1 ELECTRONIC AND OPTICAL PROPERTIES OF NANOMATERIALS

1.1 Introduction

Figure 1-1: Size quantization effect. Electronic state transition from bulk metal/semiconductor to small cluster.

Nanocrystalline particles represent a state of matter in the transition region between bulk solid and single molecule. As a consequence, their physical and chemical properties gradually change from solid state to molecular behaviour with decreasing particle size. The reasons for this behaviour can be summarised as two basic phenomena:

First, as we have already discussed, owing to their small dimensions, the surface-to-volume ratio increases, and the number of surface atoms may be similar to or higher than those located in the crystalline lattice core, and the surface properties are no longer negligible. When no other molecules are adsorbed onto the nanocrystallites, the surface atoms are highly unsaturated and their electronic contribution to the behaviour of the particles is totally different from that of the inner atoms. These effects may be even more marked when the surface atoms are ligated.
This leads to different electronic transport and catalytic properties of the nanocrystalline particles.ii

The second phenomenon, which occurs in metal and semiconductor nanoparticles, is totally an electronic effect. The band structure gradually evolves with increasing particle size, i.e., molecular orbital convert into delocalised band states. Figure 1-1, shows the size quantization effect responsible for the transition between a bulk metal or semiconductor, and cluster species. In a metal, the quasi-continuous density of states in the valence and the conduction bands splits into discrete electronic levels, the spacing between these levels and the band gap increasing with decreasing particle size.iii,iv

In the case of semiconductors, the phenomenon is slightly different, since a band gap already exists in the bulk state. However, this band gap also increases when the particle size is decreased and the energy bands gradually convert into discrete molecular electronic levels.v If the particle size is less than the De Broglie wavelength of the electrons, the charge carriers may be treated quantum mechanically as "particles in a box", where the size of the box is given by the dimensions of the crystallites.vi In semiconductors, the quantization effect that enhances the optical gap is routinely observed for clusters ranging from 1 nm to almost 10 nm. Metal particles consisting of 50 to 100 atoms with a diameter between 1 and 2 nm start to loose their metallic behaviour and tend to become semiconductors.vii Particles that show this size quantization effect are sometimes called Q-particles or quantum dots that we will discuss later in this chapter.

At very small particle sizes, also called clusters, determined by the so-called magic numbers, which are more frequently observed than others. Metals have a cubic or hexagonal close-packed structure consisting of one central atom, which is surrounded in the first shell by 12 atoms, in the second shell by 42 atoms, or in principle by $10n^2+2$ atoms in the nth shell.viii For example, one of the most famous ligand stabilized metal clusters is a gold particle with 55 atoms (Au$_{55}$) first reported by G. Schmid in 1981.ix


1.2 Metals

1.2.1 Introduction

Nanowires and nanocrystals having average radius $R$, in the range of the Fermi wavelength $\lambda_F$, can indeed be fabricated and have shown unusual mechanical and electronic properties. The effects of reduced size and dimensionality, and their quantum properties have been investigated actively in the last decade. Ultrathin nanowires and even monatomic chains suspended between two metal electrodes have been produced. Electrical conduction and force have been measured concomitantly in the course of stretching of nanowires. Initially, much of the work was carried out on GaAs–AlGaAs heterostructures which were grown to contain a thin conducting layer at the interface. The conducting layer is treated as a two-dimensional (2D) electron gas in which a narrow constriction of desired width $w$, and length $l$, can be created by applying a negative gate voltage.

The conductivity $\sigma$, which relates the electric current density to the electric field by $j = \sigma E$, is expressible in terms of the areal charge density $\rho_S$ for 2D electron gas of effective mass $m^*$ through the equation

$$\sigma = \frac{\rho_S e^2 \tau}{m^*} \quad (1.1)$$

The experimental quantity of interest, however, is the conductance $G = I / V$, which is the ratio of the total current $I$ to the voltage drop $V$ across the sample of length $l$ in the direction of current flow. For 2D, since $I = wj$, one can also write

$$G = \sigma \frac{w}{l} \quad (1.2)$$

For a 3D conductor, this relationship is valid provided that $w$ is replaced by the cross sectional area $A$ orthogonal to the current flow direction. Similar expressions are also valid for the thermal transport of energy. The thermal conductance related to the energy (or heat) current $J_x$ through a sample between two reservoirs is given by $k_x = J_x \Delta T$, where $\Delta T$ is the temperature gradient. Depending on whether the energy is carried by electrons ($x = e$) or by phonons ($x = p$) the thermal conductance is identified as electronic $K_e$ or phononic $K_p$. Here our focus is on quantum transport through materials of very small dimensions.
Novel size-dependent effects emerge as $w$ and $l$ are reduced towards nanometric dimensions in the nanometre range. The relationship expressed by equation $G = \sigma \frac{w}{l}$ (1.2) holds in the diffusive transport regime where both $w$ and $l$ are greater than the mean free path. As the width of the constriction decreases, there comes a point where quantum mechanics makes its presence known. The quantum confinement of a carrier in a strip of width $w$ leads to the discretization of energy levels given by $\varepsilon_n = \frac{n^2 \hbar^2}{8m^* w^2}$. The number of these $w$-dependent transverse modes, which are occupied, determines the conductance. Thus, rather than a simple linear dependence of $G$ on $w$, quantum mechanics forces this ‘indirect’ dependence on $w$. As $w$ is altered, the energy spectrum changes and so does the number of occupied modes below the Fermi energy and hence the conductance.

Simple physical considerations show that the number of transverse occupied states, $N \sim 2w/\lambda_F$, increases with the width of the constriction. Since all these modes can contribute to the conductance, one still expects the conductance to increase linearly with $w$ even in the nanodomain. This is almost the case, except with one important distinction. The width $w$ can change continuously, at least in principle. But the number of modes, being an integer, can only vary in discrete steps. The concept becomes physically more transparent if we rewrite $N \sim n \frac{E_F}{\varepsilon_n}$. The highest occupied $\varepsilon_n = E_F$ gives $N$ from a simple counting of the number of discrete eigenvalues. Since it is a rare coincidence for an eigenvalue to exactly align with the Fermi energy, $N$ is taken to be the integer which corresponds to the highest occupied level just below $E_F$. Thus the effect of quantum mechanics due to the reduced dimension $w$ is to cause the conductance to change in discrete steps in a staircase fashion. We have yet to find the step height. This simple view is necessarily modified when other factors explained later start to play a crucial role. Obviously, one then requires a more detailed analysis.

The characteristic length that comes into play is $\lambda_F$, since only those electrons having energy close to the Fermi energy carry current at low temperatures. If $w >> \lambda_F$, the
number of conducting modes is very large and so is the conductance. This is typical in metals where $\lambda_F \sim 0.2$ nanometres is very small and consequently the observation of discrete conductance variation requires $w \sim \lambda_F$. That is why the discrete conductance behaviour was first observed in semiconductor heterojunctions having very low electron density and $\lambda_F$ two orders of magnitude larger than in metals.

The effect of reduced length $l$ on the conductance is even more striking. If the ohmic regime were to hold in equation

$$G = \sigma \frac{w}{l} \quad (1.2)$$

one would expect $G$ to increase without limit (or resistance to reach zero) as $l$ was reduced towards zero. We shall see that there would always be finite residual resistance. Heisenberg’s uncertainty principle defines a natural characteristic length as the mean free path $l_e$. If $l < l_e$, carriers can propagate without losing their initial momentum, and this domain is referred to as the ballistic transport regime. If we follow the standard definition, that the conductance is a measure of current through a sample divided by the voltage difference,

$$G = \frac{I}{\Delta V} \quad (1.3)$$

the quantum of electrical conductance occurs naturally as a consequence of Heisenberg’s uncertainty principle. The current is given by the rate of charge flow $I = \Delta Q/t_{\text{transit}}$. Now charge is quantized in units of elementary charge, $e$. Hence in the extreme quantum limit, setting $\Delta Q = e$ and recognizing that the transit time should then be at least in the range of time implied by Heisenberg’s uncertainty principle, we get

$$I = \frac{e}{\Delta t} \quad (1.4)$$

Combining equation

$$G = \frac{I}{\Delta V} \quad (1.3)$$

and equation

$$I = \frac{e}{\Delta t} \quad (1.4)$$

and using the fact that the potential difference, $\Delta V$, is equal to electrochemical potential difference $\Delta E$ divided by the electronic charge $e$, one gets

$$G = \frac{e^2}{\Delta E \Delta t} \quad (1.5)$$
Next invoking Heisenberg’s uncertainty principle, $\Delta E \Delta t >> h$, the expression for ballistic conductance including the spin degeneracy becomes $G = 2e^2/h$ in the ideal case. It has a maximum value of $8 \times 10^{-5} \Omega^{-1}$. This is the step height, the conductance per transverse mode.

The corresponding resistance $h/2e^2$ has a value of 12.9 kΩ (it suffices to call it 12345Ω for ease of remembrance) and is attributed to the resistance at the contacts where the conductor is attached to the electrodes or electron reservoirs. Thus classically $G \propto w$. Quantum mechanically it increases in discrete steps. It jumps by $2e^2/h$ as $w$ increases enough to permit one more transverse mode to be occupied and hence available for conduction. More recently, the electronic and transport properties of metallic point contacts and wires having average dimension in the range of metallic $\lambda_F$ produced by STM and also by mechanical break junctions have displayed various quantum effects. The two-terminal electrical conductance, $G$, of the wire showed a stepwise variation with the stretch.

**Quantum transport of electrons**

In 1957, Landauer introduced a novel way of looking at conduction. He taught us to view the conduction as transmission and gave the famous formula, which has been a breakthrough in the conductance phenomena and in the physics of mesoscopic systems. According to Landauer, the conduction is a scattering event, and the transport is the consequence of the incident current flux. On the basis of the self-consistency arguments for reflections ($R$) and transmissions ($T$), he derived his famous formula for a one-dimensional conductor yielding the conductance

$$G = \left(\frac{2e^2}{h}\right)\frac{T}{R} \quad (1.6)$$

Where $T$ and $R = 1 - T$ are transmission and reflection coefficients, respectively.

Later, Sharvin investigated the electron transport through a small contact between two free-electron metals. Since the length of the contact is negligible, i.e. $l \rightarrow 0$, the scattering in the contact was absent and hence $T \sim 1$. By using a semiclassical approach he found an expression for the conductance,

$$G_S = \left(\frac{2e^2}{h}\right)\frac{A k_F^2}{4\pi} \quad (1.7)$$

Which has come to be known as Sharvin’s conductance ($A =$area).
The original Landauer formula, i.e. equation \( G = \frac{(2e^2/h)T}{R} \) (1.6), and Sharvin’s conductance have seemed to be at variance, since the former yields \( G \to \infty \) as \( R \to 0 \) in the absence of scattering. The confusion in the literature has been clarified by recognizing the fact that the original formula is just the conductance of a barrier in a 1D conductor. Engquist and Anderson pointed out an interesting feature by arguing that the conductance has a close relation with the type of measurement. Landauer’s formula was extended to the conductance measured between the two outside reservoirs within which the finite-length conductor is placed. The corresponding two-terminal conductance formula, \( G = (2e^2/h)T \), incorporates the resistance due to the contacts to the reservoirs. Accordingly, for perfect transmission, \( T \to 1 \), the conductance is still finite and equal to \( 2e^2/h \).

The step behaviour of \( G \) has been treated in several studies. Here we provide a simple and formal explanation by using a 1D idealized uniform constriction having a width \( w \). The electrons are confined in the transverse direction and have states with quantized energy \( \epsilon_i \). They propagate freely along the length of the constriction. The propagation constant \( \gamma_i \) for an electron with \( \epsilon_i < E_F \) is

\[
\gamma_i = \left[ \frac{2m^*}{\hbar^2} (E_F - \epsilon_i) \right]^{1/2}
\]  

Whenever the width of the constriction increases by \( \lambda_F /2 \), a new subband with energy \( \epsilon_i + \hbar^2 \gamma_i^2/2m \) dips below the Fermi level and contributes to the current under the small bias voltage \( \Delta V \). The current is

\[
I = \sum_{j=1}^{i} 2n_i e \vartheta_{\gamma_i} \left[ D_i(E_F + e\Delta V) - D_i(E_F) \right]
\]  

Here \( j \) is the index of the highest subband that lies below the Fermi level, i.e. \( \epsilon_i \leq E_F + e\Delta V \) and \( \epsilon_{j+1} > E_F + e\Delta V \), and \( n_i \) is the degeneracy of the state \( i \). By assuming perfect transmission in the absence of any contact resistance and barrier inside the constriction, i.e. \( T = 1 \), and by expressing the group velocity \( \vartheta_{\gamma_i} \) and the density of states \( D_i(\epsilon) \) in terms of the subband energy \( \epsilon = \epsilon_i + \hbar^2 \gamma_i^2/2m^* \) and dividing \( I \) by \( \Delta V \) we obtain

\[
G = \sum_{i=1}^{j} \frac{2e^2}{\hbar} n_i
\]  

(1.10)
Accordingly, each current-transporting state with energy in the range $E_F < \epsilon < E_F + \epsilon \Delta V$ contributes to $G$ an amount $2e^2n_i/h$.

For a uniform, infinite wall constriction, the states are non-degenerate, i.e. $n_i = 1$, and hence the increase of $w$ by $\lambda_F / 2$ causes $G$ to jump by $2e^2/h$. As a result, the $G(w)$ curve exhibits a staircase structure. Since the level spacing in the transverse quantization is rather small for the low electron density in the 2D electron gas system, and $\Delta \epsilon \sim \lambda_F^{-2}$, the sharp step structure is likely to be smeared out at $T \sim 10$ K or at finite bias voltage.

For a finite-length constriction the scattering at the contacts to the reservoirs (i.e. the contact resistance) and at the non-uniformities or the potential barriers inside the constriction affect the transmission. Then, the conductance of a single channel expressed as

$$ G = (2e^2/h)T \quad (1.11) $$

may deviate from the perfect quantized values. As a result, the effects, such as the contact and potential barrier, surface roughness, impurity scattering, cause the sharp step structure of $G(w)$ to smear out. The local widening of the constriction or impurity potential can give rise to quasi-bound (0D) states in the constriction and to resonant tunnelling effects.

The length of the constriction, $l$, is another important parameter. In order to get sharp step structure, $l$ has to be greater than $\lambda_F$, but smaller than the electron mean free path $l_e$; $G(w)$ is smoothed out in a short constriction ($l < \lambda_F$). Therefore, $G(w)$ exhibits sharp step structure if the constriction is uniform, and $w \sim \lambda_F$ and $\lambda_F << l < l_e$. On the other hand, the theoretical studies predict that the resonance structures occur on the flat plateaus due to the interference of waves reflected from the abrupt connections to the reservoirs. The stepwise variation of $G$ with $w$ or $E_F$ has been identified as the quantization of conductance. This is, in fact, the reflection of the quantized constriction states in the electrical conductance.

We now extend the above discussion to analyse the ballistic electron conductance through a point contact or a nanowire, in which the electronic motion is confined in two dimensions, but freely propagates in the third dimension. The point contact (or quantum contact) created by the indentation of the STM, a nanowire (or a connective neck) that is produced by retracting the tip from an indentation and also a metallic
SWNT are typical systems of interest. Nanowires created by STM are expected to be round (though not perfectly cylindrical) and have radius $R \sim \lambda_F$ at the neck. The neck is connected to the electrodes by horn-like ends, and hence the radius increases as one goes away from the neck. An extreme case for $l \to 0$ is Sharvin’s conductance, $G_S = \left(\frac{2e^2}{h}\right)\left(\frac{\pi R}{\lambda_F}\right)^2$, with contact radius $R$, where the step structure is almost smeared out and plateaus disappear. In the quantum regime, where the cross section $A \sim \lambda_F^2$, $G_S$ should vanish when $A$ is smaller than a critical cross section set by the uncertainty principle. As $l$ increases, a stepwise behaviour for $G_S$ develops.

### 1.2.2 Electrical Conductivity

An atomic size contact and connective neck first created by Gimzewski and Möller by using a STM tip exhibited abrupt changes in the variation of the conductance with the displacement of the tip. Initially, the observed behaviour of the conductance was attributed to the quantization of conductance. At that time, from calculating the quantized conductance of a perfect but short connective neck, Ciraci and Tekman concluded that the observed abrupt changes of the conductance can be related to the discontinuous variation of the contact area. Later, Todorov and Sutton performed an atomic scale simulation of indentation based on the classical molecular dynamics (MD) method and calculated the conductance for the resulting atomic structure using the s-orbital tight-binding Green’s function method. They showed that sudden changes of conductance during indentation or stretching are related to the discontinuous variation of the contact area. Recently, nanowires of better quality have been produced using STM and also by using the mechanical break junction. The two-terminal electrical conductance of these wires showed abrupt changes with the stretching.

The radius of the narrowest cross section of the wire prior to the break is only a few ångströms; it has the length scale of $\lambda_F$, where the discontinuous (discrete) nature of the metal dominates over its continuum description. Since the level spacing $\Delta\varepsilon$ is in the region of $\sim 1$ eV at this length scale, the peaks of the density of states $D(\varepsilon)$ of the connective neck become well separated and hence the transverse quantization of states becomes easily resolved even at room temperature. Furthermore, any change in the atomic structure or the radius induces significant changes in the level spacing.
and in the occupancy of states. This, in turn, leads to detectable changes in the related properties. Therefore, the ballistic electron transport through a nanowire should be closely related to its atomic structure and radius at its narrowest part. On the other hand, irregularities of the atomic structure and electronic potential enhance scattering that destroys the regular staircase structure. In the following section, we summarize results that emerged from recent experimental and theoretical studies on stretched nanowires.

### 1.2.2.1 Atomic structure and mechanical properties

Computer simulations of the atomic structure of connective necks created by STM were first performed in the seminal works by Sutton and Pethica, and Landman et al. The deformation (or elongation) generally occurred in two different and consecutive stages that repeat while the wire is stretched.

1. In the first stage, which was identified as quasi-elastic, the stored strain energy and average tensile force increase with increasing stretch $s$, while the atomic layers are maintained. The variation of the applied tensile force, $F_z(s)$, in this stage is approximately linear, but it deviates from linearity as the number of atoms in the neck decreases. Fluctuations in $F_z(s)$ can occur possibly due to displacement and relocation of atoms within the same layer or atom exchange between adjacent layers. Also, intralayer and interlayer atom relocations can give rise to conductance fluctuations.

2. The second stage that follows each quasi-elastic stage is called the yielding stage. A wire can yield by different mechanisms depending on its diameter. The motion of the dislocation and/or the slips on the glide planes are generally responsible for the yielding if the wire maintains an ordered (crystalline) structure and has a relatively large cross section. The type of the ordered structure and its orientation relative to the $z$-axis (or stretching direction) are expected to affect the yielding. On the other hand yielding can occur by order–disorder transformation and single-atom exchange if the cross section of the wires is relatively small. Once the elongation reaches approximately the interlayer spacing at the end of the quasi-elastic stage, the structure becomes disordered.

But after further stretching, it recovers with the formation of a new layer. In the yielding stage, $|F_z|$ decreases abruptly; the cross section of the layer formed at the
end of the yielding stage is abruptly reduced by a few atoms. As a typical example, the force variation and atomic structure calculated by the MD method are illustrated in Figure 1-2.

![Figure 1-2: The variation of the tensile force $F_z$ (in nanonewtons) with the strain or elongation $s$ along the z-axis of the nanowire having Cu(001) structure. The stretch $s$ is realized in $m$ discrete steps. The snapshots show the atomic positions at relevant stretch steps $m$. The MD simulations are performed at $T = 300\,\text{K}$ [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]}

When the neck becomes very narrow (having 3–4 atoms), the yielding is realized, however, by a single atom jumping from one of the adjacent layers to the interlayer region.

Under certain circumstances, atoms at the neck form a pentagon that becomes staggered in different layers. The interlayer atoms make a chain passing through the centre of the pentagon rings. In this new phase, the elastic and yielding stages are intermixed and elongation, which is by more than one interlayer distance, can be accommodated. As the cross section of the wire is further decreased the pentagons are transformed to a triangle. In the initial stage of pulling off, the single-atom process, in which individual atoms also migrate from central layers towards the end layers, can give rise to a small and less discontinuous change in the cross section. The tendency to minimize the surface area, and hence to reduce the strain energy of the system, is the main driving force for this type of neck formation. While quasi-elastic and yielding stages are distinguishable initially, the force variation becomes more complex and more dependent on the migration of atoms for atomic necks. Atomic migrations have important implications such as dips in the variation of
conductance with stretch. The simulation studies on metal wires with diameters ∼λ_F at the neck, but increasing gradually as one goes away from the neck region, have shown structural instabilities. Such wires displayed spontaneous thinning of the necks even in the absence of any tensile strain. Under prolonged stretching, shortly before the break, the cross section of the neck is reduced to include only 2–3 atoms. In this case, the hollow-site registry may change to the top-site registry. This leads to the formation of a bundle of atomic chains (rope) or of a single atomic chain (see Figure 1-3). We consider this a dramatic change in the atomic structure of the wire that has important implications. For example, first-principles calculations indicated that a chain of single Al atoms has an effective Young modulus stronger than that of the bulk.

Figure 1-3: The top view of three layers at the neck showing atomic positions and their relative registry at different levels of stretch. m = 15 occurs before the first yielding stage. The atomic positions in the layers 2, 3 and 4 are indicated by +, • and ◊, respectively. m = 38 and m = 41 occur after the second yielding stage. m = 46, 47 and m = 49 show the formation of bundle structure (or strands). In the panels for m = 38–49 the positions of atoms in the third, fourth and fifth (central) layers are indicated by +, • and ◊, respectively. Atomic chains in a bundle are highlighted by square boxes. [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]

1.2.2.2 Electrical conductance of nanowires

The overall features of electrical conductance have been obtained from a statistical analysis of the results of many consecutive measurements to deduce how frequently a measured conductance value occurs. Many distribution curves exhibited a peak near G_0 = 2e²/h for metal nanowires, and a relatively broad peak near 3G_0, and
almost no significant structure for larger values of conductance. It appears that the cross section of a connective neck can be reduced down to a single atom just before the wire breaks. In certain situations, the connective neck can be a monatomic chain comprising of a few atoms arranged in a row. In this case, a transverse state quantized in the neck at the Fermi level is coupled to the states of the electrodes and forms a conducting channel yielding a plateau in the G(s) curve, and hence a peak in the statistical distribution curve. The step structure for large necks comprising of a few atoms cannot occur at integer multiples of G₀ due to the scattering from irregularities, and hence due to the channel mixing.

It should be noted that in the course of stretching, elastic and yielding stages repeat; the surface of the nanowire roughens and deviates strongly from circular symmetry. The length of the narrowest part of the neck is usually only one or two interlayer separations, and is connected to the horn-like ends. Under these circumstances, the quantization is not complete and the contribution of the tunnelling is not negligible. Results of atomic simulations point to the fact that neither adiabatic evolution of discrete electronic states, nor perfect circular symmetry can occur in the neck. Consequently the expected quantized sharp structure shall be smeared out by channel mixing and tunnelling.

Contradicting these arguments, the changes in the conductance are, however, abrupt. This controversial situation has been explained by the combined measurements of the conductance and force variation with the stretch. The abrupt changes of conductance in the course of stretching coincide with the sudden release (or relief) of the measured tensile force. The tensile stress is released suddenly following the yielding stage, whereby the cross section of the wire is reduced discontinuously, and hence the electronic structure and the electronic level spacing undergo an abrupt change near the neck. The variation of the conductance, i.e. G(s), calculated for stretching the nanowire is presented as an example in Figure 1-4.
1.2.3 Surface Plasmons

Gold colloidal nanoparticles are responsible for the brilliant reds seen in stained glass windows. Silver particles are typically yellow. These properties have been of interest for centuries, and scientific research on metal nanoparticles dates at least to Michael Faraday. It was therefore one of the great triumphs of classical physics when in 1908, Mie presented a solution to Maxwell’s equations that describes the extinction spectra (extinction = scattering + absorption) of spherical particles of arbitrary size. Origin of surface plasmon resonance in noble metal nanoparticles

The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is ~50 nm, therefore in particles smaller than this, no scattering is expected from the bulk. Thus, all interactions are expected to be with the surface. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance conditions as represented in Figure 1-5.
Light in resonance with the surface plasmon oscillation causes the free-electrons in the metal to oscillate. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light's frequency causing a standing oscillation. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material. This is referred to as the surface plasmon resonance, since it is located at the surface. As the shape or size of the nanoparticle changes, the surface geometry changes causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering.

Changing the dielectric constant of the surrounding material will have an effect on the oscillation frequency due to the varying ability of the surface to accommodate electron charge density from the nanoparticles. Changing the solvent will change the dielectric constant, but the capping material is most important in determining the shift of the plasmon resonance due to the local nature of its effect on the surface of the nanoparticle. Chemically bonded molecules can be detected by the observed change they induce in the electron density on the surface, which results in a shift in the surface plasmon absorption maximum. This is the basis for the use of noble metal nanoparticles as sensitive sensors. Mie originally calculated the surface plasmon resonance by solving Maxwell’s equations for small spheres interacting with an electromagnetic field. Gan was able to extend this theory to apply to ellipsoidal geometries. Modern methods using the discrete dipole approximation (DDA) allow one to calculate the surface plasmon resonance absorption for arbitrary geometries. Calculation of the longitudinal plasmon resonance for gold nanorods generates an

**Figure 1-5:** Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei. [K. Lance Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, 2003, Journal of Physical Chemistry]
increase in the intensity and wavelength maximum as the aspect ratio (length divided by width) increases. Thus, the plasmon resonance can be tuned across the visible region by changing the aspect ratio. The increase in the intensity of the surface plasmon resonance absorption leads to an enhancement of the electric field, as exploited in many applications.

1.2.3.1 Dipole plasmon resonances

When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently (Figure 1-5). When the electron cloud is displaced relative to the nuclei, a restoring force arises from Coulomb attraction between electrons and nuclei that results in oscillation of the electron cloud relative to the nuclear framework. The oscillation frequency is determined by four factors: the density of electrons, the effective electron mass, and the shape and size of the charge distribution. The collective oscillation of the electrons is called the dipole plasmon resonance of the particle (sometimes denoted “dipole particle plasmon resonance” to distinguish from plasmon excitation that can occur in bulk metal or metal surfaces). Higher modes of plasmon excitation can occur, such as the quadrupole mode where half of the electron cloud moves parallel to the applied field and half moves antiparallel. For a metal like silver, the plasmon frequency is also influenced by other electrons such as those in d-orbitals, and this prevents the plasmon frequency from being easily calculated using electronic structure calculations. However, it is not hard to relate the plasmon frequency to the metal dielectric constant, which is a property that can be measured as a function of wavelength for bulk metal.

To relate the dipole plasmon frequency of a metal nanoparticle to the dielectric constant, we consider the interaction of light with a spherical particle that is much smaller than the wavelength of light. Under these circumstances, the electric field of the light can be taken to be constant, and the interaction is governed by electrostatics rather than electrodynamics. This is often called the quasistatic approximation, as we use the wavelength-dependent dielectric constant of the metal particle, \( \varepsilon_i \), and of the surrounding medium, \( \varepsilon_0 \), in what is otherwise an electrostatic theory.

Let’s denote the electric field of the incident electromagnetic wave by the vector \( \mathbf{E}_o \). We take this constant vector to be in the x direction so that \( \mathbf{E}_o = \mathbf{E}_o \hat{x} \), where \( \hat{x} \) is a unit vector. To determine the electromagnetic field surrounding the particle, we solve
LaPlace’s equation (the fundamental equation of electrostatics), $\nabla^2 \phi = 0$, where $\phi$ is the electric potential and the field $E$ is related to $\phi$ by $E = -\nabla \phi$. In developing this solution, we apply two boundary conditions: (i) that $\phi$ is continuous at the sphere surface and (ii) that the normal component of the electric displacement $D$ is also continuous, where $D = \varepsilon E$.

It is not difficult to show that the general solution to the LaPlace equation has angular solutions which are just the spherical harmonics. In addition, the radial solutions are of the form $r^l$ and $r^{-(l+1)}$, where $l$ is the familiar angular momentum label ($l = 0, 1, 2, ...$) of atomic orbitals. If we restrict our considerations for now to just the $l = 1$ solution and if $E_o$ is in the $x$ direction, the potential is simply $\phi = A r \sin \theta \cos \Phi$ inside the sphere ($r < a$) and $\phi = (-E_o r + B/r^2) \sin \theta \cos \Phi$ outside the sphere ($r > a$), where $A$ and $B$ are constants to be determined. If these solutions are inserted into the boundary conditions and the resulting $\phi$ is used to determine the field outside the sphere, $E_{out}$, we get

$$E_{out} = E_o \hat{x} - \alpha E_o \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$$  \hspace{1cm} (1. 12)

Where $\alpha$ is the sphere polarizability and $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the usual unit vectors. We note that the first term in eq $E_{out} = E_o \hat{x} - \alpha E_o \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$ (1. 12) is the applied field and the second is the induced dipole field (induced dipole moment = $\alpha E_o$) that results from polarization of the conduction electron density.

For a sphere with the dielectric constants indicated above, the LaPlace equation solution shows that the polarizability is

$$\alpha = g_d a^3$$  \hspace{1cm} (1. 13)

with

$$g_d = \frac{\varepsilon_i - \varepsilon_0}{\varepsilon_i + 2 \varepsilon_0}$$  \hspace{1cm} (1. 14)

Although the dipole field in eq $E_{out} = E_o \hat{x} - \alpha E_o \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$ (1. 12) is that for a static dipole, the more complete Maxwell equation solution shows that this
is actually a radiating dipole, and thus, it contributes to extinction and Rayleigh scattering by the sphere. This leads to extinction and scattering efficiencies given by

\[ Q_{\text{ext}} = 4 \pi \text{Im}(g_d) \]  
\[ Q_{\text{scat}} = \frac{8}{3} x^4 |g_d|^2 \]

where \( x = 2\pi a(e_0^{1/2}/\lambda). \) The efficiency is the ratio of the cross-section to the geometrical cross-section \( \pi a^2. \) Note that the factor \( g_d \) from eq \((1.14)\) plays the key role in determining the wavelength dependence of these cross-sections, as the metal dielectric constant \( e_i \) is strongly dependent on wavelength.

### 1.2.3.2 Quadrupole plasmon Resonances

For larger particles, higher multipoles, especially the quadrupole term \((l=2)\) become important to the extinction and scattering spectra. Using the same notation as above and including the \( l=2 \) term in the LaPlace equation solution, the resulting field outside the sphere, \( E_{\text{out}} \), now can be expressed as

\[ E_{\text{out}} = E_o \hat{x} + ikE_o (x\hat{x} + z\hat{z}) - \alpha E_o \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) - \beta E_o \left[ \frac{x^2 + y^2}{r^5} - 5z(x^2\hat{x} + y^2\hat{y} + xz\hat{z}) \right] \right] \]

and the quadrupole polarizability is

\[ \alpha = g_d a^5 \]  
\[ g_d = \frac{e_i - e_0}{e_i + 3/2 e_0} \]

Note that the denominator of eq \((1.19)\) contains the factor 3/2 while in eq \((1.14)\) the corresponding number is 2. These factors arise from the exponents in the radial solutions to LaPlace’s equation, e.g., the factors \( r^l \) and \( r^{-(l+1)} \) that were discussed above. For dipole excitation, we have \( l=1, \) and the magnitude of the ratio of the exponents is \((l+1)/l = 2, \) while for quadrupole excitation \((l+1)/l = 3/2. \) Higher partial waves work analogously.
Following the same derivation, we get the following quasistatic (dipole + quadrupole) expressions for the extinction and Rayleigh scattering efficiencies:

\[
Q_{\text{ext}} = 4\pi \text{Im} \left[ g_d + \frac{x^2}{12} g_a + \frac{x^2}{30} (\varepsilon_i - 1) \right] \tag{1.20}
\]

\[
Q_{\text{ext}} = \frac{8}{3} x^4 \left\{ |g_d|^2 + \frac{x^4}{240} |g_a|^2 + \frac{x^4}{900} (\varepsilon_i - 1)^2 \right\} \tag{1.21}
\]

1.2.3.3 Extinction for silver spheres

We now evaluate the extinction cross-section using the quasistatic expressions, eqs (1.24), (1.25) and (1.29), (1.30) as well as the exact (Mie) theory. We take dielectric constants for silver that are plotted in Figure 1-6 a) and the external dielectric constant is assumed to be 1 (i.e., a particle in a vacuum). The resulting efficiencies for 30 and 60 nm spheres are plotted in Figure 1-6 b), c), respectively.

![Figure 1-6:](image)

Figure 1-6: (a) Real and imaginary part of silver dielectric constants as function of wavelength. (b) Extinction efficiency, i.e., the ratio of the extinction cross-section to the area of the sphere, as obtained...
from quasistatic theory for a silver sphere whose radius is 30 nm. (c) The corresponding efficiency for a 60 nm particle, including for quadrupole effects, and correcting for finite wavelength effects. In b and c, the exact Mie theory result is also plotted. [K. Lance Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, 2003, Journal of Physical Chemistry]

The cross-section in Figure 1-6 b) shows a sharp peak at 367 nm, with a good match between quasistatic and Mie theory. This peak is the dipole surface plasmon resonance, and it occurs when the real part of the denominator in eq \( g_d = \frac{\varepsilon_i - \varepsilon_0}{\varepsilon_i + 2\varepsilon_0} \) vanishes, corresponding to a metal dielectric constant whose real part is -2. For particles that are not in a vacuum, the plasmon resonance condition becomes

\[ \text{Re } \frac{\varepsilon_i}{\varepsilon_0} = -2, \]

and because the real part of the silver dielectric constant decreases with increasing wavelength (Figure 1-6 a), the plasmon resonance wavelength for \( \varepsilon_0 > 1 \) is longer than in a vacuum. The plasmon resonance wavelength also gets longer if the particle size is increased above 30 nm. This is due to additional electromagnetic effects that will be discussed later.

Figure 1-6 c) presents the \( l = 2 \) quasistatic (dipole + quadrupole) cross-section as well as the full Mie theory result for a radius 60 nm sphere. The quasistatic result also includes a finite wavelength correction. We see that the dipole plasmon wavelength has shifted to the red, and there is now a distinct quadrupole resonance peak at 357 nm. This quadrupole peak occurs when the real part of the denominator in eq (1.28) vanishes, corresponding to a metal dielectric constant whose real part is -3/2. For a sphere of this size, there are clear differences between the quasistatic and the Mie theory results; however, the important features are retained. Although Mie theory is not a very expensive calculation, the quasistatic expressions are convenient to use when only qualitative information is needed.

### 1.2.3.4 Electromagnetic fields for spherical particles

So far, we have emphasized the calculation of extinction and Rayleigh scattering cross-section; however, for certain properties, such as surface enhanced Raman spectroscopy, SERS, and hyper-Raman scattering (HRS) intensities, it is the electromagnetic field at or near the particle surfaces that determines the measured intensity. Thus, if \( E(\omega) \) is the local field for frequency \( \omega \), then the SERS intensity is
determined by $\langle |E(\omega)|^2 |E(\omega')|^2 \rangle$ where $\omega'$ is the Stokes-shifted frequency and the brackets are used to denote an average over the particle surface. The HRS intensity is similarly (but approximately) determined by $\langle |E(\omega)|^2 |E(2\omega)|^2 \rangle$. Also, when one makes an aggregate or array of metal nanoparticles, the interaction between the particles is determined by the polarization induced in each particle due to the fields $E$ arising from all of the other particles.

At the dipole (dipole + quadrupole) level, the field outside a particle is given by eq

$$E_{\text{out}} = E_0 \hat{x} - \alpha E_0 \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$$  \hspace{1cm} (1. 12)

$$E_{\text{out}} = E_0 \hat{x} + i k E_0 (x\hat{x} + z\hat{z}) - \alpha E_0 \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) - \beta E_0 \left( \frac{x\hat{x} + z\hat{z}}{r^3} - \frac{5z}{r^7} (x^2\hat{x} + y^2\hat{y} + xz\hat{z}) \right) \right]$$  \hspace{1cm} (1. 17)

These expressions determine the near-fields at the particle surfaces quite accurately for small enough particles; however, the field beyond 100 nm from the center of the particle exhibits radiative contributions that are not contained in these equations. To describe these, we need to replace the dipole or quadrupole field by its radiative counterpart. In the case of the dipole field, this is given by

$$E_{\text{dipole}} = k^2 e^{ikr} \frac{r \times (r \times P)}{r^3} + e^{ikr} (1 - i kr) \frac{r^2 P - 3r (r \cdot P)}{r^3}$$  \hspace{1cm} (1. 22)

where $P$ is the dipole moment. Note that this reduces to the static field in eq

$$E_{\text{out}} = E_0 \hat{x} - \alpha E_0 \left[ \frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$$  \hspace{1cm} (1. 12) in the limit $k \to 0$ where only the term in square brackets remains. However, at long range, the first term becomes dominant as it falls off more slowly with $r$ than the second.
Figure 1-7: E-field contours for radius 30 and 60 nm Ag spheres in a vacuum. Two cross-sections are depicted for each sphere. (a, b) The plane containing the propagation and polarization axes and (c, d) the plane perpendicular to the propagation axis. The 30 nm sphere refers to 369 nm light, the main extinction peak for this size, whereas the larger sphere is for 358 nm light, the quadrupole peak for this size. Labeled points 1 and 2 illustrate locations for Figure 1-8. [K. Lance Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, 2003, Journal of Physical Chemistry]

Figure 1-7 presents contours of the electric field enhancement $|E|^2$ around 30 and 60 nm radius silver spheres, based on a Mie theory calculation in which all multipoles are included. Two planes are chosen for these plots, the xz plane that is formed by the polarization and $k$ vectors and the yz plane that is perpendicular to the polarization vector. The wavelength chosen for the 30 nm particle is the dipole plasmon peak, so since the dipole field dominates, we see the characteristic p-orbital shape around the sphere in Figure 1-7 a,c. Note that a small quadupole component to the field makes the p-orbital lobes slightly asymmetrical. At long range, the radiative terms in eq $E_{dipole} = k^2 e^{ikr} \frac{r \times (r \times P)}{r^3} + e^{ikr} (1 - ikr) \frac{r^2 P - 3 r (r \cdot P)}{r^5}$

become more important, and then, the field has a characteristic spherical wave appearance.

The wavelength for the 60 nm particle has been chosen to be that for the peak in the quadrupole resonance, and as a result, the field contours close to the particle in Figure 1-7 b look like a $d_{xz}$-orbital (slightly distorted by a small dipole component that is also present). In addition, Figure 1-7 d, which is a nodal plane for the $d_{xz}$-orbital, only shows the weak dipolar component. Note that the peak magnitude of the field for
the 30 nm particle occurs at the particle surface, along the polarization direction. This peak is over 50 times the size of the applied field, while that for the 60 nm particle is over 25 times larger. This is responsible for the electromagnetic enhancements that are seen in SERS, and they also lead to greatly enhanced HRS.

**Figure 1-8:** Comparison of extinction efficiency, surface-averaged E-field enhancement, and E-field enhancement for specific points for radius 30 nm (top) and 60 nm (bottom) Ag spheres in a vacuum. The two points chosen are point 1, along the polarization direction, and point 2, at a 45° angle relative to the polarization direction and in the \(xz\) plane. [K. Lance Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, 2003, Journal of Physical Chemistry]

Figure 1-8 plots the surface-averaged E-field enhancement for the 30 and 60 nm spheres as a function of wavelength, along with the extinction efficiency. In addition, the figure includes the E-field enhancement associated with two points on the sphere: (a) along the polarization direction (point 1) and (b) rotated 45 degrees away from the polarization direction (point 2). The E-field enhancement associated with specific points on the surface would be appropriate for understanding a single molecule SERS experiment, should this be possible for a spherical particle. For both sphere sizes, the field enhancement due to the dipole resonance peaks to the red of the extinction. Quasistatic theory predicts that both peaks should occur at the same wavelength; however, the finite wavelength corrections to the quasistatic result lead
to depolarization of the plasmon excitation on the blue side of the extinction peak, resulting in a smaller average field and a red-shifted peak.

For the smaller sphere (top panel of Figure 1-8), the E-field enhancement associated with point 1 is about three times larger than the surface-averaged value, and the lineshapes are the same. Point 2 shows a smaller enhancement, and it peaks toward the blue, indicating the influence of a weak quadrupole resonance. For the larger sphere (bottom), the maximum for point 1 is about 3.5 times greater than the surface average for the dipole peak. For point 2, we see a maximum at the quadrupole resonance wavelength, and the enhancement is about three times greater than for the quadrupole peak in the surface-averaged result. Thus, for the larger sphere, it is possible for the largest SERS enhancement to be at a location on the surface that is not along the polarization direction.

1.3 Carbon Nanotubes

Nanotubes were discovered by Iijima in the form of multiple coaxial carbon fullerene shells (multi-wall nanotubes, MWNTs). Later, in 1993 single fullerene shells (single-wall nanotubes, SWNTs) were synthesized using transition metal catalysts. A nanotube can be simply described as a sheet of graphite (or graphene) coaxially rolled to create a cylindrical surface (as shown in Figure 1-9(a)).

\[ \mathbf{C} = n \mathbf{a}_1 + m \mathbf{a}_2 \]

Tubes are called ‘zigzag’ if either one of the integers is zero \((n, 0)\) or called ‘armchair’ if both integers are equal \((n, n)\). [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]

In this way the 2D hexagonal lattice of graphene is mapped onto a cylinder of radius \(R\). The mapping can be realized with different helicities resulting in different
nanotubes. Each nanotube is characterized by a set of two integers \((n, m)\) indicating the components of the chiral vector \(C = na_1 + ma_2\) in terms of the 2D hexagonal Bravais lattice vectors of graphene, \(a_1\) and \(a_2\), as illustrated in Figure 1-9(b). The chiral vector is a circumferential vector and the tube is obtained by folding the graphene such that the two ends of \(C\) are coincident. The radius of the tube is given in terms of \((n, m)\) through the relation 
\[
R = a_0 \sqrt{n^2 + m^2 + nm / 2\pi}
\]
where \(|a_1| = |a_2| = a_0\). When \(C\) involves only \(a_1\) (corresponding to \((n, 0)\)) the tube is called ‘zigzag’, and if \(C\) involves both \(a_1\) and \(a_2\) with \(n = m\) (corresponding to \((n, n)\)) the tube is called ‘armchair’. The chiral \((n, n)\) vector is rotated by \(30^\circ\) relative to that of the zigzag \((n, 0)\) tube. SWNTs are found in the form of nanoropes, each rope consisting of up to a few hundred nanotubes arranged in a hexagonal lattice structure.

1.3.1 Electronic structure

As a nanotube is in the form of a wrapped sheet of graphite, its electronic structure is analogous to the electronic structure of a graphene. Graphene has the lowest \(\pi^*\)-conduction band and the highest \(\pi\)-valence band, which are separated by a gap in the entire hexagonal Brillouin zone (BZ) except at its K corners where they cross. In this respect, graphene lies between a semiconductor and a metal with Fermi points at the corners of the BZ. You can imagine an unrolled, open form of nanotube, which is graphene subject to periodic boundary conditions on the chiral vector. This in turn imposes quantization on the wave vector. This is known as zone folding, whereby the BZ is sliced with parallel lines of wave vectors, leading to subband structure. A nanotube’s electronic structure can thus be viewed as a zone-folded version of the electronic band structure of the graphene. When these parallel lines of nanotube wave vectors pass through the corners, the nanotube is metallic. Otherwise, the nanotube is a semiconductor with a gap of about 1 eV, which is reduced as the diameter of the tube increases. Within this simple approach, \((n, m)\) nanotubes are metallic if \(n - m = 3x\) integer. Consequently, all armchair tubes are metallic. The conclusion that you draw from the above paragraph is that the electronic structures of nanotubes are determined by their chirality and diameter, i.e. simply by their chiral vectors \(C\).

The first theoretical calculations were performed and the above simple understanding was provided much earlier than the first conclusive experiments were carried out.
these early calculations, a simple one-band $\pi$-orbital tight-binding model was used. However, different calculations have been at variance on the values of the band gap. For example, while the $\sigma^*-\pi^*$ hybridization due to the curvature can be treated well by calculations, simple tight-binding methods may have limitations for small-radius nanotubes.

![Figure 1-10](image)

**Figure 1-10:** (a) The band structure, (b) density of states and (c) conductance of a (10, 10) nanotube. The tight-binding model is used to derive the electronic structure. The conductance is calculated using the Green’s function approach with the Landauer formalism. [K. S. Ciraci, A. Buldum, I. P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]

In Figure 1-10(a) and (b) the band structure and density of states (DOS) of a (10, 10) tube are given, based on a tight-binding calculation. Samples prepared by laser vaporization consist predominantly of (10, 10) metallic armchair SWNTs. As can be seen in Figure 1-10 (a), band crossing is allowed, and the bonding $\pi$- and antibonding $\pi^*$-states cross the Fermi level at $k_z = 2\pi/3$.

In Figure 1-10 (b) the density of states is plotted for the (10, 10) tube. The $E^{-1/2}$-singularities which are typical for 1D energy bands appear at the band edges. The curvature of nanotubes introduces hybridization also between $sp^2$ and $sp^3$ orbitals, but these effects are small when the radius of a SWNT is large. However, the $\pi^*$- and $\sigma^*$-state mixing was enhanced for small-radius zigzag SWNTs. Recently, it has been shown that the electronic properties of a SWNT can undergo dramatic changes owing to the elastic deformations. For example, the band gap of a semiconducting
SWNT can be reduced or even closed by the elastic radial deformation. The gap modification and the eventual strain-induced metallization seem to offer new alternatives for reversible and tunable quantum structures and nanodevices.

1.3.2 Quantum transport properties

A nanotube can be an ideal quantum wire for electronic transport; two subbands crossing at the Fermi level should nominally give rise to two conducting channels. Under ideal conditions each channel can carry current with unit quantum conductance $2e^2/h$; the total resistance of an individual SWNT would be $h/4e^2$ or $\sim 6 \text{ kΩ}$. The contribution of each subband to the total conductance is clearly seen in Figure 1-10 (c) illustrating the calculated conductance of the $(10, 10)$ nanotube. The first electronic transport measurements of nanotubes were carried out using MWNTs. These measurements found MWNTs to be highly resistive due to defect scattering and weak localization. The first electronic transport measurements of individual SWNTs and nanoropes were performed by Tans et al. and Bockrath et al. In these measurements nanotubes or nanoropes were placed on an insulating (oxidized silicon) substrate containing metallic electrodes.

(a) An AFM image of a carbon nanotube on top of a Si/SiO$_2$ substrate with Pt electrodes. A gate voltage $V_g$ is applied to the third electrode in the upper left corner to vary the electrostatic potential of the nanotube.

(b) Current–voltage curves of nanotubes for different $V_g$ values (A: 88.2 mV, B: 104.1 mV and C: 120.0 mV).

**Figure 1-11: a) and b) [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]**

In Figure 1-11 (a) an AFM image of an individual SWNT on a silicon dioxide substrate is shown with two Pt electrodes. A gate voltage $V_g$ is applied to the third electrode in the upper left corner to shift the electrostatic potential of the nanotube. The
measurements were performed at 5 mK and step-like features are observed in current–voltage curves shown in Figure 1-11 (b). Note that the voltage scale is mV and these steps are not due to the quantized increase of conductance with subbands shown in Figure 1-10 (c). These steps are due to resonant tunnelling of electrons to the states of a finite nanotube. The presence of metallic electrodes introduces significant contact resistances and changes the bent part of the nanotube into a quantum-dot-like structure. The same phenomena were seen in individual ropes of nanotubes with oscillations in the conductance at low temperatures.

An interesting transport experiment was performed by Frank et al. MWNTs were dipped into liquid metal with the help of a scanning probe microscope tip and the conductance was measured simultaneously. Figure 1-12 (a) and Figure 1-12 (b) show the nanotube contact used in the measurements.

![Figure 1-12](image_url)

**Figure 1-12:** (A) A transmission electron micrograph (TEM) image of the end of a nanotube fibre which consists of carbon nanotubes and small graphitic particles. (B) A schematic diagram of the experimental set-up. Nanotubes are lowered under SPM control to a liquid metal surface. (C) Variation of conductance with nanotube fibre position. Plateaus are observed corresponding to additional nanotubes coming into contact with the liquid metal. [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]

The nanotubes were straight with lengths of 1 to 10 μm. As the nanotubes were dipped into the liquid metal one by one, the conductance increased in steps of $2e^2/h$ as shown in Figure 1-12(c). Each step corresponds to an additional nanotube coming into contact with liquid metal. The electronic transport is found to be ballistic, since
the step heights do not depend on the different lengths of nanotubes coming into
contact with the metal.

1.3.3 Nanotube junctions and devices

Current trends in microelectronics are to produce smaller and faster devices. Owing
to the novel and unusual mechanical and electronic properties, carbon nanotubes
appear to be potential candidates for meeting the demands of nanotechnologies.
There are already nanodevices which use nanotubes. Single-electron transistors
were produced by using metallic tubes; the devices formed therefrom have operated
at low temperatures. For example, a field-effect transistor that consists of a
semiconductor nanotube and operates at room temperature. The nanotube placed on
two metal electrodes and a Si substrate which is covered with SiO₂ is used as a
back-gate. The nanotube is switched from a conducting to an insulating state by
applying a gate voltage.

Two or more nanotubes can form nanoscale junctions with unique properties. A
simple intermolecular nanotube junction can be formed by bringing two tube ends
together. Figure 1-13 (a) illustrates such a junction with two semi-infinite (10, 10)
tubes in parallel and pointing in opposite directions.

![Figure 1-13: (a) An intermolecular nanotube junction formed by bringing two semi-infinite (10, 10) tubes together. l is the contact length. (b) The conductance, G, of a (10, 10)–(10, 10) junction as a function of energy, E, for l = 64 Å. Interference of electron waves yields resonances in conductance. (c) Current–voltage characteristics of a (10, 10)–(10, 10) junction at l = 46 Å. [K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter] These junctions have high conductance values and exhibit negative differential resistance behaviour. Interference of electron waves reflected and transmitted at the]
tube ends gives rise to the resonances in conductance shown in Figure 1-13 (b). The current–voltage characteristics of this junction presented in Figure 1-13 (c) show a negative differential resistance effect, which may have applications in high-speed switching, memory and amplification devices.

A four-terminal junction can be constructed by placing one nanotube perpendicular to another and forming a cross-junction (Figure 1-14 (a)).

![Figure 1-14](image)

**Figure 1-14**: (a) A four-terminal cross-junction with two nanotubes perpendicular to each other. (b) The resistance of an (18, 0)–(10, 10) junction as a function of tube rotation. The rotation angle, Θ, and terminal indices are shown in the inset. The tube which is labelled by 2 and 4 is rotated by Θ. The contact region structure is commensurate at Θ = 30°, 90°, 150°.[K. S. Ciraci, A. Buldum, I.P. Batra, Quantum effects in electrical and thermal transport through nanowires, 2001, Journal of Physics Condensed Matter]

The conductance of such intermolecular junctions strongly depends on the atomic structure in the contact region. Conductance between the tubes was found to be high when the junction region structure was commensurate and conductance was low when the junction was incommensurate. Figure 1-14 (b) shows the variation of the resistance with the rotation of one of the tubes. The junction structure is commensurate at angles 30°, 90° and 150°, and hence the resistance values are lower. Similar variation of the resistance with the atomic structure in the contact region is observed in nanotube–surface systems. This significant variation of transport properties with atomic scale registry was found also in mechanical/frictional properties of nanotubes. Recently, Rueckes et al introduced a random-access memory device for molecular computing which is based on cross-junctions. They showed that crossjunctions can have bistable, electrostatically switchable on/off states and an array of such junctions can be used as an integrated memory device.
1.4 Semiconductor

1.4.1 Introduction

Over decades, the ability to control the surfaces of semiconductors with near atomic precision has led to a further idealization of semiconductor structures: quantum wells, wires, and dots. Ignoring for a moment the detailed atomic level structure of the material, it is possible to imagine simple geometric objects of differing dimensionality (2, 1, and 0), in each case made out of homogeneous semiconductor material and with perfect surface termination. Such structures should exhibit the idealized variations in density of electronic states predicted by simple particle in a box type models of elementary quantum mechanics, with the continuous levels of the 3D case evolving into the discrete states of the 0-dimensional case (Figure 1-15).

![Idealized density of states for one band of a semiconductor structure of 3, 2, 1, and “0” dimensions. In the 3D case the energy levels are continuous, while in the “0D” or molecular limit the levels are discrete. [A.P. Alivisatos, Perspectives on the physical chemistry of semiconductor nanocrystals, 1996, Journal of Physical Chemistry](#) From the perspective of solid state physics and materials science, it is perhaps surprising that nanocrystals of inorganic solids, coated with organic ligands, may prove one of the most diverse and powerful ideals of a “quantum dot.” This is so because, as a molecule, the nanocrystal can now be considered not just a component embedded in the surface of a solid state device, but rather a chemical reagent. In this form the nanocrystal may be dissolved in a fluid, spun into a polymer, attached to an electrical circuit, bound to other nanocrystals as dimers, trimers, etc. or someday perhaps bound to biological molecules. It is important to realize that, in the construction of optical and electronic materials using components of nanometer size, it is not only the physical properties of matter that change but also the chemical methods by which the materials are constructed.
1.4.2 Band Gap modification

Independent of the large number of surface atoms, semiconductor nanocrystals with the same interior bonding geometry as a known bulk phase often exhibit strong variations in their optical and electrical properties with size. These changes arise through systematic transformations in the density of electronic energy levels as a function of the size of the interior, known as quantum size effects. Nanocrystals lie in between the atomic and molecular limit of discrete density of electronic states and the extended crystalline limit of continuous bands (Figure 1-16).

![Figure 1-16: Density of states in metal (a) and semiconductor (b) nanocrystals. In each case, the density of states is discrete at the band edges. [A.P. Alivisatos, Perspectives on the physical chemistry of semiconductor nanocrystals, 1996, Journal of Physical Chemistry]](image)

1.4.2.1 Quantum Size Effects

The most striking property of semiconductor nanocrystals is the massive changes in optical properties as a function of the size. As size is reduced, the electronic excitations shift to higher energy, and there is concentration of oscillator strength into just a few transitions. These basic physical phenomena of quantum confinement arise by changes in the density of electronic states and can be understood by
considering the relationship between position and momentum in free and confined particles:

\[ \Delta p \Delta x \geq \hbar / 2 \]  \hspace{1cm} (1.23)

For a free particle or a particle in a periodic potential, the energy and the crystal momentum \( \hbar k \) may both be precisely defined, while the position is not. As a particle is localized, the energy may still be well-defined; however, the uncertainty in position decreases, so that momentum is no longer well-defined. The energy eigenfunctions of the particle may then be viewed as superpositions of bulk \( k \) states. In the extended case, there is a relationship between energy and momentum, and to a first approximation, the change in energy as a function of the size can be estimated simply by realizing that the energy of the confined particle arises by superposition of bulk \( k \) states of differing energy.

For a free particle, the dependence of energy on wavevector is quadratic:

\[ E = \hbar k^2 / 2m \]  \hspace{1cm} (1.24)

In the effective mass approximation, this relationship is assumed to hold for an electron or hole in the periodic potential of the semiconductor, with a reduced mass which is inversely proportional to the width of the band. Given the relationship between confinement in space and momentum superposition, this leads directly to the approximate dependence of energy on size as \( 1/r^2 \), as expected for a simple particle in a box. For large sizes, the approximation is nearly correct but breaks down for even moderately sized because energy does not depend quadratically on \( k \) in real crystallites.

To gain a physical understanding of the variation of \( E \) with \( k \), it is at this point useful to switch to a molecular picture of bonding in the solid (Figure 1-17) and of the quantum confinement process.
The single-particle wave functions for electrons and holes in the extended solid can be viewed as linear combination of unit cell atomic orbitals, multiplied by phase factors between the unit cells. When all the cells are in phase, the wavevector, \( k = (2\pi/\lambda) \), is equal to 0; when adjacent cells are out of phase, \( k \) takes on its maximum value, \( \pi/a \). In a simple one-dimensional single band tight binding model, the dependence of \( E \) on \( k \) is

\[
E = \alpha + 2\beta \cos(ka)
\]

(1.25)

where \( \alpha \), the energy of the linear combination of atomic orbitals inside the unit cell, determines the center position of the band in energy. \( 2\beta \) gives the width of the band and is directly related to the strength of nearest-neighbor coupling and inversely proportional to the effective mass. An expansion of the \( \cos(ka) \) term for small \( k \)
yields a quadratic term as its first term, so that one can see why the effective mass approximation only describes the band well near either its minimum or its maximum. Considering now a real binary semiconductor, such as CdSe, the single particle states can be viewed as products of unit cell atomic orbital combinations and phase factors between unit cells (Figure 1-17 A). For example, the highest occupied molecular orbital or top of the valence band may be viewed as arising from Se 4p orbitals, arranged to be in phase between unit cells. This will be the maximum of the valence band, since adjacent p orbitals in phase are $\sigma$-antibonding (and $\pi$-bonding). Similarly, the lowest unoccupied molecular orbital will be comprised of Cd 5s atomic orbitals, also in phase between unit cells. This is the minimum of the conduction band, since s orbitals in phase constructively interfere to yield a bonding level. In this case, the minimum of the conduction band and the maximum of the valence band have the same phase factor between unit cells.

1.4.2.2 Quantization and energy level spacing

As the size is reduced, the electronic states may be viewed as superpositions of bulk states. Hence, there is a shift to higher energy, the development of discrete features in the spectra, and concentration of the oscillator strength into just a few transitions. Qualitatively, all of these effects can be readily observed in the spectra of Figure 1-18, which show data for CdSe.

![Figure 1-18: Optical absorption vs size for CdSe nanocrystals shows the shift to higher energy in smaller sizes, as well as the development of discrete structure in the spectra and the concentration of oscillator strength into just a few transitions. [A.P. Alivisatos, Perspectives on the physical chemistry of semiconductor nanocrystals, 1996, Journal of Physical Chemistry](image)]
The quantitative analysis of these spectra remains a difficult subject, for several reasons:

- The foregoing picture is a single-particle one and does not include the substantial effects of correlation. In molecules this is analogous to trying to use the highly approximate molecular orbital theory, instead of more advanced quantum chemistry methods. Regrettably, the nanocrystals are too large to describe using even moderately advanced methods that are routinely applied to small molecules.

- Further, in CdSe at least, the large atomic number of the Se ensures that the coupling between spin and orbital momenta is very strong in the valence bands (p bands). This coupling is in the \( j-j \), and not the Russell-Saunders, \( L-S \), coupling regime. When translational symmetry is removed, the mixing of \( \mathbf{k} \) vectors can also result in different bands mixing together.

- The shape of the crystallites, which is regular (tetrahedral, hexagonal prisms), or spherical, or ellipsoidal, will determine the symmetry of the nanocrystals and will influence the relative spacing of the levels.

- Finally, surface energy levels are completely excluded from this simple quantum confinement picture. Yet it seems apparent that surface states near the gap can mix with interior levels to a substantial degree, and these effects may also influence the spacing of the energy levels.

Theoretical approaches that directly include the influence of the surface, as well as electronic correlation, are being developed rapidly.

1.4.3 Electrical properties

We talk about single-electronics whenever it is possible to control the movement and position of a single or small number of electrons. To understand how a single electron can be controlled, one must understand the movement of electric charge through a conductor. An electric current can flow through the conductor because some electrons are free to move through the lattice of atomic nuclei. The current is determined by the charge transferred through the conductor. Surprisingly this transferred charge can have practically any value, in particular, a fraction of the charge of a single electron. Hence, it is not quantized.
This, at first glance counterintuitive fact, is a consequence of the displacement of the electron cloud against the lattice of atoms. This shift can be changed continuously and thus the transferred charge is a continuous quantity (see left side of Figure 1-19).

**Figure 1-19**: The left side shows, that the electron cloud shift against the lattice of atoms is not quantized. The right side shows an accumulation of electrons at a tunnel junction.

If a tunnel junction interrupts an ordinary conductor, electric charge will move through the system by both a continuous and discrete process. Since only discrete electrons can tunnel through junctions, charge will accumulate at the surface of the electrode against the isolating layer, until a high enough bias has built up across the tunnel junction (see right side of Figure 1-19). Then one electron will be transferred. Likharev has coined the term ‘dripping tap’ as an analogy of this process. In other words, if a single tunnel junction is biased with a constant current \( I \), the so called Coulomb oscillations will appear with frequency \( f = \frac{I}{e} \), where \( e \) is the charge of an electron (see Figure 1-20).

**Figure 1-20**: Current biased tunnel junction showing Coulomb oscillations.
Charge continuously accumulates on the tunnel junction until it is energetically favorable for an electron to tunnel. This discharges the tunnel junction by an elementary charge $e$. Similar effects are observed in superconductors. There, charge carriers are Cooper pairs, and the characteristic frequency becomes $\omega = I/2e$, related to the so called Bloch oscillations.

**Figure 1-21:** The electron-box can be filled with a precise number of electrons.

The current biased tunnel junction is one very simple circuit, that shows the controlled transfer of electrons. Another one is the electron-box (see Figure 1-21). A particle is only on one side connected by a tunnel junction. On this side electrons can tunnel in and out. Imagine for instance a metal particle embedded in oxide, as shown in Figure 1-22.

**Figure 1-22:** Metal particle embedded in oxide. Tunneling is only possible through the thin top layer of oxide.

The top oxide layer is thin enough for electrons to tunnel through. To transfer one electron onto the particle, the Coulomb energy $E_C = e^2/2C$, where $C$ is the particles capacitance, is required. Neglecting thermal and other forms of energy, the
only energy source available is the bias voltage $V_b$. As long as the bias voltage is small enough, smaller than a threshold $V_{th} = e/C$, no electron can tunnel, because not enough energy is available to charge the island. This behavior is called the Coulomb blockade. Raising the bias voltage will populate the particle with one, then two and so on electrons, leading to a staircase-like characteristic.

It is easily understandable, that these single-electron phenomena, such as **Coulomb oscillations** and **Coulomb blockade**, only matter, if the Coulomb energy is bigger than the thermal energy. Otherwise thermal fluctuations will disturb the motion of electrons and will wash out the quantization effects. The necessary condition is,

$$E_c = \frac{e^2}{2C} > k_BT$$

(1.26)

Where $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature. This means that the capacitance $C$ has to be smaller than 12 nF for the observation of charging effects at the temperature of liquid nitrogen and smaller than 3 nF for charging effects to appear at room temperature. A second condition for the observation of charging effects is, that quantum fluctuations of the number of electrons on an island must be negligible. Electrons need to be well localized on the islands. If electrons would not be localized on islands one would not observe charging effects, since islands would not be separate particles but rather one big uniform space. The charging of one island with an integer number of the elementary charge would be impossible, because one electron is shared by more than one island. The Coulomb blockade would vanish, since no longer would a lower limit of the charge, an island could be charged with, exist. This leads to the requirement that all tunnel junctions must be opaque enough for electrons in order to confine them on islands. The ‘transparency’ of a tunnel junction is given by its tunnel resistance $R_T$ which must fulfill the following condition for observing discrete charging effects, where $h$ is Planck’s constant. This should be understood as an order-of-magnitude measure, rather than an exact threshold.

$$R_T > \frac{h}{e^2} = 25813\Omega$$

(1.27)

Therefore, these effects are experimentally verifiable only for very small high-resistance tunnel junctions, meaning small particles with small capacitances and/or
very low temperatures. Advanced fabrication techniques, such as the production of granular films with particle sizes down to 1 nm, and deeper physical understanding allow today the study of many charging effects at room temperature. Based on the Coulomb blockade many interesting devices are possible, such as precise current standard, very sensitive electrometers, logic gates and memories with ultra low power consumption, down-scalability to atomic dimensions, and high speed of operation. Altogether, single-electronics will bring new and novel devices and is a very promising candidate to partly replace MOS technology in the near future.

1.4.4 Optical Properties

1.4.4.1 Line widths: Size distributions and intrinsic broadening

As a consequence of their being a new type of material, the properties of semiconductor nanocrystals can be expected to evolve with improvements in sample preparation. Spectra which at first seemed featureless and diffuse have gradually acquired definition, with multiple discrete states apparent in the latest generation of samples. Essentially all of this progress derives from narrowing the distribution of sizes in the sample. Since the energies of the transitions depend so strongly on the size, size variation is a special form of inhomogeneous broadening at work here, which over time has been largely reduced. Today it is really the intrinsic, or single particle, line widths that are a matter of greater concern.

Illuminescence and electroluminescence

Narrow band (15-20 nm), size-tunable luminescence, with efficiencies at least of order 10%, is observed at room temperature from semiconductor nanocrystals. The origin of this luminescence remains the topic of some controversy. For some time researchers thought that this luminescence arose from partially surface trapped carriers. Other experiments strongly suggest that the luminescence in fact arises from low-lying “dark” states of the nanocrystal interior, and surface modifications only influence the quantum yield by modulating the non radiative rates. Just as in organic molecules a singlet state may be optically prepared, followed by rapid relaxation to triplet states with long decay times, so in semiconductor nanocrystals, where \( j-j \) coupling dominates, an angular momentum allowed state is initially prepared, and on the time scale of picoseconds or longer, there is a decay to a lower lying angular-
momentum-forbidden state, which decays relatively slowly (nanoseconds to microseconds). One success of this dark state model is the accurate prediction that the magnitude of the exchange splitting increases as $r^{-3}$, thus explaining one long puzzling feature of the luminescence. As the size is reduced, the shift between the absorbing and emitting state is observed to increase. The rigorous separation of interior and surface states is somewhat artificial in nanocrystals in any case, since substantial mixing may be expected. Indeed, other features of the spectra suggest that there may well be substantial surface character associated with the emitting state. For example, electric field modulation of the luminescence yields signals a factor of 100 or larger than modulation of absorption, indicating that the emitting state is not as well confined spatially. Further evidence for surface localization of the emitting state comes from low-temperature studies of the vibronic coupling of the emission, which show that there is a well-defined localization temperature.

Independent of the exact origin of the luminescence, it does appear to be one property which can be manipulated in useful ways. For example, two reports of light-emitting diodes made with polymers and CdSe nanocrystals have appeared within the past year. In the first instance, nanocrystals were assembled in layers a few nanocrystals thick on the surface of PPV, an electroluminescent polymer. The PPV itself was grown on a layer of indium tin oxide, a transparent hole-injecting contact. Finally, the nanocrystal layer was coated with a film of Mg/Ag, the electron-injecting contact. This complete assembly electroluminesces when a voltage is applied. The recombination of electrons and holes may take place either in the polymer layer (which emits green light) or in the nanocrystal layer. The nanocrystal emission shifts with size. Thus, these LEDs provide a variety of means for tuning the output color. This advance is particularly important, since it constitutes the first example of electrical, rather than purely optical, investigation of semiconductor nanocrystals.

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