High-Current Field Emission from an Atomic Quantum Wire

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Abstract

Linear chains of carbon atoms have been proposed as the electron emitting structures of open tip carbon nanotubes subject to an electric field. To better understand the implications of the results of Smalley and collaborators, the electromagnetic response of linear carbon chains to both static and dynamics fields have been studied, making use of ab-initio methods. It is found that the associated emission currents, plotted as a function of the bias potential, follow Fowler-Nordheim intensity-voltage curves typical of the field emission of metallic tips. Under standard bias conditions, linear carbon chains of one nanometer of length are expected to deliver currents of the order of one microampère. These systems behave, furthermore, as conducting needles in photoabsorption processes. Linear carbon chains are thus likely to constitute the ultimate atomic-scale realization of metallic wires.
In studying the field emission of electrons from individually mounted carbon nanotubes, Smalley and collaborators have found a conspicuous increase of the yield when the nanotube tips were opened by laser evaporation, an increase which became accentuated when the open tips cooled down to room temperature. This behaviour lead the authors to conclude that the emitting structure was an “atomic wire” of 10 to 100 sp-bonded carbon atoms pulled from the open graphene sheet of the nanotube by the electric field.

Triggered by these remarkable results, we have studied the quantal properties of $C_n$ chains ($n = 3 - 11$), making use of ab-initio methods. We have found that when the linear chains of carbon atoms, which display an electronic structure very close to the cumulenic form ($\cdots = C = C = C = C :$), are subject to a bias field of intensity $0.6 - 0.7 \text{ V/Å}$, currents of the order of $1 \mu \text{A}$ are obtained, in overall agreement with the experimental findings. Even-n chains lead to currents which are a factor $\approx 10^2$ more intense than those associated with the field emission of electrons from odd-n chains. Shining photons on the $C_n$ chains leads to a frequency-dependent photoabsorption cross section which essentially coincides with that of a classical metallic needle of the same shape. These results lend strong support to the conjecture that linear chains of carbon atoms can be viewed as atomic-scale metallic wires. The electronic structure calculations of the $C_n$ chains have been carried out in the local density approximation (LDA) including exchange-correlation effects according to the parametrization of Perdew and Zunger, while the role of the carbon atoms were taken into account in terms of norm-conserving pseudopotentials. The resulting bond length is constant and equal to $1.31 \text{ Å}$ for n-odd chains, while it alternates by less than 2% around this value in the case of n-even chains. The constancy of the bond length can be seen from Fig.1(A), where the electronic density of the linear chain $C_8$ is displayed. It is also found an almost complete screening of the field along the chain, as it is the case for perfect conductors (Fig.1(B), cf. also ref. [5]).

The electron emission characteristic were calculated in the WKB approximation making use of the LDA potential felt by the electron. Typical current versus voltage (I-V) curves are shown in Fig. 2. They can be compared with the Fowler-Nordheim equation for the field
emission \( I = aF^2 \exp(-b/F) \), where \( a \) and \( b \) are constants that depend on the electronic work-function of the system as well as on the image correction term, a quantity which depends weakly on the electric field strength at the emitting surface \( F = V/kR_0 \). Here \( R_0 \) is the radius of the tip and \( k \) is a constant of the order of 10. Making use of the fact that the linear chains under discussion have a value \( R_0 \approx 1.2\AA \) and of the results shown in Fig.2, it is seen that emission currents of the order of 1 \( \mu \)A are obtained with a bias voltage \( V \) of the order of 40V, in overall agreement with the experimental findings. Because the emitted electrons arise essentially from the occupied levels lying closest to the Fermi energy (HOMO), the emitted electrons are rather monoenergetic with energies that fluctuate less than 5 % around the mean value of 5eV.

To gain further insight into the properties of the \( C_n \)-chains, we have subject them to a time dependent electromagnetic field. The associated longitudinal photoabsorption cross section calculated in the time-dependent LDA (cf. ref. [4]), essentially displays a single peak which collects \( \approx 90\% \) of the oscillator strength. The corresponding energy centroids \( \hbar \omega(C_n) \) are displayed in Fig.3. Theory provides an excellent account of the experimental findings [13] (cf. also ref. [12]).

The values of \( \hbar \omega(C_n) \) shown in Fig.3 can be compared with the results of the relation \( \hbar \omega_s = \sqrt{L} \hbar \omega_0 \) (cf. refs. [14] and [12]). This expression is a generalization of the Mie resonance expression, and describes the surface plasmon of elongated metallic particles, in terms of the bulk plasmon frequency \( \omega_0 \). The quantity \( L = \frac{1-e^2}{e^2} (-1 + \frac{1}{2e \log(1+e)}) \) is the depolarization factor for vibrations along the symmetry axis of the system. The quantity \( e \) is related to the ratio of short to long axis \( R_\perp/R_\parallel \) according to \( e^2 = 1 - (R_\perp/R_\parallel)^2 \). The quantity \( \hbar \omega_s \) provides a very good fit to the centroid energies \( \hbar \omega(C_n) \) with \( \hbar \omega_0 = 24 \text{eV} \) (cf. Fig.3). This value is quite close to the one obtained inserting, in the standard plasmon relation \( \omega_0^2 = 4\pi e^2 n/m \), the density of graphite.

We have also calculated the polarizability of the system, and displayed it in Fig.4. These results can again be compared with the polarizability associated with a perfect conductor of the same dimension, that is \( \alpha_s = v[(\epsilon-1)/(1+L(\epsilon-1))] \) (cf.ref. [15]). In this expression \( v \) and
$\epsilon$ are the volume and the dielectric constant of the system, respectively. The long wavelength limit of the time dependent LDA results are accurately reproduced by the function $\epsilon = 0.34N^{1.24} + 1$, which already for a 10 nm linear chain leads to a dielectric constant of the order of $10^2$, indicating the conducting properties of the system.

Linear carbon chains seem to pass with ease, some of the most obvious and stringent tests needed to qualify as metallic atomic wires. In particular, chains with an even number of atoms behave as prolific emitters of monoenergetic electrons as well as sensitive antennas.

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[9] In keeping with this discussion, it is noted that for one-dimensional systems like the ones under discussion, quantal size effects (QSE) are of importance, and the total current emitted under the influence of an external electric field is the summed contribution of each single-particle quantum level. Thus, the equivalent to the Fowler-Nordheim (FN) equation for field emission from a carbon chain, taking into account QSE is \( I = a'F \exp(b'/F) \), that is, a relation similar to the FN-equation but with a prefactor linear in the electric field. While the standard FN-equation provides a reasonable fit to the numerical results displayed in Fig.2, the results of the expression linear in F essentially coincides with the WKB results.

[10] To be noted is that even-n carbon chains are stable when they are closed [11,12]. Under the influence of an external field these chains can be assumed to be linear, and the plasmon frequency essentially coincides with that of the neighbouring odd-n Carbon
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FIG. 1. (A) Electronic density of C\textsubscript{8} calculated in the local density approximation as described in the text. (B) Difference \(\Delta U\) between the total potential felt by the electrons when the C\textsubscript{8}-chain is subject to an electric field \(F = 0.8\) eV/Å, and when the external field is switched off.
FIG. 2. Current $I$ (in nA) versus electric field $(V/\text{Å})$ for two typical $C_n$-chains, as calculated in the WKB approximation making use of the LDA self-consistent potential.

Inset) Fowler-Nordheim plot, that is the quantity $(I/F^2)$ is displayed as a function of $1/F$. The linearity of this curve testifies to the fact that the calculated field emission follows the pattern expected for electron emission from a metallic system.
FIG. 3. Energy centroids $\hbar \omega (C_n)$ for linear carbon chains with $n = 3 - 11$, calculated in the time dependant LDA (solid dots), in the comparison with the experimental findings [13]. The continuous curve displays the results of the relation $\hbar \omega_s = \overline{\hbar \omega}_0 [15]$ (cf. text).
FIG. 4. Polarizability for carbon chains with $n = 3 - 11$ atoms, calculated in the long wavelength limit of the time dependent LDA. The continuous curve displays the results of the relation

$$\alpha_s = v[(\epsilon - 1)/(1 + L(\epsilon - 1))]$$

with $\epsilon = 0.34N^{1.24} + 1$ (cf. text and ref. [15]).