

11. Excitons in Nanowires and Nanotubes

We have seen that confinement in quantum wells leads to enhanced excitonic effects in the optical response of semiconductors. The binding energy of the strongest bound excitons increase by a factor of 4 in the ideal 2D case. Consequently, one expects this trend to continue to 1D-structures with even stronger binding of excitons. As we will see, this is precisely what happens even to the point, where excitons completely dominate the response.

Following the previous chapter, we will limit ourselves to variational calculations of excitons in 1D-structures. These structures are assumed to be infinite along the long-axis direction and strongly confining in the two transverse dimensions. Also, the system is excited along the long-axis so that centre-of-mass momentum for this direction is to remain zero throughout. We take the z -axis as the long-axis and so the confined electron-hole pair is described by the Hamiltonian

$$\hat{H}_{eh} = \hat{h}_e(x_e, y_e) + \hat{h}_h(x_h, y_h) + E_g - \frac{d^2}{dz^2} - \frac{2}{\sqrt{(x_e - x_h)^2 + (y_e - y_h)^2 + z^2}}. \quad (11.1)$$

Here, $\hat{h}_e(x_e, y_e) = -m_e^{-1}(d^2/dx_e^2 + d^2/dy_e^2) + V_e(x_e, y_e)$ is the Hamiltonian for the transverse motion of the electron confined by the potential V_e and \hat{h}_h is the analogous term for the hole. In this expression, the effective electron and hole masses should be taken in units of the reduced electron-hole pair mass, which is taken as the unit of mass. In a purely variational treatment, we attempt to describe the exciton state by the variational ansatz $\Psi_{exc}(\vec{r}_e, \vec{r}_h) = \varphi_e(x_e, y_e)\varphi_h(x_h, y_h)\Psi(z)$. The corresponding expectation value for the energy is then

$$E = \tilde{E}_g + \langle \Psi(z) | -\frac{d^2}{dz^2} + V(z) | \Psi(z) \rangle, \quad (11.2)$$

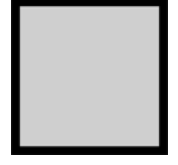
with $\tilde{E}_g = E_g + E_1^e + E_1^h$ and an effective potential

$$V(z) = -2 \iint \frac{|\varphi_e(x_e, y_e)\varphi_h(x_h, y_h)|^2}{\sqrt{(x_e - x_h)^2 + (y_e - y_h)^2 + z^2}} dx_e dy_e dx_h dy_h. \quad (11.3)$$

At this point, it is instructive to consider some specific examples of transverse confinement:

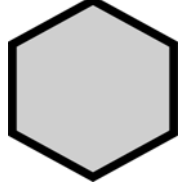
A. Rectangular nanowire with transverse dimensions $d \times d$ (Ref. [1]):

$$\varphi(x, y) = \frac{2}{d} \sin\left(\frac{\pi x}{d}\right) \sin\left(\frac{\pi y}{d}\right)$$



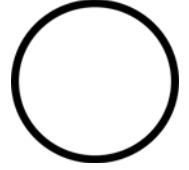
B. Hexagonal nanowire with diameter d (Ref. [2]):

$$\varphi(x, y) \approx \frac{8\pi}{3^{1/4}(16 + 5\pi^2)^{1/2}d} \cos\left(\frac{\pi x}{d}\right) \cos\left(\frac{\pi(x - \sqrt{3}y)}{2d}\right) \cos\left(\frac{\pi(x + \sqrt{3}y)}{2d}\right)$$



C. Circular nanotube with radius r (Ref. [3]):

$$|\varphi(x, y)|^2 = \frac{1}{2\pi r} \delta(\sqrt{x^2 + y^2} - r)$$



We note that in the nanotube model, the wave function is completely localized to the cylinder wall and rather than giving the wave function itself, we give the normalized square. In cases A and B, the effective potential can only be computed numerically. However, for the nanotube model an analytic result can be found. To this end, we introduce polar transverse coordinates $x = \rho \cos \theta$ and $y = \rho \sin \theta$. Due to the complete localization on the cylinder wall, we always have $\rho = r$. In this manner, $(x_e - x_h)^2 + (y_e - y_h)^2 = 4r^2 \sin^2((\theta_e - \theta_h)/2)$. Hence, in polar coordinates,

$$\begin{aligned} V(z) &= -\frac{2}{(2\pi r)^2} \int_0^{2\pi} \int_0^\infty \int_0^{2\pi} \int_0^\infty \frac{\delta(\rho_e - r)\delta(\rho_h - r)}{\sqrt{4r^2 \sin^2((\theta_e - \theta_h)/2) + z^2}} \rho_e \rho_h d\rho_e d\theta_e d\rho_h d\theta_h \\ &= -\frac{1}{\pi} \int_0^{2\pi} \frac{1}{\sqrt{4r^2 \sin^2(\theta/2) + z^2}} d\theta \\ &= -\frac{4}{\pi |z|} K\left(-\frac{4r^2}{z^2}\right). \end{aligned} \quad (11.4)$$

In the last line, K is a so-called complete elliptic integral of the 1. kind defined by

$$K(x) \equiv \int_0^{\pi/2} \frac{1}{\sqrt{1 - x \sin^2 \theta}} d\theta.$$

From this definition, it is seen that $K(0) = \pi/2$ and the potential approaches the bare 1D Coulomb potential $V(z) = -2/|z|$ in the limit $r \rightarrow 0$. From Eq.(11.3) it is clear that this must always be the limit of a 1D effective potential whenever the confining potential becomes sufficiently narrow that $x_e \approx x_h$ and $y_e \approx y_h$ because of the confinement.

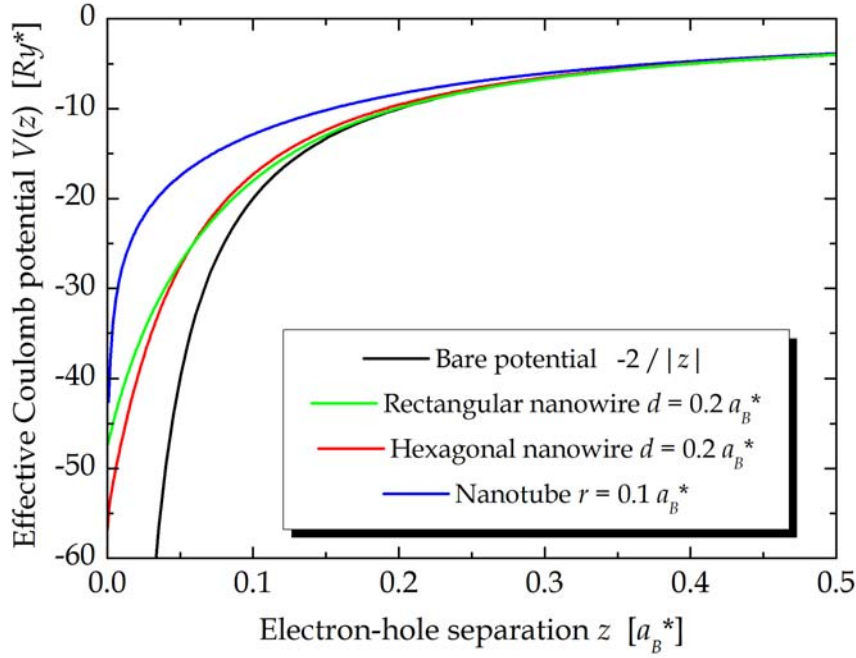


Figure 11.1 Effective Coulomb potential for three different 1D confinements compared to the bare potential.

The actual effective potentials for the three models listed above are illustrated in Fig. 11.1. When compared to the bare Coulomb potential, it is clear that the behaviour as $z \rightarrow 0$ is much less singular. Hence, for models A and B, the singularity is completely removed and for C, the singularity is now logarithmic instead of $\sim 1/|z|$. However, in all cases the bare potential $-2/|z|$ is found as a limit when the diameter of the nanowire or -tube becomes very small. It might then be thought that a viable and simple model for 1D excitons would result from using the pure 1D potential $V(z) = -2/|z|$ in Eq.(11.2) similarly to the 2D quantum well case. To look at the properties of this simple model we need to start with a “regularized” potential, however. For this purpose, we will take $V(z) = -2/(|z|+c)$ as our potential, where c is a positive constant, which should eventually be taken to zero. This “Loudon” model was originally analyzed by R. Loudon [4]. The form is mathematically simpler than any of the alternatives above. As our variational ansatz we will, as usual, try the exponential $\Psi(z) = \sqrt{\alpha} e^{-\alpha|z|}$. Differentiating twice leads to $d^2\Psi(z)/dz^2 = \alpha^2\Psi(z) - 2\alpha\Psi(0)\delta(z)$. Thus, the expectation value Eq.(11.2) is

$$E = \tilde{E}_g + \alpha^2 - 4\alpha \int_0^{\infty} \frac{e^{-2\alpha z}}{z+c} dz.$$

Evaluating this integral leads to yet another complicated function: the exponential integral Ei :

$$E = \tilde{E}_g + \alpha^2 + 4\alpha e^{2\alpha c} Ei(-2\alpha c).$$

However, as c should go to zero we can use an expansion based on partial integration valid for small c

$$\begin{aligned}
E &= \tilde{E}_g + \alpha^2 - 4\alpha \int_0^\infty \frac{e^{-2\alpha z}}{z+c} dz \\
&= \tilde{E}_g + \alpha^2 - 4\alpha \left[e^{-2\alpha z} \ln(z+c) \right]_0^\infty - 8\alpha^2 \int_0^\infty e^{-2\alpha z} \ln(z+c) dz \\
&= \tilde{E}_g + \alpha^2 + 4\alpha \ln(c) - 8\alpha^2 \int_0^\infty e^{-2\alpha z} \ln(z+c) dz \\
&\approx \tilde{E}_g + \alpha^2 + 4\alpha \ln(c) - 8\alpha^2 \int_0^\infty e^{-2\alpha z} \ln(z) dz \\
&= \tilde{E}_g + \alpha^2 + 4\alpha(\gamma + \ln(2\alpha c)),
\end{aligned} \tag{11.5}$$

where the integral $\int_0^\infty e^{-\beta z} \ln(z) dz = -(\gamma + \ln(\beta)) / \beta$ with $\gamma = 0.577\dots$ as Euler's constant has been applied. Differentiating, one finds $0 = 2\alpha + 4(\gamma + \ln(2\alpha c)) + 4$. With a few manipulations this condition can be reformulated as

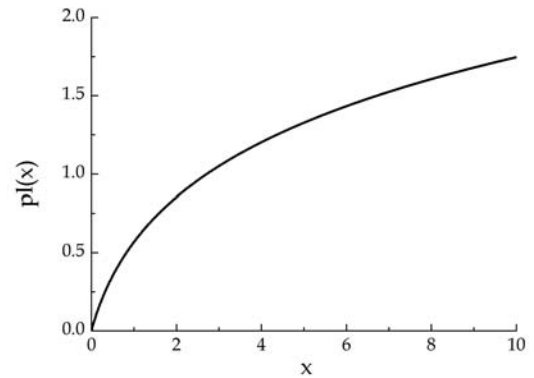
$$\frac{\alpha}{2} \exp\left(\frac{\alpha}{2}\right) = \frac{1}{4ce^{1+\gamma}}.$$

The formal solution to the equation $w \exp(w) = x$ is sometimes called the "product logarithm" (pl), i.e. $w = \text{pl}(x)$. Thus, the solution for α is

$$\alpha = 2 \text{pl}\left(\frac{1}{4ce^{1+\gamma}}\right) \approx 2 \ln\left(\frac{1}{4ce^{1+\gamma}}\right) - 2 \ln\left(\ln\left(\frac{1}{4ce^{1+\gamma}}\right)\right),$$

where the second expression is the expansion for low c . Accordingly, the energy is

$$E = \tilde{E}_g - 8 \text{pl}\left(\frac{1}{4ce^{1+\gamma}}\right) - 4 \text{pl}^2\left(\frac{1}{4ce^{1+\gamma}}\right).$$



As the plot of the product logarithm to the right shows, it is a monotonically increasing function that diverges logarithmically as the argument increases. The extremely important conclusion is this: as c goes to zero, we find $\alpha \rightarrow \infty$ and $E \rightarrow -\infty$. Hence, the wave function becomes completely localized to the point $z=0$. This is *not* an artefact of the variational approach because the variational estimate for the energy is always higher than the true value. We therefore conclude that the 1D Coulomb model is "pathological" in that

the ground state collapses and the ground state energy diverges. In Fig. 11.2, we illustrate the behaviour of the energy as c becomes smaller.

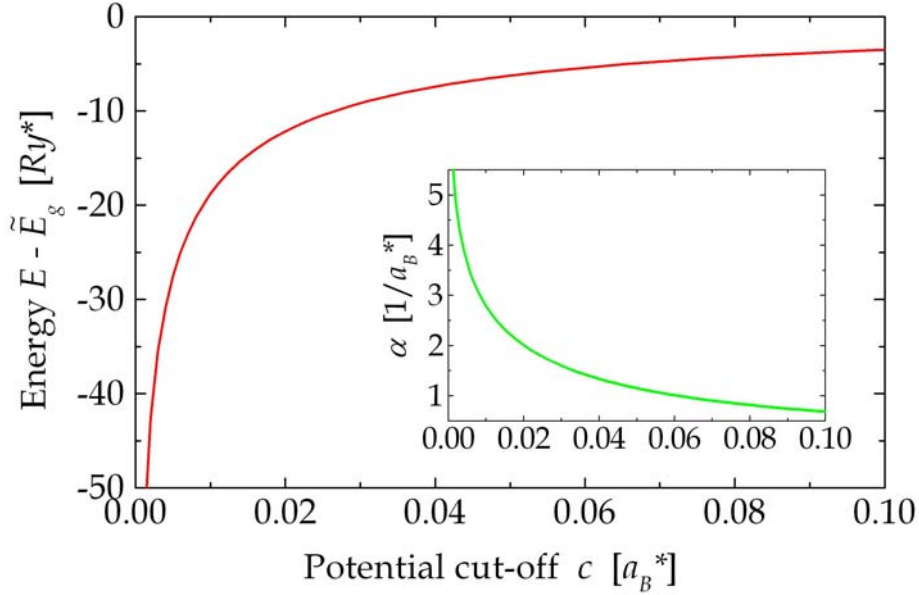


Figure 11.2 Binding energy and variational parameter (inset) in the Loudon model as a function of the potential cut-off.

Even though the pure 1D Coulomb model is clearly unphysical, it is still correct that the true potential for all realistic models approaches this strange situation as the confinement becomes stronger. Hence, even if actual exciton binding energies obviously do not diverge, they can still grow extremely large compared to bulk values. As an example of this, we now consider the true nanotube potential given by Eq.(11.4). With the same exponential ansatz as above, we find the energy expectation value

$$E = \tilde{E}_g + \alpha^2 + 2\pi\alpha J_0(2\alpha r) Y_0(2\alpha r) - \frac{32\alpha^2 r}{\pi} {}_2F_3\left[1, 1; \frac{3}{2}, \frac{3}{2}, \frac{3}{2}; -4\alpha^2 r^2\right],$$

where J_0 and Y_0 are Bessel functions of first and second kind, respectively, and ${}_2F_3$ is a generalized hypergeometric function [5]. The similarity with the Loudon model above becomes apparent if we again use partial integration to approximate to lowest order in r . Using the definition of the elliptic integral, we have

$$E = \tilde{E}_g + \alpha^2 - \frac{8\alpha}{\pi} \int_0^{\pi/2} \int_0^{\infty} \frac{e^{-2\alpha z}}{\sqrt{z^2 + 4r^2 \sin^2 \theta}} dz d\theta.$$

The indefinite integral of $1/\sqrt{z^2 + x^2}$ is $\ln(z + \sqrt{z^2 + x^2})$ and it follows that

$$\begin{aligned}
E &= \tilde{E}_g + \alpha^2 - \frac{8\alpha}{\pi} \int_0^{\pi/2} \left[e^{-2\alpha z} \ln(z + \sqrt{z^2 + 4r^2 \sin^2 \theta}) \right]_0^\infty + 2\alpha \int_0^\infty e^{-2\alpha z} \ln(z + \sqrt{z^2 + 4r^2 \sin^2 \theta}) dz \Big\} d\theta \\
&= \tilde{E}_g + \alpha^2 - \frac{8\alpha}{\pi} \int_0^{\pi/2} \left[-\ln(2r \sin \theta) + 2\alpha \int_0^\infty e^{-2\alpha z} \ln(z + \sqrt{z^2 + 4r^2 \sin^2 \theta}) dz \right] d\theta \\
&\approx \tilde{E}_g + \alpha^2 + 4\alpha \ln(r) - \frac{16\alpha^2}{\pi} \int_0^{\pi/2} \int_0^\infty e^{-2\alpha z} \ln(2z) dz d\theta \\
&= \tilde{E}_g + \alpha^2 + 4\alpha(\gamma + \ln(\alpha r)).
\end{aligned}$$

Comparing to Eq.(11.5), we see that r takes the place of $2c$. We therefore expect to find precisely the same behavior as above when r goes to zero. It should be noted that this similarity is obtained even though the nanotube potential is actually (logarithmically) divergent at the origin whereas the Loudon model potential is finite. The exciton binding energy for the nanotube model is illustrated in Fig. 11.3.

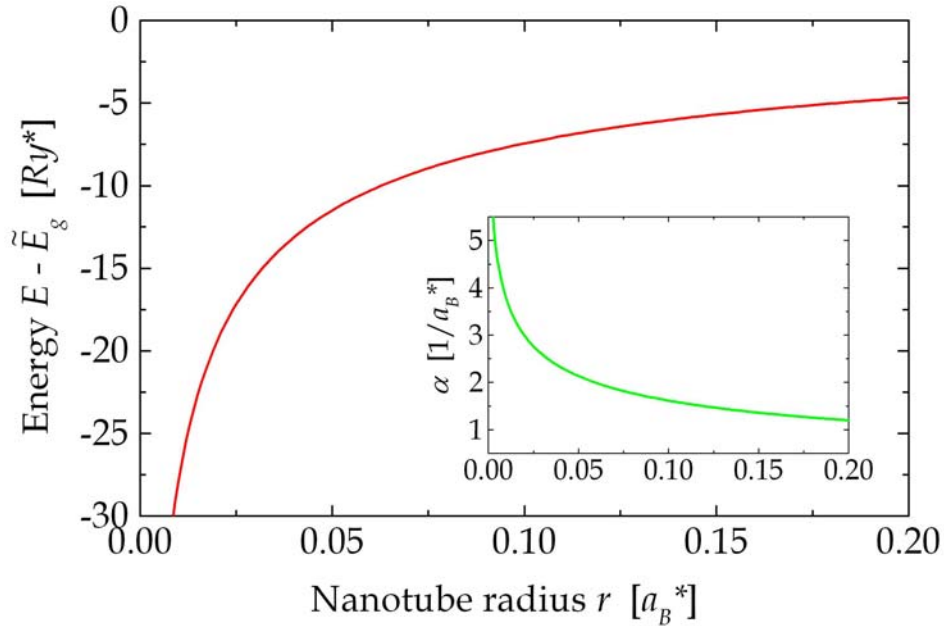


Figure 11.3 Binding energy and variational parameter (inset) of excitons in carbon nanotubes as a function of nanotube radius, all in natural exciton units.

From Fig. 11.3 it is apparent that the exciton binding energy may become very large if the nanotube radius is sufficiently small. The question is then: what are the actual values of a_B^* and Ry^* ? We recall that $a_B^* = 0.529\text{\AA} \cdot \epsilon m / m_{eh}$ and $Ry^* = 13.6\text{eV} \cdot m_{eh} / m\epsilon^2$. Hence, to answer this question we need the reduced effective electron-hole pair mass and a value of the dielectric constant. The latter is relatively straight-forward since most experiments are performed in liquid suspensions and a reasonable value describing the screening in this case is $\epsilon = 3.5$ [3]. To compute m_{eh} we need to consider the band structure. For nanotubes excited along the long-axis the allowed transitions are between bands symmetrically

positioned above and below the Fermi level. In a simple nearest-neighbor tight-binding model the transition energy is given by

$$E_{cv}(\vec{k}) = 2\gamma \sqrt{1 + 4\cos^2\left(\frac{k_y a}{2}\right) + 4\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{\sqrt{3}k_x a}{2}\right)}, \quad (11.6)$$

where $\gamma \approx 3$ eV is the hopping integral and $a = 2.46$ Å is the lattice constant. The nanotube is characterized by the chiral indices (n, m) and in terms of these, the components of the k -vector are

$$\begin{aligned} k_x &= k \frac{\sqrt{3}(n+m)}{2L} - q \frac{n-m}{2L} \\ k_y &= k \frac{n-m}{2L} + q \frac{\sqrt{3}(n+m)}{2L}. \end{aligned}$$

Here, k is the continuous long-axis component of the k -vector and q is the quantized short-axis component given by $q = p/r$, where p is an integer and r is the radius. Also, $L = \sqrt{n^2 + m^2 + nm}$ is the radius in units of $a/2\pi$, i.e. $2\pi r = aL$. An important point about the energy dispersion Eq.(11.6) is that $E_{cv}(\vec{K}) = 0$ with $\vec{K} = (\sqrt{3}, 1) \cdot 2\pi/3a$. Thus, the band gap is found at the allowed k -point closest to \vec{K} . To simplify the analysis, we expand the dispersion in the vicinity of \vec{K} and find

$$E_{cv}(\vec{k}) \approx \sqrt{3}a\gamma |\vec{k} - \vec{K}|.$$

We introduce \hat{l} and \hat{s} as unit vectors for the long-axis and short-axis, respectively. If we express \vec{K} and \vec{k} in terms of the projections along these directions we find $\vec{k} = k\hat{l} + q\hat{s}$ and similarly $\vec{K} = K\hat{l} + Q\hat{s}$, where it can be shown that $Q = (2n+m)/3r$. Hence, setting $q = Q$, leads to the condition $p = (2n+m)/3$. This condition can *only* be fulfilled if $(2n+m)/3$ is an integer in which case the nanotube is a metal. If not, the minimum difference becomes $|q - Q|_{\min} = 1/3r$. In this case, the minimum transition energy, i.e. the band gap \tilde{E}_g , then becomes

$$\tilde{E}_g = \sqrt{3}a\gamma |q - Q|_{\min} = \frac{a\gamma}{\sqrt{3}r}.$$

To find the effective mass, we consider an approximately parabolic dispersion

$$E_{cv}(\vec{k}) \approx \tilde{E}_g + \frac{\hbar^2}{2m_{eh}} (k - K)^2$$

so that, to lowest order, the square becomes $E_{cv}^2(\vec{k}) \approx \tilde{E}_g^2 + \hbar^2(k-K)^2\tilde{E}_g/m_{eh}$. On the other hand, the square of the energy dispersion for the nanotube near the minimum is

$$\begin{aligned} E_{cv}^2(\vec{k}) &\approx 3a^2\gamma^2 \{(k-K)^2 + |q-Q|_{\min}^2\} \\ &= \tilde{E}_g^2 + 3a^2\gamma^2(k-K)^2 \end{aligned}$$

Hence, a comparison demonstrates that $m_{eh} = \hbar^2\tilde{E}_g/3a^2\gamma^2$. Consequently the effective mass is proportional to the band gap. Plugging in the numbers it turns out that $\tilde{E}_g = 4.2 \text{ eV}\text{\AA}/r$ and $m_{eh}/m = 0.19\text{\AA}/r$. An extremely important point is then that the effective Bohr radius $a_B^* = 0.529\text{\AA} \cdot \epsilon m/m_{eh}$ becomes a linear function of r given by $a_B^* = 9.7r$. As a consequence, the radius r measured in units of a_B^* is *always* roughly 0.1!. At this value, the exciton binding energy as computed above and illustrated in Fig. 11.3 is around $-7.44 Ry^*$. A more accurate calculation [3] finds a binding energy of approximately $-8.1 Ry^*$. It is noted that these values are substantially higher than the maximum value $-4 Ry^*$ found for 2D structures. In analogy with the effective Bohr radius, the effective Rydberg also depends on r and inserting values we find $Ry^* = 0.21 \text{ eV}\text{\AA}/r$. It therefore follows that the ratio between exciton binding energy and band gap is a near constant of around -40%. This is obviously a huge value, which will completely rearrange the optical response.

As an example, we consider the (7,6) nanotube with a radius of $r = 4.4 \text{ \AA}$. For this structure, the exciton binding energy is then -0.39 eV . Unfortunately, there is no simple way to sum all the contributions to the optical response analytically. Instead, a numerical calculation of bound and unbound excitons can be made using a finite basis set [6]. Summing the different terms leads to the spectrum shown in Fig. 11.4, where the independent-particle result is included for comparison. The very large red-shift of the resonance corresponds to the value of the exciton binding energy. Also, it is noticed that the peak is now much more symmetric than the inverse square-root of the independent-particle spectrum.

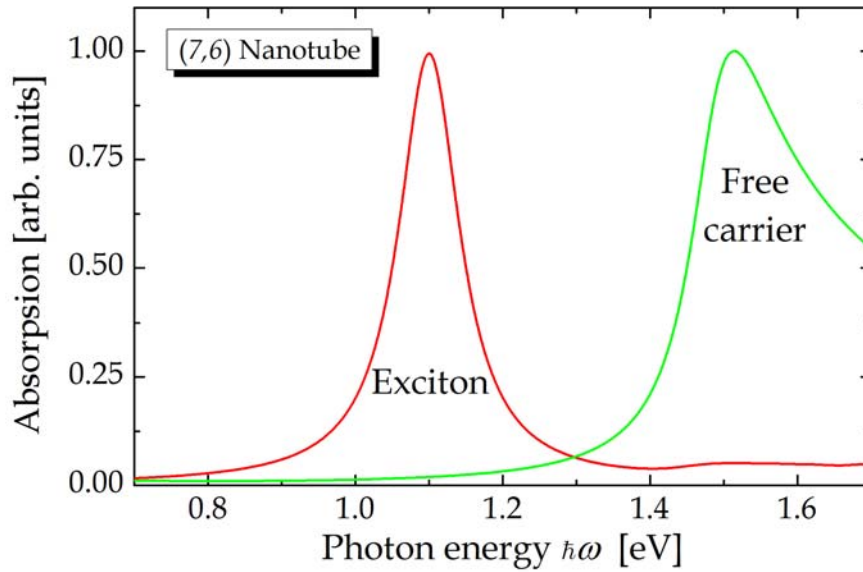


Figure 11.4 Normalized absorption spectra of a (7,6) carbon nanotube. The curves show the spectra including and neglecting excitonic effects, respectively.

Exercise: $2p$ nanotube excitons

In this exercise, we will attempt to compute the energy of the $2p$ exciton in a nanotube and for this purpose the ansatz $\Psi(z) = \sqrt{2\beta^3} z e^{-\beta|z|}$ will be used. Note that it is always orthogonal to the ground state.

a) show that $\Psi(z)$ is normalized and that the kinetic energy is β^2 .

The difficult part lies in determining an approximate expression for the Coulomb energy valid for small but finite r . It is given by

$$U = -\frac{8}{\pi} \int_0^{\pi/2} \int_0^{\infty} \frac{\Psi^2(z)}{\sqrt{z^2 + 4r^2 \sin^2 \theta}} dz d\theta.$$

As a start, we will consider the definite integral

$$W = \int_0^{\infty} \frac{f(z)}{\sqrt{z^2 + x^2}} dz.$$

The first few indefinite integrals of the square-root are denoted $S_n(z, x)$ so that

$$\begin{aligned}
S_0(z, x) &\equiv \frac{1}{\sqrt{z^2 + x^2}} \\
S_1(z, x) &\equiv \int S_0(z, x) dz = \ln\left(z + \sqrt{z^2 + x^2}\right) \\
S_2(z, x) &\equiv \int S_1(z, x) dz = z \ln\left(z + \sqrt{z^2 + x^2}\right) - \sqrt{z^2 + x^2} \\
S_3(z, x) &\equiv \int S_2(z, x) dz = \frac{1}{4}(2z^2 - x^2) \ln\left(z + \sqrt{z^2 + x^2}\right) - \frac{3}{4}z\sqrt{z^2 + x^2}.
\end{aligned}$$

b) Under the assumption that $f(\infty) = 0$, show by repeated use of partial integration that

$$\begin{aligned}
W &= -f(0) \ln x - \int_0^\infty f'(z) S_1(z, x) dz \\
&= -f(0) \ln x - f'(0)x + \int_0^\infty f''(z) S_2(z, x) dz \\
&= -f(0) \ln x - f'(0)x + \frac{1}{4} f''(0) x^2 \ln x - \int_0^\infty f'''(z) S_3(z, x) dz.
\end{aligned}$$

At this stage, no approximations have been made. However, to actually calculate the integral, we will now use the small- x expansion

$$S_3(z, x) \approx \frac{1}{4}(2z^2 - x^2) \ln(2z) - \frac{1}{4}(3z^2 + x^2).$$

In the present example, f is the function $f(z) = \Psi^2(z) = 2\beta^3 z^2 e^{-2\beta z}$ and so

$$f'(z) = 4\beta^3 z(1 - \beta z) e^{-2\beta z}, \quad f''(z) = 4\beta^3(1 - 4\beta z + 2\beta^2 z^2) e^{-2\beta z}, \quad f'''(z) = -8\beta^4(3 - 6\beta z + 2\beta^2 z^2) e^{-2\beta z}.$$

With this form and the approximate $S_3(z, x)$ we find

$$\int_0^\infty f'''(z) S_3(z, x) dz \approx -\frac{\beta}{2} - \frac{\beta^3 x^2}{2} \{1 + 2\gamma + 2 \ln \beta\}.$$

In turn, W becomes $W \approx \frac{\beta}{2} + \frac{\beta^3 x^2}{2} \{1 + 2\gamma + 2 \ln \beta x\}$ and we then have

$$\begin{aligned}
U &= -\frac{8}{\pi} \int_0^{\pi/2} \left[\frac{\beta}{2} + 2\beta^3 r^2 \sin^2 \theta \{1 + 2\gamma + 2 \ln(2\beta r \sin \theta)\} \right] d\theta \\
&= -2\beta - 8\beta^3 r^2 \{1 + \gamma + \ln(\beta r)\}.
\end{aligned}$$

The total energy is therefore $E_{2p} = \tilde{E}_g + \beta^2 - 2\beta - 8\beta^3 r^2 \{1 + \gamma + \ln(\beta r)\}$.

c) Show that the minimum energy is approximately

$$E_{2p} \approx \tilde{E}_g - 1 - 8r^2 \{1 + \gamma + \ln r\}.$$

This result is plotted below.

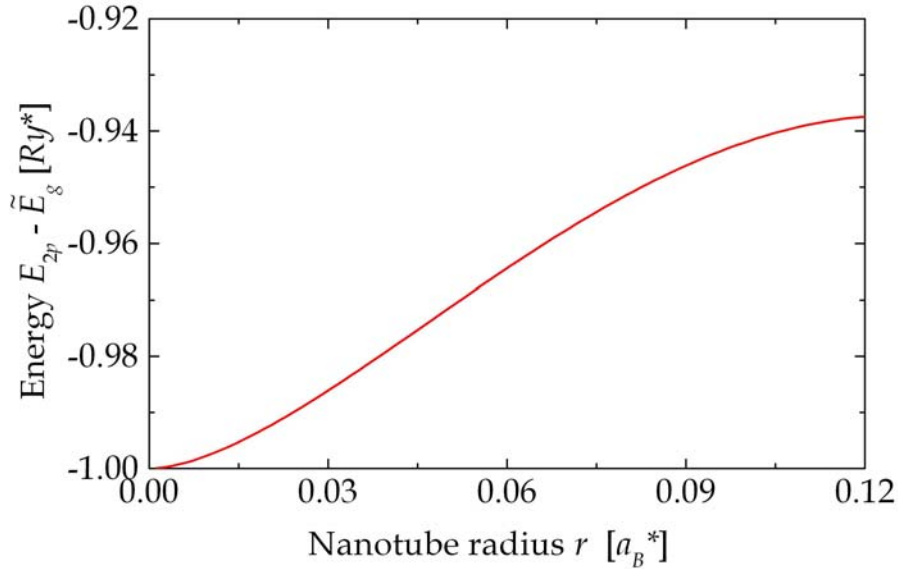


Figure 11.5 Variational 2p exciton binding energy.

References

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