Bands of Image States in Nanowire Lattices and Infrared-Control of Proteins on Nanotube Ropes

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Abstract: We show that suspended arrays of parallel nanowires support bound electron image states with rich band structures. These states could be controlled by electric and magnetic fields and used in building of waveguides, mirrors, and storage places for Rydberg-like electrons. We also exploit the possibility of controlling proteins attached to hybrid nanotube ropes. Near infrared excitation of such ropes causes their depolarization, leading to the change of protein’s conformation.

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ELECTRON IMAGE STATES IN ARRAYS OF PARALLEL NANOWIRES

Atomic and molecular systems support extended Rydberg-electron states that can preserve their coherence properties for a relatively long time (1). Extended electron states are also formed above bulk metals, when an electron above the surface is attracted to its oppositely charged image in the material (2). Unfortunately, practical applications of these states are limited by their picosecond lifetimes, mostly given by their spatial overlap with the surface states of the material.

Recently, we discovered a new class of electronic image states, which are highly detached from the material surface (3). They are formed above freely suspended cylindrical nanowires, such as metallic carbon nanotubes, when they carry a nonzero angular momentum, $l$. The resulting centrifugal barrier protects the electronic wave functions from a radial collapse on the material surface, thus prolonging their lifetimes. We have shown that the image states can be longitudinally localized along the nanowire axis by designed inhomogeneities (4) (see Fig. 1, left), and can be tuned by external electric and magnetic fields (5). Damping of their angular momenta is relatively slow, due to emission of phonons with “string-like” deformations of the nanowires (6). Recently, the predicted image states were observed experimentally above nanotubes (7). These tunable states would create opportunities for developing unique electronic devices.

Here, we briefly describe electron image states formed in arrays of parallel nanowires (8), which can serve as basic building blocks in nanoscale devices for “Rydberg-like electronics.” In Fig. 1 (right), we show the general configuration of such a periodic array of parallel (10, 10) metallic nanotubes, of radius $a = 0.68$ nm, surrounded by the electron image states. The tubes are aligned along the $z$ direction, with their axes placed at the $x = pd$ and $y = qd$ positions ($p, q = 0, \pm 1, \pm 2, \ldots$; with

Figure 1. Electron image states above a nanotube heterojunction (left) and arrays of parallel nanowires (right).
q = 0, for a 1D array), where d is the lattice constant. Typically, d/a = 10–100 and the image-state energies are proportionally decreased with respect to those in solids.

In the first approximation, we can model each of the linear conductors by a metallic cylinder of radius a. A point charge, at distances ρ₀ ≫ a above the cylinder, generates a potential Φ₀, which polarizes the tube and induces the potential Φ_{ind}. The total potential Φ_{tot} = Φ₀ + Φ_{ind} vanishes at the metallic nanotube surface, and this determines Φ_{ind}(ρ, φ, z). The electron potential energy is given by V(ρ) = (1/2) e Φ_{ind}(ρ, 0, 0), which at ρ₀ ≫ a can be approximated by (3)

\[
V(ρ) ≈ \frac{2e^2}{πa} \sum_{n=1,3,5,...} \ln[(a/ρ)^n], \quad \ln(x) = \int_0^x \frac{dt}{\ln(t)}
\]

In a single-nanowire, the effective potential energy of the image-state electron, V_{eff}(ρ) = V(ρ) + 2 (l² - (1/4))/(2mₑ ρ²), is composed of the attractive induced part and the repulsive centrifugal term. The wave functions, \(ψ_{n,l,k}(ρ, φ, z) = \psi_{m,k}(x, y) e^{ikφ} φ_k(z)/\sqrt{2 \pi ρ}\), have the eigenenergies E_{n,l,k} = E_{n,l} + E_k, where E_{n,l} ≈ 1 – 10 meV is related with the radial electron motion, and E_k is the kinetic energy for the longitudinal motion along the wire. The states with angular momenta l > 5 are radially separated 10 – 50 nm from the surface (3) and can be axially localized by inhomogeneities in the wire (4).

In a 1D array of nanotubes (see Fig. 1, right), the total attractive potential fulfills V_T(x, y) = V_T(x + R, y) for all R in a Bravais lattice. Thus, the transverse Bloch components of the total wave functions \(ψ(x, y, z) = ψ_{m,k}(x, y) φ_k(z)\), with energies \(ε_{m,k} + E_k\), fulfill

\[
ψ_{m,k}(x, y) = e^{ikx}f_{m,k}(x, y) = e^{ikx}f_{m,k}(x + R, y)
\]

They can be obtained from the Schrödinger equation parameterized by k as,

\[
\left\{-\frac{\hbar^2}{2m_e} \left( \frac{∂}{∂x} + ik \right)^2 + \frac{∂^2}{∂y^2} \right\} + V_T(x, y) \right\}f_{m,k}(x, y) = ε_{m,k}f_{m,k}(x, y)
\]

We can apply an analogous expression, with the k = (kₓ, kᵧ) wave vectors, for a 2D (square) lattice of nanotubes. We solve Eq. (3) numerically, using a multidimensional discrete variable representation (DVR) algorithm (9). For simplicity, we use the single-tube potential (1), and include in V_T the interaction due to the central tube in the cell and its neighbors.

We briefly examine a square 2D arrays of nanotubes, where the unit cell spans the region from −d/2 to d/2 on both axes. In Fig. 2, we display an example of 2D-wave function densities. In the left panel, we show for d = 50 nm the probability density of a state, of an approximate l = 6 and n = 2 nodal counting, which is detached from the tubes’ surfaces. It corresponds to the Γ point in Fig. 2 (right). In contrast, as we move through the band to the X
point, the state partially collapses on the tubes’ surfaces (central panel). Similar states can also be obtained for other distances of the nanotubes (8).

In Fig. 2 (right), we present the band structure for the 2D-lattice of nanotubes, with \( d = 50 \text{ nm} \), between the \( \Gamma (k = (k_x, k_y) = (0, 0)) \), \( X (k = (\pi/d, 0)) \) and \( M (k = (\pi/d, \pi/d)) \) points. We display the (50-73)-th bands, where the square (circle) denotes the \( X (\Gamma) \) point of the 68 (70)-th band, with wave function densities plotted in Fig. 2’s central (left) panel. The band gaps present at lower energies could block the transport of Rydberg-like electrons. Higher bands \((m > 60)\) are broader and denser, causing a number of avoided crossings and the band gaps to disappear. These bands of image states could be used in building of waveguides, mirrors and storage places for Rydberg-like electrons. They also play a role when molecules are adsorbed on the nanotubes, as we show below.

**CONTROL OF PROTEINS ON NANOTUBES**

Biosystems and artificial nanosystems can coexist and supplement each other in a number of directions, in particular, during the release of drugs (11). Their coevolution can lead to the formation of new hybrid bio-nano systems, with unprecedented organizational and functional level. A potentially interesting hybrid system can be obtained from nanotubes dressed with bio-molecules, via structure-selective (12, 13) or less specific hydrophobic coupling (14).

Here, we discuss the use of a near-infrared (NIR) radiation (0.74–1.2 \( \mu \text{m} \)) for control of proteins attached to nanotubes (15). We consider a hybrid nanotube rope, which is formed of two adjacent metallic C nanotubes, where one is (peapod) filled with metallofullerenes and the other is empty. In isolated metallofullerenes like \( \text{Dy@C}_{82} \), several electrons are passed from Dy to \( \text{C}_{82} \). When these are used in a peapod, the transferred electrons can be passed further to the nanotube (16). In a double-rope formed by this peapod and a “twin” (empty) nanotube, the last would absorb the excessive
charge too, so the two would become oppositely charged. This process can be partly inverted at elevated temperatures, obtained during NIR-excitation.

In Fig. 3, we schematically show this NIR-control of protein (enzyme) activity. The NIR-excitation heats the two nanotubes, so that electrons, released in equilibrium from the fullerenes to the peapod (16) and the twin tube, are transferred back. This resulting recharging of the tubes and the change of the local electric field causes deformation of proteins (17, 18), which are selectively attached to the nanotubes. Their new conformation can have different catalytic activity (19). The system thus works in an opposite way than some biosensors (20), where antibodies bind to proteins attached to material surfaces, bend them, and thus change the surface electric parameters. We can tune the system by using different nanotubes, fullerenes and their filling, and especially proteins, to be controlled. The attached proteins might also help to dissolve the hydrophobic nanotubes in water.

We consider that the system is formed by two metallic (10, 10) carbon nanotubes of the radius $r_T \approx 0.68\,\text{nm}$, where one of them is the peapod. In a double-rope (21, 22), their centers are separated by $D_T \approx 1.7\,\text{nm}$, which determines the tunneling time, $\tau_T \approx 1\,\text{ps}$, of electrons between the tubes. The fullerenes are separated one from another by $d_F \approx 2\,\text{nm}$ (23).

We can excite the metallic nanotubes at deliberate NIR frequencies. By using some assumptions about the NIR-induced recharging (15), we obtain the induced linear charge density $\sigma = 0.2\,e/d_F \approx 0.1\,\text{e nm}^{-1}$ in each nanotube. From this $\sigma$, we can calculate the change of electric field between the two tubes. If these two are ideal metallic cylinders of the length $L$, their electric capacity is (10) $(\varepsilon = \varepsilon_0\varepsilon_r)\,C = \pi\varepsilon L/\cos\theta^{-1}(D_T/2\tau_T)$. Thus, the potential difference between them is $\Delta \phi = \sigma L/C \approx 0.1\,\text{V}$, where we use the permittivity of water $\varepsilon_r \approx 4.6$. Similar voltage was used in manipulation of proteins attached to metals (10).

Activation of the attached protein by this NIR-radiation induced potential can be realized by moving a charged tip of one of its domains (20) (see Fig. 3). We model this process, by evaluating the total potential energy of the system

![Figure 3](image.png)

**Figure 3.** (Left) Scheme of a hybrid nanotube system that controls protein activity. (Right) The related bend and shear types of protein motion.
and using it to find the protein conformation with a minimal energy. To do so, let us first find the potential energy of a charge \( q \) at the position \( \mathbf{r} = (x, y) \). The two cylinders with charge densities \( \sigma \) and \( -\sigma \) have their centers at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), respectively. The potential energy of the charge \( q \) is formed by the direct Coulombic component (10)

\[
V_C(\mathbf{r}) = -\frac{\sigma q}{2\pi\epsilon} \ln \left( \frac{|\mathbf{r} - \mathbf{r}_1|}{|\mathbf{r} - \mathbf{r}_2|} \right),
\]

which can be either positive or negative, depending on which of the oppositely charged tubes is closer. It also has a negative screening component (3), originating in the reflection of the external charge in the metallic tube, which close to the surface of both tubes has the form

\[
V_S(\mathbf{r}) \approx -\frac{q^2}{16\pi\epsilon} \left( \frac{1}{|\mathbf{r} - \mathbf{r}_1| - r_T} + \frac{1}{|\mathbf{r} - \mathbf{r}_2| - r_T} \right).
\]

Here, we simply add the screening potentials of the two tubes, neglecting thus multiple reflections.

We also need to estimate the deformation energy \( V_R(\mathbf{r}) \) of the protein. Typically, structural domains in proteins perform hinge or shear motion (17, 18). These domains are often formed by (rigid) \( \alpha \)-helices, connected by (flexible) \( \beta \)-sheets. The structures (conformations) of deformed proteins in nature are usually close in energies, so that they can be flipped over by room temperature energies \( k_B T \) (17). The different conformations of the externally controlled proteins should be more energetically distant.

In the present system, where the control of protein’s motion is realized via dynamical charging of nanotubes, we can also consider these two generic (hinge and shear) configurations, shown schematically in Fig. 3 (right panel). Since, the tubes are different and become charged in equilibrium, the proteins should be able to distinguish them and deposit on them asymmetrically. In the bend configuration (left), the trajectory of the controlled protein domain is practically vertical, toward one of the tube’s centres. In the shear configuration (right), the trajectory of the domain goes approximately in parallel with the vector connecting the tube’s centers of masses.

We assume that the balance of internal forces in the protein, in the presence of equilibrium charging of the tubes, adjusts the charged tip to a position \( \mathbf{r}_0 = (x_0, y_0) \). The dependence of the protein energy around (close to) this position can be considered to be

\[
V_R(\mathbf{r}) \approx C_x(x - x_0)^2 + C_y(y - y_0)^2,
\]

where the constants \( C_x, C_y \) describe rigidity of the deformed protein (18). Their values should be such that the difference in energies \( \Delta E \) between the used conformations is \( k_B T \leq \Delta E < 100 \text{kJ/mol (1 eV)} \), where the last value is the lower energy limit required to deform individual protein domains (18).

Finally, we estimated which of the configurations, in Fig. 3, can be more easily controlled. We have calculated (15) the distance over which the protein
domains move during the NIR-radiation induced charge transfer. The tip moves from the equilibrium position \( r_0 \) to a new position \( r_0' \), given by the local minimum of the total potential, \( V_T(r) = V_C(r) + V_R(r) \). The results show that the “hinge” configuration, in Fig. 3 (left), gives a rather small motion. On the other hand, the “shear” configuration, shown in Fig. 3 (right), leads to a shift of the domain of the size \( \approx 0.3 \text{ nm} \). This might be sufficient to change the protein’s conformation and thus its activity in vivo. Since the two conformations are shifted in energy by \( \Delta E \approx 50 \text{ meV} \), they would not flip one to another at room temperatures \( kT < 30 \text{ meV} \) or during the irradiation, causing heating of the system. In the first approximation, we could thus neglect the effect of temperatures on the protein motion. At the same time, we can protect the rest of the biosystem from heating by putting the double-tube system in liposomes with a large surface. We are also studying other mechanisms of controlling catalytic activities of molecules adsorbed on nanotube surfaces.

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