C). In the case of this experiment, all of these are made of Cu.

Figure 2. An outline of the set-up for the experiment. The nanowires are made by vibrating the macroscopic Cu wires by a speaker driven at about 10 Hz; the current is measured by a transimpedance amplifier and an oscilloscope.
Figure 3. These are two representative curves. A shows the expected \( G_0 \) step size. B shows half the expected step size. The \( G_0/2 \) steps are evidence of breaking of the spin degeneracy.

Figure 4. A typical conductance histogram, showing the \( G_0/2 \) steps.

Our experiments suggest that in this case this spin degeneracy has been lifted. A possible explanation of the mechanism is that while Cu in the bulk state is paramagnetic and has no overall spin, atomic Cu has a ground state of \( ^2S_1/2 \), i.e. atomic Cu has a net spin. In the nanofilaments it is possible that the nearly isolated Cu atoms at the thinnest part of the nanowire revert to the spin-polarized atomic state, acting therefore as ‘loose spins’ giving rise to the \( G_0/2 \) quantization observed. Such nearly isolated atoms can occur due to the low atomic coordination of the Cu atoms at the thinnest part of the nanowire (area B in figure 1).

To summarize, we have observed quantum conduction in non-magnetic Cu nanowires with both \( G_0 \) and \( G_0/2 \) steps. We interpret this as evidence for breaking of the spin degeneracy in Cu nanowires from nearly isolated Cu atoms, which may revert to the spin-polarized atomic state and act as ‘loose spins’. We hope that our finding of spin polarization effects in non-magnetic nanowires will stimulate further theoretical and experimental work on spin-polarized quantum transport.
The authors would like to thank Professor E M Forgan of the University of Birmingham for valuable discussions and the EPSRC for funding.

References

$e^2/h$ quantization of the conduction in Cu nanowires

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We have investigated the quantum transport behavior of Cu nanowires created by bringing two macroscopic Cu wires into and out of contact at room temperature. We have observed quantum conductance with steps of both $e^2/h$ and $2e^2/h$. We conclude that the spin degeneracy can be broken in nonmagnetic Cu nanowires. © 2003 American Institute of Physics.

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I. INTRODUCTION

In the past couple of decades nanowires and point contacts have been investigated. Quantum conduction has been seen in metallic nanowires and in two-dimensional electron gas devices. The study of metallic nanowires has received more attention recently because of their technological potential for creating nanoscale electronic devices. There are a variety of methods which can be used to make nanowires: for example, retracting a scanning tunneling microscope (STM) tip after it has hit a metallic surface, growth via an electrochemical process and taping macroscopic wires together.

The general structure of a nanowire is a narrow constriction between two reservoirs. Most studies have reported that the conductance is quantized in units of $2e^2/h$ as expected from the Landauer formula for nonmagnetic materials:

$$G = G_0 \sum_i T_i,$$

where $G$ is the conductance, $G_0 = 2e^2/h$ and $T_i$ is the transmission coefficient for the $i$th conduction channel which will be either open or closed (1 or 0). So if there are $n$ conduction channels open $G = 2ne^2/h$. The factor of 2 appears due to the spin degeneracy expected for nonmagnetic materials. Recent studies however have reported that in ferromagnetic Fe and Ni nanocontacts this spin degeneracy is lifted, as expected.

II. EXPERIMENTAL DETAILS

In a low dimensional structure such as a nanowire the spin polarized electronic structure and spin order can be different from the corresponding bulk quantities depending on the physical structure of the contact. It is therefore of interest to search for possible spin dependent effects in nonmagnetic nanocontacts. In the present work we carried out an investigation of quantum transport in Cu nanowires. The nanowires were made by taping macroscopic Cu wires together in air at room temperature. The Cu wires were vibrated at frequency in the range of 5–10 Hz. A voltage source supplying approximately of 10 mV was connected to the wires and the current flowing through the wires was measured via a current to voltage converter. Both the current and the voltage were captured by a Tektronix TDS430A digital oscilloscope. Nanowires were not created everytime a contact was broken, so the data sets had to be filtered to separate those which demonstrated quantum conduction.

The formation of the nanowires is important in this experiment. Thin filaments extend from each Cu wire because the wire is not smooth on an atomic scale. When the wires separate separate these filaments can remain in contact with the other wire and be stretched. As the wires are being stretched the filaments get thinner and quantum conductance can arise. As the wire gets still thinner the various conduction channels will become closed so the conductance will fall into the familiar staircase curve. Towards the end of the stretching process there will be a very small number of atoms that remain in contact between the wires.

III. RESULTS

Figure 1 shows representative conductance against time curves for Cu nanowires. The nanowires are made and broken on the millisecond time scale. Quantum conductance is seen in making [e.g., Fig. 1(a)] and breaking contacts [e.g., Fig. 1(b)]. Figure 1(a) shows the $G_0$ quantization of the conductance this is as expected from Eq. (1). Figure 1(b) reveals

![Graph showing conductance over time](image)

**FIG. 1.** Two representative conductance–time curves taken at room temperature: (a) expected step size $G_0$; (b) half the expected step size. The $G_0/2$ steps are evidence of broken spin degeneracy.
a different story, also showing quantization but in this case in units of $G_{0}/2$. Both quantization behaviors can be seen in making and breaking contacts: usually the contacts are quantized in steps of $G_{0}$ but in 5%–10% of the quantized data steps of $G_{0}/2$ quantization are seen.

Figure 2 shows two conduction histograms for Cu nanowires which are constructed of approximately 20 conductance-time curves. Quantization is clearly visible in both Figs. 2(a) and 2(b). Above $2G_{0}$ the peaks are shifted away from integer and half integer values of $G_{0}$ due to changes in the topography of the nanowires. The data in Fig. 2(b) were gathered in the absence of a magnetic field and the peaks at integer values of $G_{0}$ dominate. In Fig. 2(b) when a 5 Oe external magnetic field is applied two effects can be seen. First the $G_{0}/2$ quantization becomes more prominent: either because the field encourages the formation of $G_{0}/2$ steps or because it stabilizes the $G_{0}/2$ steps is not clear at the moment. The second effect is that the peaks are lower and broader when the field is applied.

IV. DISCUSSION

The importance of these measurements is that the observation of $G_{0}/2$ steps is not consistent with Eq. (1) for a nonmagnetic material. This is because in deriving Eq. (1) we have assumed spin degeneracy which gives rise to the factor of 2 in $G_{0}$. Our results suggest that in our experiment the spin degeneracy has been lifted. A possible mechanism is that, while Cu in the bulk state is diamagnetic and has no overall spin, atomic Cu has a ground state of $^{2}S_{1/2}$, i.e., isolated Cu atoms are paramagnetic and have a net spin. In nanofilaments it is possible that the nearly isolated Cu atoms at the thinnest part of the nanowire revert back to the spin polarized atomic state, act as “loose spins” and hence give rise to the observed $G_{0}/2$ quantization. Such nearly isolated atoms can occur due to the low atomic concentration of the Cu atoms at the thinnest part of the nanowire (area B in Fig. 3).

V. CONCLUSION

To summarize, we have observed quantum conduction in nonmagnetic Cu nanowires with both $G_{0}$ and $G_{0}/2$ steps. We interpret this as evidence of the breaking of spin degeneracy in Cu nanowires by nearly isolated Cu atoms, which may revert back to the spin polarized atomic state and act as loose spins. We hope that our finding of spin polarization effects in nonmagnetic nanowires will stimulate further theoretical and experimental work on spin polarized quantum transport.

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