

Polarization Component of Cohesion Energy in Single–Wall Carbon Nanotube–DNA Complexes[¶]

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Within the framework of a quantum mechanical model, the polarization component of the energy of cohesion of an ionized DNA molecule to the surface of a nanotube has been calculated. Neglecting the polarization of the DNA, and in the absence of external screening, the binding energy is ~ 0.47 eV per elementary charge. The effective nanotube screening parameter is ~ 2 and cannot be reduced to classical expressions for metallic and dielectric screening.

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1. INTRODUCTION

Our study deals with the nature of binding between a single-wall carbon nanotube and DNA that makes a periodic spiral wrap around the surface of the cylinder of the nanotube. The experimental data confirming formation of such complexes may be found in a number of papers [1–3]. At present, it is accepted that the binding of the complex is noncovalent. It is established that there exists a van der Waals component of the cohesion energy of the complex. The conformational (entropic) contribution to the free energy is also studied. Taking into account the hydrophobic nature of the DNA macromolecule is also essential for understanding the physics of the complex formation. However, there is another important component of the cohesion energy that is noncovalent but cannot be reduced to any of the above components, and this is the energy of the polarization interaction.

The polarization interaction appears in complexes of DNA with highly polarizable substrates, because the backbone of the DNA molecule possesses substantial charge density in solution [4]. The ionization of phosphate groups between bases of single-stranded DNA results in the DNA having a one dimensional charge density $\sim e/7$ Å, neglecting compensation due to counterions in solution. This charge decreases when including the counterion contribution and polarization of the solvent, which may be addressed phenomenologically by changing the elementary charge to a smaller effective charge, $e \rightarrow e^*$.

Calculation of the polarization interaction is a more complex problem than calculation of any of the afore-

mentioned components of cohesion energy, which do not require knowledge of the microscopic electronic structure of the complex. The calculation of the polarization interaction in principle must self-consistently take into account evolution of the Hamiltonian of the system during complex formation. In this paper, we present the simplest approach to solving the problem; namely, we use the geometry of the complex obtained by the molecular dynamics method with force constants parameterized without specifics of the polarization interaction and construct the Hamiltonian of the system with the “frozen” coordinates of the atoms. Moreover, we assume that the polarization of the electronic subsystem of the DNA molecule is much weaker than the polarization of the electronic subsystem of the nanotube and neglect the former compared to the latter. This approximation is valid because all valence electrons of the single-wall nanotube are divided into two classes, the sigma electron subsystem and the pi electron subsystem, forming rigid covalent bonds of the nanotube framework and forming a highly polarizable electron shell around it, respectively. In graphitic structures, the pi electron subsystem has one of the highest molecular polarizabilities, close to that of metal with the density of states $4/\pi\hbar V_F$, where $V_F \approx 10^8$ cm/s is the Fermi velocity in the nanotube.

The polarization interaction is associated with the rearrangement of the nanotube electronic density in response to the perturbing electrostatic potential of the spiral “wrap” of the DNA around it. The classical model of the electrostatic interaction of point charges and their images in a metal or dielectric cylinder was used to estimate the polarization interaction in [5]. The main problem is to take into account the essential anisotropy of the nanotube dielectric function and its

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nonlocality. The anisotropy appears at the macroscopic level as the existence of essentially different longitudinal and transverse dielectric constants in the response tensor, especially for metallic nanotubes in which the longitudinal dielectric constant diverges with increasing the length of the nanotube segment. An even more complex problem is to take into account the nonlocality of the nanotube response function. To date, there is no general solution to the problem of the nanotube dielectric function. The dielectric function changes the nature of screening, which is one dimensional (in the long wavelength limit) and two dimensional (in the short wavelength limit) [6–9].

In this work, we calculate the exact nanotube response function within the framework of a semiempirical model for each specific choice of the perturbation potential. This work uses a quantum mechanical approach to analyze the polarization response of a nanotube to a perturbation of spiral symmetry.

With high accuracy, the electronic subsystem of an isolated nanotube may be computed by the tight binding method. This semiempirical approach, which is a variant of the method of linear combination of atomic orbitals, is a compromise for numerical computations, because the perturbation potential as shown below is a sufficiently smooth function of the coordinates on the surface of the nanotube, and its numerical value is small compared to the atomic scale. In this case, the perturbation-induced variation of the atomic orbitals can be neglected, and the envelopes of the wave functions allow estimation of the density matrix and calculation of all basic properties of the electronic subsystem.

2. MODEL DESCRIPTION

The specific choice of the tight binding Hamiltonian and its parameterization follow previous work [10]:

$$\hat{H}_0 = \sum_{ij} \gamma a_i^\dagger a_j, \quad (1)$$

where $\gamma \approx 2.9$ eV is the hopping integral (characteristic energy scale of the model) and the sum is taken over all nearest neighbors in the nanotube lattice. The tight binding Hamiltonian in the nearest neighbor approximation is the simplest quantum mechanical model that reproduces the electronic spectrum of the nanotube and allows analytical solution for specific cases (the qualitative symmetry analysis of the helical perturbation of the electronic subsystem of the armchair nanotube was given in [11] in the framework of perturbation theory). In this work, the perturbation operator is chosen as

$$\hat{V} = \sum_i V(i) a_i^\dagger a_i = \sum_i e \varphi^{\text{act}}(i) a_i^\dagger a_i, \quad (2)$$

where the sum with respect to i runs over all atoms of the unit cell of the complex and the acting electrostatic potential at the lattice site, φ^{act} , must be calculated in a self-consistent way. Choice of the unit cell of the com-



Fig. 1. Charge density induced on the surface of the [7, 0] zigzag nanotube in response to the potential of the phosphate groups of the DNA wrapped around the nanotube (gradient from gray to white/black corresponds to increasing positive/negative charge). Three unit cells are shown unfolded onto a plane.

plex is a nontrivial problem; a commensurate one-dimensional periodic structure of the complex does not exist for every (helically symmetric) DNA potential and given nanotube symmetry. The nanotube lattice itself may possess spiral symmetry incommensurate with the DNA. All of these issues require special consideration and have not been included in this work in which we consider only a commensurate structure of the complex where the nanotube is not chiral and the angle of the DNA wrap is chosen such that one wind (or more winds) covers an integer number of nanotube lattice constants. In particular, the results presented below were obtained for the complex of DNA with the zigzag nanotube [7, 0], with the lattice constant (along the axis of the nanotube cylinder) $a = 4.31$ Å and the unit cell length of the complex $6a = 25.88$ Å (one wind of the DNA covers a single unit cell with the length of six lattice constants of the nanotube, see Fig. 1).

We also consider other complexes that exhibit similar response to the external perturbation. The perturbation potential is computed so as it would be produced by static point charges placed at the equilibrium positions of the phosphorus atoms between the bases of the DNA macromolecule. We idealize the actual charge distribution of the DNA using the effective potential φ^{st} induced by a chain of point charges e^* . All charges are placed equidistant along a circular helix (at the same distance $\delta \approx 4.35$ Å from the nanotube surface). Such a charge distribution produces an electrostatic potential of the correct symmetry, which is smooth on the nanotube surface, because the ion chain is at a considerable distance from the surface. We use periodic boundary conditions; that is, the nanotube and DNA are considered to be infinite. In this work, we completely neglect both possible displacement of the phosphate groups from the chosen positions and possible contribution to the perturbation potential from other partially polarizable DNA atoms. Thus, the Hamiltonian of the DNA subsystem is not involved in the model (refinement of the result of this model is work in progress [12]).

3. CALCULATION OF THE SELF-CONSISTENT POTENTIAL ENERGY OF THE PERTURBATION

The Hamiltonian given by Eqs. (1) and (2) depends parametrically on the self-consistent electrostatic

potential on the nanotube surface, ϕ^{act} . The calculation of this quantity is the most complicated part of the problem, because it includes in principle complete consideration of the polarization of the nanotube itself, as well as the polarization of the DNA and the medium surrounding the complex. In the framework of the model, we include only the polarization of the nanotube itself, i.e., the contribution of the potential produced by the polarization charge of the nanotube. The contribution of the polarization of the DNA and medium is considered only phenomenologically through the use of the effective charge of the phosphate groups, e^* .

The nanotube responds to the external potential produced by the helical chain of point charges by redistributing the electronic charge density so as to maximize screening of the external potential. As a result, the total (acting) potential is substantially lower than the external (bare) potential, which may be described through the macroscopic dielectric constant of the nanotube. We emphasize the difference in description of the depolarization of the external potential of the helical wrap of the DNA and the classical formalism of the dielectric function of the medium; the “dielectric function” of the complex depends on the nanotube type, on the symmetry of the DNA wrap, and even on the properties of the surrounding medium, because the polarization charge of the nanotube is sensitive to all of these parameters. However, for a complex of given symmetry in vacuum, we can calculate accurately the polarization charge at each of the atoms and compute the screening factor.

It is interesting that (within the model) we found very weak dependence of the screening factor (local dielectric function) on the atomic position within the unit cell. It will be shown below that the distribution of the polarization charge follows the external potential and is very nonuniform along the perimeter and axis of the nanotube. At the same time, the ratio of the external potential to the total potential is nearly constant and is 2.2 ± 0.5 , meaning that the external potential is attenuated approximately by half.

The method of calculation of the polarization charge is as follows: Given the exact self-consistent potential ϕ , the charge density is determined as the trace of the density matrix calculated from the Hamiltonian with the perturbation proportional to ϕ , minus the trace of the density matrix determined from the Hamiltonian with zero perturbation. At zero (low) temperature only the occupied electronic states should be counted, i.e., the states below the Fermi level:

$$\delta\rho(\mathbf{x}) = \delta\langle ea^\dagger a \rangle = e \sum_{\lambda \leq \lambda_F} (|\psi_\lambda(\mathbf{x})|_\phi^2 - |\psi_\lambda(\mathbf{x})|_0^2), \quad (3)$$

where $\rho = e\langle a^\dagger a \rangle$ is the quantum mechanical charge density, λ denotes all quantum numbers, and λ_F denotes the last occupied state with the highest energy. Know-

ing the charge density, we can calculate the induced (screening) potential via the Poisson equation

$$\phi^{\text{ind}}(\mathbf{x}) = \int \frac{\delta\rho(\xi)}{|\mathbf{x} - \xi|} d\xi. \quad (4)$$

Then, the total potential equals the sum of two components:

$$V = e\phi^{\text{act}} = e(\phi^{\text{xt}} + \phi^{\text{ind}}), \quad (5)$$

where ϕ^{xt} is the “bare” potential of the charges on the DNA.

In practice, Eqs. (3)–(5) are solved by the iteration method. We use the charge density calculated at the previous step to refine the total screened potential, which is used to diagonalize the tight binding Hamiltonian. The details of the numerical method were given in [12]. However, we note that, because the Coulomb kernel of the one dimensional Poisson equation is significantly singular, the method requires using an adaptive mesh and an additional damping parameter for improving convergence (a typical calculation takes 10–20 iteration steps). In addition, we use a long wavelength cutoff and an extended supercell for more accurate treatment of the long distance component of the Coulomb potential. We have compared the results of the computations for different choices of these calculation parameters and confirmed that the final self-consistent result is independent of the specific choice of the parameters, starting from some critical value of a parameter. For example, for numerical integration of the Coulomb kernel, we used the long wavelength cutoff parameter $\sim 40\text{--}50$ Å, and a triple sized supercell for calculating ϕ^{ind} . The initial damping parameter was chosen $\sim 2\text{--}10$ and was adaptively changed in the process of the iterations.

The result of the calculation for a typical case of the [7, 0] nanotube wrapped by fully ionized DNA with the charge of a phosphate group $e = e^*$ is shown in Fig. 1. In this given complex, the DNA has four bases per unit cell. The positions of the phosphate groups are easily distinguished in Fig. 1 as the maxima of the positive charge density shown in white.

4. DISCUSSION OF THE RESULT AND CONCLUSIONS

Knowing the electron density induced on the nanotube surface by the DNA charges, we calculated the contribution to the cohesion energy from the polarization interaction. The reduced cohesion energy (per single base of the DNA) equals

$$\delta\mathcal{E} = \frac{l}{\mathcal{L}} \sum_{\text{DNA}} \int \frac{e_{\text{DNA}}^* \delta\rho(\xi)}{|\mathbf{x}_{\text{DNA}} - \xi|} d\xi, \quad (6)$$

where \mathcal{L} is the length of the DNA per period of a single unit cell and l is the distance between bases (i.e., their ratio is the number of charges of the DNA per unit cell,

which is equal to four in our case). We obtain the value $\delta\mathcal{E} \approx 0.47$ eV for the complex under consideration. The effective screening factor of the nanotube, which is discussed above, is approximately equal to two in our case. Correspondingly, the polarization component of the cohesion energy is halved as compared to the nonself-consistent value ≈ 0.96 eV at the first iteration (Fig. 2).

The classical attraction energy of an elementary charge to a metal surface

$$\delta\mathcal{E}_{cl} \sim e^2/2\delta, \quad (7)$$

where $\delta \approx 4.35$ Å corresponds to the distance between a phosphate group and the nanotube surface, is four times higher than the energy of the polarization interaction. Thus, the estimate of the polarization interaction via the interaction with the metal surface gives an essentially overestimated value. On the other hand, the transverse dielectric constant of the nanotube has a typical value of $\epsilon \approx 5$, and for the interaction of an elementary charge with the charge of the image in the insulator $e\frac{\epsilon-1}{\epsilon+1}$, we obtain a quantity more than two times higher than the actual one.

5. SUMMARY

We have calculated quantum mechanically the energy of the interaction of a single-wall carbon nanotube with a DNA molecule that is due to the appearance of polarization charges on the nanotube surface. Our estimate for the polarization cohesion energy for the given nanotube–DNA complex is ~ 0.47 eV per DNA base, which is ~ 14 eV for complexes that use oligomers 30 bases long (as in experimental works [1, 3]). This theoretical result confirms the high stability of nanotube–DNA complexes.

The polarization charges induced by the ionized phosphate groups have been computed numerically in the framework of the tight binding method in the nearest neighbor approximation. The calculation includes obtaining a self-consistent electrostatic potential, which is substantially screened by the charge on the nanotube as compared to the potential of the DNA in vacuum. We obtained a constant characterizing the effective screening factor for the complex under consideration. Up to small atom-to-atom fluctuations, the acting potential on the nanotube surface is approximately half the bare (initial) potential.

We have shown that an estimate of the energy of the polarization interaction using the image charge model

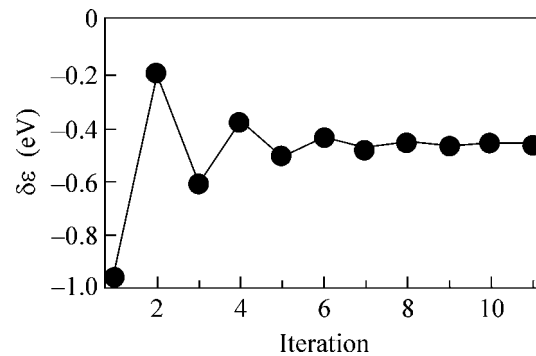


Fig. 2. Convergence of the polarization component of the cohesion energy for the nanotube–DNA complex described in the work. Eleven steps of iteration are shown, including the nonself-consistent value for the first step.

in a metal or dielectric surface of the nanotube is substantially overestimated as compared to the accurate result. We assume that this discrepancy is related mainly to the nonlocal character of the nanotube polarization.

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