Electronic kinetic energy decrease as two metallic parallel C nanotubes are brought together from infinity

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Abstract

By utilising the virial theorem, an expression is derived from the recent work of Dobson et al. for the initial decrease of electronic kinetic energy as two metallic parallel C nanotubes of equal diameter are brought together from infinity to a (still large) separation. To yield the dispersion energy proposed by Dobson et al. [J.F. Dobson, A. White, A. Rubio, Phys. Rev. Lett. 96 (2006) 073201], it is shown that it is the initial drop in the kinetic energy that is responsible for the long-range attractive interaction.

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In a very recent study, Dobson et al. [1] have given a form for the long-range dispersion energy between two parallel metallic C nanotubes at a large separation D. Here we apply the integral quantum-mechanical virial theorem to propose the microscopic way in which such a form of attractive dispersion force can come about. Throughout we shall work with energies per unit length. Then, for a single nanotube assumed to have a radius a, the virial reads

\[ 2T_1 + U_1 = -a \frac{dE_1}{da}, \]  

where \( T \) and \( U \) denote respectively kinetic and potential energy while \( T + U = E \). Since the nanotube for finite diameter is never in equilibrium under pure Coulomb forces, the right-hand side of Eq. (1) reflects the fact that external forces, which are radius dependent, must act on the nanotube.

Next, we denote by \( E_2(D, a) \) the total energy ground-state energy at separation \( D \) of the assembly of two metallic parallel C nanotubes of equal radii \( a \). The result of Dobson et al. [1] is then embraced by writing:

\[ E_2(D, a) - 2E_1(a) \equiv \Delta E(D, a) = -A(a)D^{-2} \left[ \ln(BD) \right]^{-n} + \cdots, \]  

where \( B \) depends on \( a \) and \( A(a) \) is positive. Dobson et al. [1] found the value \( n = 3/2 \) from their plasmon zero-point energy calculation. It seems clear, on physical grounds, that at sufficiently large \( D \) for Eq. (2) to be valid, the force exhibited on the rhs of Eq. (1) can play no role in determining the kinetic and potential energy changes \( \Delta T \) and \( \Delta U \) as the two equal diameter nanotubes are brought together from infinite separation to a (still large) separation \( D \). With that single assumption, we can proceed to use the virial theorem in the form

\[ 2\Delta T + \Delta U = -D \frac{d\Delta E}{dD}, \]  

to derive these kinetic and potential energy changes for the Dobson et al. [1] result (2). Since \( \Delta T + \Delta U = \Delta E \), it is a straightforward matter to find, with \( n = 3/2 \):

\[ \Delta T(D, a) = -A(a)D^{-2} \left[ \ln(BD) \right]^{-n} + \text{higher order terms} \]  

and hence

\[ \Delta U(D, a) = O(\Delta T/\ln D). \]
What we stress from Eqs. (4) and (5) is that, as the two nanotubes are moved from infinite separation to a distance $D$ which is still large, it is the initial decrease in electronic kinetic energy that is responsible for the entire dispersion energy in leading order, the potential energy change only entering at $O(\Delta T/\ln D)$. This is the main finding of the present study, but it seems of interest for the future to make a number of further points. Though the points below seem to us to be rather general, for purposes of presentation we shall find it helpful to appeal to the generalisation of the so-called March model of the buckyball $C_{60}$ [2,3]. There, the 60 $\pi$-electrons are taken to move in the central field created by a uniform positive neutralising surface charge distribution on a sphere having the radius of the European football [4]. The nanotube analogue of this model smears the discrete nuclear neutralising charges of the $\pi$-electrons uniformly over the cylindrical surfaces of the two nanotubes, assumed oriented along the $z$-axis. Drawing it in the $(x, y)$ plane, the electron density in this model is then characterised solely by $\rho(x, y, D, a)$, which in turn from density functional theory characterises the kinetic energy functional $T(\rho)$ say. Of course, we recognise that in the present problem the correlation kinetic energy will play an essential role and that this functional remains as yet unknown. However, by way of illustration, suppose we use LDA for the single-particle kinetic energy $T_s^{\text{LDA}}[\rho]$, taking into account the two-dimensionality of $\rho(x, y)$ set out above. Then this suggests that $T_s^{\text{LDA}}[\rho] = c_k \int \rho^2(x, y) \, dx \, dy$, where $c_k$ is a known kinetic constant from the theory of the homogeneous electron gas. If at sufficiently large separation $D$ we take $\rho(x, y, D, a)$ for the nanotube complex as the superposition density of the single nanotube densities, $\rho$, say, then $\Delta T_s$ is evidently given by the overlap of the $\rho$ densities which of course is positive, in direct contrast to the result (4) from the present investigation. It may be of some interest for the future to examine whether density gradient corrections to the above LDA form of $T_s[\rho]$ can be constructed to (a) reproduce the $D^{-2}[\ln(BD)]^{-3/2}$ dependence in Eq. (4) and (b) give at least a zero-order approximation to $A(a)$. However, as emphasised already, a fully quantitative solution of this problem must await progress on understanding the correlation kinetic energy functional. As a further point, our invoking a two-dimensional density $\rho(x, y)$ above suggests that the $\ln D$ factor entering the result (2) of Dobson et al. [1] is a rather direct consequence of dimensionality. This is supported, but not proved because of the considerable differences in the two assemblies considered by Amovilli and March [5] of planar rings of H atoms, and also of C ring clusters (with suitable modification then to allow for $\sigma$ bonds). In the approximation, for H rings, in which the protons are smeared out uniformly around the ring of radius $R$, Amovilli and March demonstrate scaling of the potential energy curve $E(R)$, a $\ln R$ term then appearing naturally in their two-dimensional model.

To summarise, the main result of the present Letter is embodied in Eq. (4), which shows that at sufficiently large separations $D$ of the two metallic nanotubes, the decrease in electronic kinetic energy equals the dispersion energy (2) obtained by Dobson et al. [1]. The increase in potential energy represented in Eq. (5) is $O(\Delta T/\ln D)$ smaller at large $D$. The study of the kinetic energy functional at large $D$ for this assembly, and particularly the possible role of low-order density gradient terms seems to us to be an area worthy of further investigation in the future. Finally, we should refer to the very recent work by Dobson [6] who stresses the importance of using ultrasensitive force detection methods to distinguish between the $D^{-2}[\ln(BD)]^{-3/2}$ dependence of the dispersion energy discussed here for metallic nanotubes and the much smaller energy for their semiconducting counterparts.

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