Variational approach to excitons in carbon nanotubes

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Excitons in quasi-one-dimensional semiconductors may lower the optical transition energies by a substantial amount. To quantify the effect in carbon nanotubes, we apply a simple variational approach. In excitonic units, a power law with exponent ~ -0.6 is obtained for the binding energy dependence on nanotube radius. When converted to ordinary units, the ratio of binding energy to tight-binding band gap yields a roughly constant value of nearly 40%. This substantial ratio implies that exciton effects are of prime importance for the optical properties of carbon nanotubes.

Following their discovery in 1991,[1] carbon nanotubes (CN's) have been at the focus of tremendous interest. These materials have been investigated using nearly every conceivable experimental technique. This has established the fact that CN's possess quite remarkable mechanical, electronic and optical properties.[2] As noninvasive techniques, optical absorption and fluorescence spectroscopy are ideal tools for studies of the electronic structure of CN samples. Recently, optical spectra of unprecedented high resolution have been recorded due to improvements in growth control[3] and means of isolating individual CN's.[4,5] Especially noteworthy are the absorption and emission spectra of the Rice group[5] with a line width of only 0.025 eV. From these and similar high-quality spectra fundamental energy gaps have been extracted[5] and the composition of samples have been determined.[3,4] Of central importance for this purpose is the relation between the electronic (quasiparticle) band structure and the optical spectra. Usually, absorption or emission features are tacitly attributed to transitions between extrema of occupied and empty bands.[4,5] However, as demonstrated by Ichida *et al.*[3,6] and pointed out several decades ago by Loudon[7] the exciton effect in quasi-one-dimensional semiconductors is *not* a minor correction. Essentially, this means that optical transitions cannot be associated with the bare quasiparticle energy difference. Rather, they are red-shifted by a substantial exciton binding energy. Hence, whereas the exciton binding energy in ordinary three-dimensional semiconductors is on the order of 10 meV, the corresponding figure in one-dimensional materials such as conjugated polymers is typically in the range 100 meV to 1 eV.[8]

An exciton is an electron-hole pair bound by the attractive $-1/r$ Coulomb potential. In low-dimensional structures, the spatial confinement increases the electron-hole overlap, thereby enhancing the exciton binding energy. Hence, in the pure two-dimensional (quantum well) limit the binding energy is increased by a factor of four compared to the three-dimensional case.[9] For one-dimensional semiconductors, however, the situation is even more dramatic. To study this problem, Loudon[7] considered the eigenstates of the truncated one-dimensional Coulomb potential $-1/(|x|+a)$, with a being a positive constant. This potential approaches the bare potential at large distances $|x| \gg a$ but is regularized when $|x| \ll a$ and remains finite in the limit $x \to 0$. Such potentials naturally arise as effective potentials for one-dimensional

systems, where a is approximately the width of the transverse potential well.[10,11] The acceptable eigenstates are given by Whittaker functions and writing the energy eigenvalue in the form $E = -1/\alpha^2$, the condition for the lowest eigenvalue becomes[7]

$$\frac{1}{2\alpha} + \ln\left(\frac{2a}{\alpha}\right) = 0, \tag{1}$$

where a is assumed small. Here and throughout the mathematical presentation, we use natural exciton units, in which distances are measured in units of the effective Bohr radius a_B^* and energies in units of the effective Rydberg Ry^*. The conversion into ordinary units is considered below. Now, solving Eq. (1) for α readily shows that that $\alpha \to 0$ as the transverse potential width a goes to zero. Thus, the eigenvalue diverges and it can be shown that the square of the corresponding wave function approaches a delta function $\delta(x)$.[7] Hence, there is no lower bound for the exciton binding energy in the extreme one-dimensional limit. Obviously, for real materials with a finite width the value remains finite. Still, if a is much smaller than the effective Bohr radius, as in the case of typical conjugated polymers, a very large binding energy is found.

The purpose of the present Brief Report is to calculate the binding energy of the lowest exciton in semiconducting CN's. Being one-dimensional conjugated systems, a large binding energy is expected, especially for small-diameter nanotubes. In fact, we will show below that an expression very similar to Eq. (1) can be derived with the role of a played by the nanotube radius. To our knowledge, the only previous theoretical study of excitons in CN's was published by T. Ando.[12] In that work, however, only the sum of exciton binding energy and quasi-particle corrections was considered, producing, in fact, an overall blue shift. Hence, the diameter-dependence of the exciton binding energy cannot be extracted. Moreover, no information on the spatial form of the exciton wave function was given. In the present work, we apply a variational approach combined with the effective-mass approximation to obtain the properties of the lowest exciton as a function of CN radius r. We assume that electrons and holes are bound to move on the surface of an infinitely long cylinder of radius r, as illustrated in Fig. 1. This assumption is expected to break down for the very
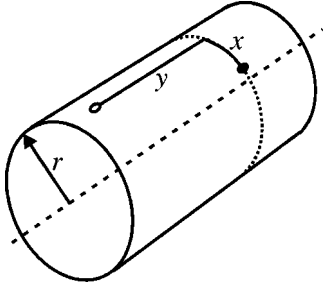
FIG. 1. Geometry of an electron (open circle) and a hole (closed circle) moving on the surface of a cylinder with radius r.
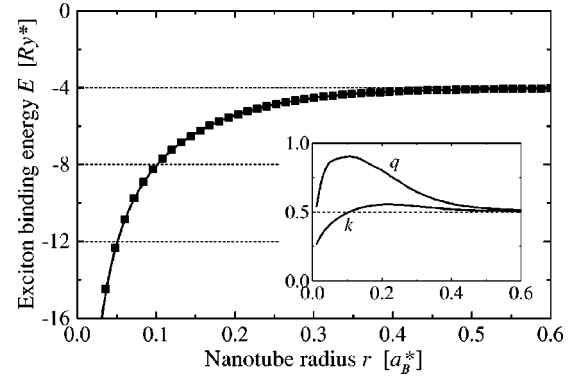

FIG. 2. Variational exciton binding energy as a function of nanotube radius. Inset: the r-dependence of decay lengths k and q of the trial wave function.

smallest nanotubes, when the radius r becomes comparable to the extension of the individual carbon atoms. For larger tubes, however, this approximation is reasonable. Recently, a similar approach was successfully applied to donors in metallic CN's.[13] While mathematically similar, the focus of the present work is on an entirely different physical problem. Hence, the application to excitons in semiconducting CN's attests further to the power of this variational technique.

In the variational approach, we consider a trial (un-normalized) wave function $\psi(x,y)$ and minimize the energy expectation value $E=(K-V)/N$ with respect to the parameters governing the spatial behavior of $\psi(x,y)$. Here, $N=\langle\psi|\psi\rangle$ is the normalization integral, $K=-\langle\psi|\partial^2/\partial x^2+\partial^2/\partial y^2|\psi\rangle$ is the kinetic energy and $V=2\langle\psi|d^{-1}(x,y)|\psi\rangle$ is the Coulomb energy with the electron-hole separation d given by $d(x,y)=\sqrt{4r^2\sin^2(x/2r)+y^2}$. Note that we use an x-coordinate that circles the circumference of the cylinder as shown in Fig. 1. This is the reason for the complicated dependence of d. Our choice of trial wave function should conform to the appropriate limits as $r\to0$ and $r\to\infty$. In the latter case, the tube becomes flat and the exact solution is the well-known exponential $\exp[-(x^2+y^2)^{1/2}/k]$ with $k=1/2a_B^*$ and an eigenvalue of $E=-4Ry^*$.[9] On the other hand, as $r\to0$ different decay lengths are expected for the x- and y-directions. A trial form that accommodates both of these limits is

$$\psi(x,y)=\exp[-(x^2/q^2+y^2/k^2)^{1/2}], \qquad (2)$$

where k and q are variational parameters that are adjusted to minimize the energy. Due to the nonseparable form, the required integrals are somewhat involved, however. A rather tedious calculation yields

$$N=\frac{\pi\beta}{2}qk\{\mathrm{L}_1(\beta)K_0(\beta)+\mathrm{L}_0(\beta)K_1(\beta)\} \qquad (3)$$

and

$$K=\frac{\beta^2}{4}\left(\frac{k}{q}-\frac{q}{k}\right)\{\pi-2\beta K_0(\beta)-2K_1(\beta)\}$$
$$+\left(\frac{1-\beta^2}{2q^2}+\frac{1+\beta^2}{2k^2}\right)N. \qquad (4)$$

Here, $\beta=2\pi r/q$ and K_n and L_n are the nth modified Bessel function of the second kind and Struve function,[14] respec-

tively. Notice that in the expression for K, a contribution from the "seam" at $x=\pm\pi r$ is included. No analytic expression for V has been obtained, unfortunately, and Gaussian quadrature is adopted for its numerical evaluation. Using a steepest-decent method, the optimum wave function is obtained as a function of r. The energy and decay lengths found in this manner are shown in Fig. 2. Here, several important features are noted. First, the exciton state rapidly approaches the zero-curvature solution ($k=q=1/2a_B^*$ and $E=-4Ry^*$) as r increases. Secondly, the exciton binding energy clearly diverges as the radius decreases. Hence, a significant enhancement factor is predicted for small-diameter nanotubes. Third, the exciton becomes highly asymmetric for smaller tubes, with a ratio q/k of more than 2. To illustrate the spatial properties of the wave functions, we have plotted cases representative of small ($r=0.1a_B^*$) and large ($r=0.5a_B^*$) radius in Fig. 3. In the former case, we find $q=0.90a_B^*$ and $k=0.49a_B^*$, whereas the larger tube has $q=0.53a_B^*$ and $k=0.51a_B^*$. Thus, these examples illustrate cases of $q\gg r$ and $q\sim r$, respectively. The consequences are clearly visible in Fig. 3. Most notably, the smaller nanotube has a large wave function amplitude at the seam $x=\pm\pi r$. Hence, with a hole located on one side of the tube there is a relatively large probability of finding the electron on the opposite side. In contrast, this probability if virtually zero for the larger nanotube.

In order to study the divergent behavior in the small r limit, we now focus specifically on an approximate solution for $q\gg r$ or equivalently $\beta\ll1$. In this limit, we find the following analytic expression for the energy:

$$E\approx\frac{1}{k^2}+\frac{2\pi}{k}J_0\left(\frac{2r}{k}\right)Y_0\left(\frac{2r}{k}\right)$$
$$-\frac{32r}{\pi k^2}\,_2F_3\left[1,1;\frac{3}{2},\frac{3}{2},\frac{3}{2};-\frac{4r^2}{k^2}\right], \qquad (5)$$

where J_0 and Y_0 are Bessel functions of first and second kind, respectively, and $_2F_3$ is a generalized hypergeometric function.[14] This expression can then be simplified even further if the additional condition $r/k\ll1$ is assumed. In this limit, we obtain the extremely simple result
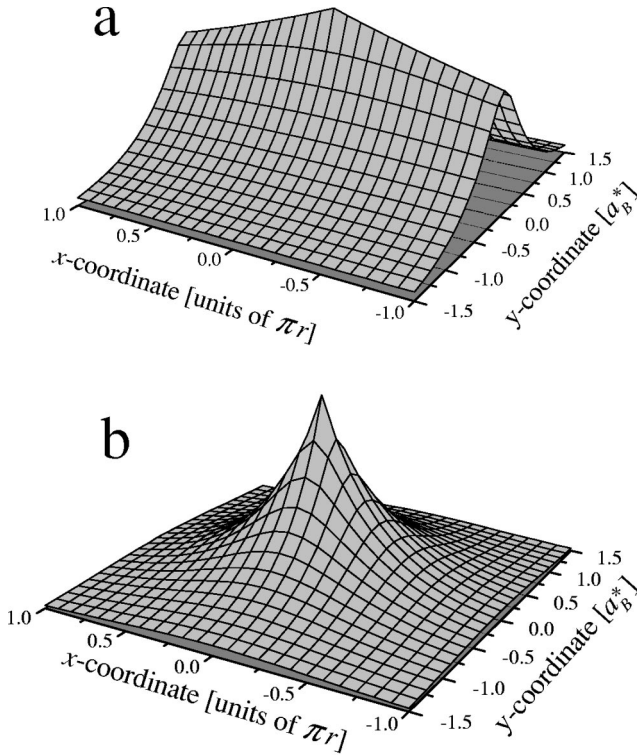
FIG. 3. Illustration of the exciton wave function for nanotubes of radius $r = 0.1 a_B^*$ (a) and $r = 0.5 a_B^*$ (b).

$$E \approx \frac{1}{k^2} + \frac{4}{k}\left[\gamma + \ln\left(\frac{r}{k}\right)\right], \qquad (6)$$

where $\gamma = 0.57721...$ is Euler's constant. Minimizing this function leads to the condition

$$\frac{1}{2k} + \ln\left(\frac{r}{k}\right) + 1 + \gamma = 0. \qquad (7)$$

This condition is seen to be very similar to Loudon's original result Eq. (1) with $2a$ replaced by r. The additional constant term $1 + \gamma$ in Eq. (7) is only of minor importance when k and r are small. In fact, if Loudon's analysis of the one-dimensional hydrogen atom is carried to one higher order, an additional constant of 1 enters on the left-hand side of Eq. (1). Denoting the solution of Eq. (7) by $k(r)$ we finally find that the exciton binding energy is given by $E(r) \approx -k^{-2}(r) - 4k^{-1}(r)$ in the limit of small r. The energies given by the approximate expressions in Eqs. (5) and (6) are shown in Fig. 4 along with the result of the full expression. A log-log scale is used in order to display the power-law behavior of the r-dependence. The successive approximations leading to Eqs. (5) and (6) are seen to produce increasingly inaccurate results. However, reasonable agreement is found for the smallest tubes and, in particular, an approximately correct slope is predicted. The solid line in Fig. 4 is a power-law fit to the binding energies obtained from the full expression. The divergent behavior is seen to follow an r^{-p} dependence with $p = 0.6 \pm 0.1$. In their recent experimental study, Ichida *et al.*[3] obtained Coulomb corrections following a power law with a somewhat larger exponent $p \approx 1.3$. How-
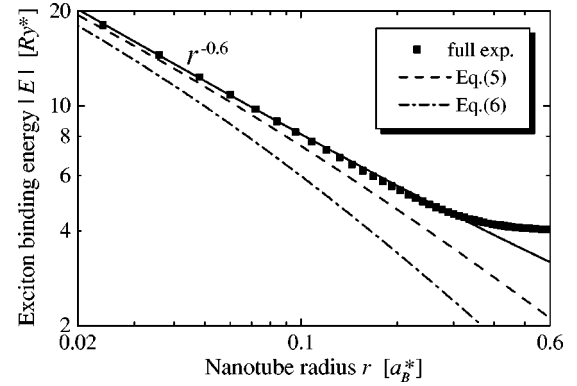

FIG. 4. Results of the full and approximate calculations of the exciton binding energy vs r. The log-log scale and the fitted solid line serve to emphasize the power-law dependence.

ever, the reported Coulomb corrections are the blue shifts including quasiparticle correction, whereas the present study only considers the exciton binding energy. The binding energy and quasiparticle corrections may well have very different r-dependencies.

To convert the calculated curves to actual numbers, we need the correct distance and energy scales. In terms of the reduced effective mass μ (in units of the free-electron mass m_0) and static dielectric constant ε, they are given by $a_B^* = 0.529$ Å $\cdot \varepsilon/\mu$ and $Ry^* = 13.6$ eV $\cdot \mu/\varepsilon^2$. In principle, both μ and ε should be different for different CN samples. We will assume, however, that screening is mainly due to external charges in e.g. the zeolite cage[4] or micelle structure,[5] etc. Hence, a sample-independent value of $\varepsilon = 3.5$ will be used. Since the energy scale varies inversely with ε, this relatively large value should lead to a conservative estimate of the exciton binding energy. The reduced mass, on the other hand, is obviously intimately connected to the band structure of the CN. To estimate the dependence of μ on CN radius, we will consider the zigzag nanotubes of type $(n,0)$ with $n = 7,10,13,...$ in the usual notation.[15] These nanotubes are all semiconductors. We will adopt the simple tight-binding zone-folding scheme[15] for the band structure calculation even though $\sigma - \pi$ mixing makes the results less reliable for the smallest nanotubes. For the present purpose of estimating μ, however, the accuracy is sufficient. In the zone-folding scheme for zigzag nanotubes, the two-dimensional (k_x, k_y) band structure of a graphene sheet is subject to the boundary condition $a \cdot k_y = 2\pi p/n$, where p is an integer between 1 and $2n$ and $a \approx 2.46$ Å is the graphene lattice constant. The tight-binding band gap E_g is located at the zone center Γ. The highest valence band is found for $p = (2n+1)/3$ (an integer for the present values of n) and the lowest conduction band is located symmetrically above the band gap. Expanding the k_x dependence of these bands around the Γ point we find band gaps and effective masses given by $E_g = 2\gamma_0|1 + 2c_n|$ and $\mu = \hbar^2/(3\gamma_0 a^2)|1/c_n + 2|$, with $\gamma_0 \approx 3$ eV the $pp\pi$ hopping matrix element and $c_n = \cos[\pi(2n+1)/3n]$. For n large, these expressions simplify to $E_g \approx 11$ eV$/n$ and $\mu/m_0 \approx 0.50/n$ implying that both of these quantities are approximately inversely proportional to the CN radius $r = an/2\pi$.[16] In Table I, band gaps and effective masses are

TABLE I. Characteristics of zigzag $(n,0)$ nanotubes with different values of n.

n	r [Å]	E_g [eV]	μ [m_0]	a_B^* [Å]	Ry^* [eV]	E [eV]
7	2.74	1.48	0.055	33	0.062	−0.55
10	3.92	1.05	0.042	44	0.046	−0.40
13	5.09	0.82	0.034	55	0.037	−0.31
16	6.26	0.67	0.028	66	0.031	−0.26
19	7.44	0.56	0.024	77	0.027	−0.22
22	8.61	0.49	0.021	88	0.023	−0.19
25	9.79	0.43	0.019	99	0.021	−0.17

listed for several zigzag nanotubes. In addition, the corresponding distance and energy scales and the binding energy E converted to electron volts are given. Remarkably, the binding energy constitutes a nearly constant fraction of the band gap, the ratio varying from 37% for $n=7$ to 39% for $n=25$. The simple reason is that r in units of a_B^* is, in fact, largely independent of n due to the n^{-1} of μ. Hence, the n-dependence of E is almost entirely that of Ry^*. As both Ry^* and E_g scale approximately as n^{-1} as well, it follows that their ratio should be roughly constant. The very large

fraction $\sim$38% is a clear demonstration of the prime importance of excitons in CN's.

In conclusion, exciton effects are *not* small corrections to the optical properties of semiconducting CN's. The present variational approach indicates that exciton binding lowers the optical transition energies by nearly 40% of the tight-binding calculated band gap. Hence, this shift should necessarily be considered whenever the electronic properties of CN's are deduced from optical spectra.

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