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Benjamin Ricaud, Thomas G. Pedersen, Horia D. Cornean. Ground and excited exciton states in semiconductor carbon nanotubes: Perturbative and variational approach. 2006. hal-00023783v1

**HAL Id: hal-00023783**

**<https://hal.science/hal-00023783v1>**

Preprint submitted on 4 May 2006 (v1), last revised 1 May 2007 (v2)

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# Ground and excited exciton states in semiconductor carbon nanotubes: Perturbative and variational approach

3rd of May, 2006

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## Abstract

The energy levels of an exciton in semiconductor nanotubes depend on the radius of the tube. Recent two-photon photoluminescence studies give accurate experimental results on the ground and first excited state energy for different nanotubes. In this study, we propose and justify a theoretical model for the exciton which gives us almost analytic expressions for eigenvalues and eigenfunctions of ground and excited states, depending on the radius of the nanotube. We compare the results with a variational approach.

## 1 Introduction

Recent experimental results on carbon nanotubes using two-photon photoluminescence [Sc02], [Sc05], [PRB05] reveal the energy levels of the excitons, especially the ground and first excited states, and point out the dependence of these energies on the radius of the nanotube. As it is, this technique appears to be a promising way to sort out nanotubes. But on the other hand, theoretical results seem to require heavy ab initio calculation like in [PRB05] [PRB05-2], to cite the most recent, in order to find the absorption peaks due to excitons. Nevertheless, simple formula for the optical response based on excitons levels [HK] can give a good approximation. It has been pointed out [PRB87] [PRB91] that the exciton binding energy in quantum wires depends on the width of the wires by a relatively simple relation. This property is also valid for nanotubes [P1]. In the first part of the paper, we provide a rigorous justification for this latter fact and provide a simple theoretical formula for the energy levels of the exciton depending on the radius of the tube, based on the mathematical paper [CDR]. In the second part we compare with a variational method and show a close relation between the results.

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## 2 The exciton model

As suggested in [P1], we suppose we can use the effective mass approximation for particles on the tube and we deal with Wannier excitons. We take as configuration space, a cylinder of radius  $r$  and infinite length, space denoted by  $\mathcal{C}_r = \mathbb{R} \times rS^1$ ,  $S^1$  being the unit circle. The coordinates on the cylinder are  $(x, y) \in (\mathbb{R} \times rS^1)$  where  $x$  is the variable along the tube axis and  $y$  is the transverse coordinate.

The two quasi-particles live in the Hilbert space  $L^2(\mathcal{C}_r \times \mathcal{C}_r)$ . We formally consider the Hamiltonian

$$\bar{H}^r = -\hbar^2 \left( \frac{\Delta_{x_1}}{2m_1} + \frac{\Delta_{x_2}}{2m_2} + \frac{\Delta_{y_1}}{2m_1} + \frac{\Delta_{y_2}}{2m_2} \right) - V^r(x_1 - x_2, y_1 - y_2), \quad (2.1)$$

where

$$V^r(x, y) := \frac{-e_1 e_2}{\varepsilon \sqrt{x^2 + 4r^2 \sin^2\left(\frac{y}{2r}\right)}} \quad (2.2)$$

$(x_i, y_i)$  are the coordinates on the cylinder of the two charged particles,  $m_i$  their masses, and  $e_i$  their charges. Here  $\varepsilon$  is the electric permittivity of the material. The potential  $V^r$  is the three dimensional Coulomb potential simply restricted to the cylinder. We justify the expression of  $V^r$  by Pythagoras's theorem. The cylinder is embedded in  $\mathbb{R}^3$ . The distance  $\rho$  from one particle to the other in  $\mathbb{R}^3$  is:

$$\rho^2 = (x_1 - x_2)^2 + 4r^2 \sin^2\left(\frac{y_1 - y_2}{2r}\right)$$

where  $|2r \sin\left(\frac{y_1 - y_2}{2r}\right)|$  is the length of the chord joining two points of coordinate  $y_1$  and  $y_2$  on the circle.

### 2.1 "Separation of the centre of mass"

Due to the restrictions imposed by the cylindrical geometry, the usual separation of the centre of mass does not work here. The standard separation with Jacobi coordinates only works for the longitudinal variable, and introducing  $M := m_1 + m_2$  and  $\mu := m_1 m_2 / (m_1 + m_2)$ , we denote  $X := (m_1 x_1 + m_2 x_2) / M$  and  $x := x_1 - x_2$ . For the transverse variable, we change to atomic coordinates  $Y = y_2$  and  $y = y_1 - y_2$ . Let us also define the effective Rydberg  $Ry^* = \mu e^4 / 2\hbar^2 \varepsilon^2$  and Bohr radius  $a_B^* = \hbar^2 \varepsilon / \mu e^2$ , where we set  $e = e_1 = e_2$ . By a scaling, the new energy and radius will be expressed in multiple of these units. This gives us the Hamiltonian:

$$H^r = -\frac{1}{M} \partial_X^2 - \frac{1}{m_2} \partial_Y^2 - \frac{1}{\mu} \partial_x^2 - \frac{1}{\mu} \partial_y^2 + \frac{2}{m_2} \partial_y \partial_Y - 2V^r(x, y).$$

First, we can separate the partial centre of mass with coordinate  $X$ . Secondly, since on the  $Y$  variable there are periodic boundary conditions, let us consider the orthonormal basis of eigenvectors of  $-\partial_Y^2$ ,

$$-\partial_Y^2 = \sum_{n=-\infty}^{\infty} E_n^r |\chi_n^r\rangle \langle \chi_n^r|$$

where

$$\chi_n^r(Y) = \frac{1}{\sqrt{2\pi r}} e^{in\frac{Y}{r}} \text{ and } E_n^r = \frac{n^2}{r^2}, n \in \mathbb{Z}.$$

One can see that for small radii, the separation between different transverse levels of energy is high. A recent theoretical study based on ab initio calculations [PRB05] shows that the probability density of the exciton is constant along the circumference and experimental results [PRL01] point out the impossibility for the exciton to absorb light polarised perpendicularly to the axis for the range of energy we are interested in. So it is reasonable to assume that the radius is so small that the system stays in the ground state of  $-\partial_Y^2$ , where  $n = 0$  and the density of probability is constant along the circumference. As a consequence, we write the eigenfunctions  $\psi$  of  $H$  to be the combination:

$$\psi(x, y) = \phi(x, y) \cdot \chi_0^r(Y) = \phi(x, y) \cdot \frac{1}{\sqrt{2\pi r}}.$$

Then, applying the Hamiltonian to these vectors, the derivatives with respect to  $Y$  cancel out, and to find the low lying spectrum, we only have to study the following operator

$$\tilde{H}^r = -\frac{1}{\mu} \partial_x^2 - \frac{1}{\mu} \partial_y^2 - 2V^r(x, y)$$

which is two dimensional and acts on  $L^2(\mathcal{C}_r)$ .

## 2.2 An effective one dimensional operator for the low lying spectrum

The potential  $V^r$  is too singular and  $\tilde{H}^r$  is not well defined. It is suitable at this point to introduce the form:

$$t_{\tilde{H}}(\psi, \phi) = \frac{1}{\mu} \langle \partial_x \psi, \partial_x \phi \rangle + \frac{1}{\mu} \langle \partial_y \psi, \partial_y \phi \rangle - 2 \langle \sqrt{V^r(x, y)} \psi, \sqrt{V^r(x, y)} \phi \rangle.$$

which is more regular than  $\tilde{H}^r$  and can be handled mathematically. This quadratic form defines the operator  $\tilde{H}^r$  since we can obtain it by an integration by parts. This integration by parts is the key point which will give us later the boundary conditions for  $\tilde{H}^r$  to be self adjoint. Now the Hamiltonian is mathematically well defined by  $t_{\tilde{H}}$  and has a clear physical meaning. Similarly to the preceding part, a good approximation of the behaviour of the eigenfunctions along the transverse variable when the radius is small is given by the ground state of the free Laplacian with periodic boundary conditions. We write the eigenfunctions  $\phi$  of  $\tilde{H}^r$  as:

$$\phi(x, y) = \varphi(x) \cdot \frac{1}{\sqrt{2\pi r}}. \quad (2.3)$$

We have that

$$\begin{aligned}
& t_{\tilde{H}}\left(\frac{\varphi}{\sqrt{2\pi r}}, \frac{\varphi}{\sqrt{2\pi r}}\right) = \\
& = \frac{1}{\mu}(\partial_x \frac{\varphi}{\sqrt{2\pi r}}, \partial_x \frac{\varphi}{\sqrt{2\pi r}}) \\
& - 2 \int_{-\infty}^{\infty} \int_{-\pi r}^{\pi r} \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}} \frac{1}{2\pi r} \varphi(x) \overline{\varphi}(x) dy dx \\
& = \frac{1}{\mu} \int_{-\infty}^{\infty} \overline{(\partial_x \varphi)}(x) (\partial_x \varphi)(x) dx - \frac{1}{\pi r} \int_{-\infty}^{\infty} V_{\text{eff}}^r(x) \varphi(x) \overline{\varphi}(x) dx
\end{aligned}$$

where

$$V_{\text{eff}}^r(x) = \frac{1}{2\pi r} \int_{-\pi r}^{\pi r} \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}} dy.$$

Let us introduce what will be our effective one-dimensional comparison operator:

$$H_{\text{eff}}^r := -\frac{d^2}{dx^2} - 2V_{\text{eff}}^r(x) \quad (2.4)$$

for which  $\varphi$  are the eigenfunctions. We have now reduced our problem of two particles on a cylinder to a one dimensional problem formed by a particle interacting with an external potential. Unfortunately, this problem cannot be solved straight away and we will use in the following perturbation theory to find an approximation of the solutions. A complete mathematical justification of these operations can be found in [CDR].

## 2.3 The one dimensional Coulomb Hamiltonian

### 2.3.1 Approximation of $H_{\text{eff}}^r$

It has been shown in [CDR] that we can approximate the one-dimensional potential  $V_{\text{eff}}^r$  for small  $r$  by the multiplication operator:

$$Y_r(x) = \frac{1}{\sqrt{x^2 + 4r^2}},$$

with the addition of a term coming from a "delta function" at  $x = 0$ , where there is a singularity. That is to say, it is demonstrated that we get the relation for  $r \leq 1$  and  $f, g$  two smooth functions

$$\langle f, V_{\text{eff}}^r g \rangle \simeq \langle f, Y_r g \rangle + \ln(4) f(0) \overline{g(0)}. \quad (2.5)$$

One can recognise in  $Y_r$  a form of the regularised Coulomb potential. In the following, our approach will be quite similar to the one of Loudon [L] in the sense that we let the regularising parameter tend to zero. But with the difference that here this parameter is the radius of the nanotube. Hence, it will give us an approximation for the exciton energies depending on the radius and allow us to estimate the error we make using this approximation. Now, for  $\varepsilon > 0$  we define

the quadratic form  $C_0(\cdot, \cdot)$  by<sup>1</sup>

$$\begin{aligned} C_0(f, f) &= - \int_0^\infty \ln(x) \cdot (|f|^2)'(x) dx + \int_{-\infty}^0 \ln(-x) \cdot (|f|^2)'(x) dx \\ &= \int_{-\varepsilon}^0 \ln(-x) \cdot (|f|^2)'(x) dx - \int_0^\varepsilon \ln(x) \cdot (|f|^2)'(x) dx \\ &\quad + \ln(\varepsilon) (|f(\varepsilon)|^2 + |f(-\varepsilon)|^2) + \int_{\mathbb{R} \setminus [-\varepsilon, \varepsilon]} \frac{1}{|x|} \cdot |f(x)|^2 dx. \end{aligned} \quad (2.6)$$

The last equality is obtained by an integration by part, one can notice the relation with a Coulomb potential in one dimension. Again from [CDR] we have

$$\langle f, Y_r g \rangle \simeq -2 \ln(r) f(0) \overline{g(0)} + C_0(f, g). \quad (2.7)$$

Eventually, let us define a new potential via a quadratic form

$$\langle f, V_C g \rangle := -2 \ln\left(\frac{r}{2}\right) f(0) \overline{g(0)} + C_0(f, g),$$

which is close to  $V_{\text{eff}}^r$  when  $r$  is small and is exactly the Coulomb potential when we look away from the origin. We will see in the following that this particular potential gives a solvable eigenvalue problem for the associated Hamiltonian. According to perturbation theory, these solutions are approximations of the solutions of the problem with  $V_{\text{eff}}^r$  with a small error. This is a good approximation at small radii.

### 2.3.2 Boundary conditions of the Coulomb Hamiltonian

The operator  $H_C$  we shall now study is defined by its associated quadratic form

$$t_C(\psi, \phi) := \int_{\mathbb{R}} \overline{\phi'(x)} \psi'(x) dx + 2 \left( 2 \ln\left(\frac{r}{2}\right) \overline{\phi(0)} \psi(0) - C_0(\phi, \psi) \right).$$

One can recognise the kinetic energy in the first term and the potential  $V_C$  in the second term. The general theory of symmetric quadratic forms gives us the existence of an associated operator  $H_C$  defined by

$$t_C(\phi, \psi) = \langle \phi, H_C \psi \rangle, \quad (2.8)$$

whenever  $\psi$  is in the domain of  $H_C$ . The difficulty here is that  $V_C$  is not a usual Schrödinger-type multiplication operator, but if  $\psi$  is smooth enough we still have that:

$$(H_C \psi)(x) = -\psi''(x) - \frac{2\psi(x)}{|x|}, \quad x \neq 0. \quad (2.9)$$

In particular, if  $\psi$  is an eigenfunction of  $H_C$  corresponding to an energy  $E$ , then we can write:

$$-\psi''(x) - \frac{2\psi(x)}{|x|} = E\psi(x), \quad x \neq 0. \quad (2.10)$$

---

<sup>1</sup>Notice that this definition of  $C_0$  differs from the one of [CDR] in which there is an additional term:  $2 \ln 2 |f(0)|^2 = \int_{-\infty}^0 \ln 2 \cdot (|f|^2)'(x) dx + \int_0^\infty \ln 2 \cdot (|f|^2)'(x) dx$ . This term is here put together with the other term depending on the function at zero.

In order to get the behaviour at the origin for the eigenfunctions of  $H_C$ , we integrate by parts and use (2.10). For  $\varepsilon > 0$  we have:

$$\begin{aligned} & \int_{\mathbb{R}} \overline{\phi'(x)} \psi'(x) dx & (2.11) \\ &= \overline{\phi(-\varepsilon)} \psi'(-\varepsilon) - \int_{-\infty}^{-\varepsilon} \overline{\phi(x)} \psi''(x) dx - \overline{\phi(\varepsilon)} \psi'(\varepsilon) - \int_{\varepsilon}^{\infty} \overline{\phi(x)} \psi''(x) dx \\ &+ \int_{-\varepsilon}^{\varepsilon} \overline{\phi'(x)} \psi'(x) dx \end{aligned}$$

where the last integral will converge to zero as  $\varepsilon$  goes to zero. On the other hand,

$$\begin{aligned} C_0(\phi, \psi) &= \int_{-\varepsilon}^0 \ln(-x) \cdot (d_x(\overline{\phi}\psi))(x) dx - \int_0^{\varepsilon} \ln(x) \cdot (d_x(\overline{\phi}\psi))(x) dx \\ &+ \ln(\varepsilon) \left( \overline{\phi(\varepsilon)} \psi(\varepsilon) + \overline{\phi(-\varepsilon)} \psi(-\varepsilon) \right) + \int_{\mathbb{R} \setminus [-\varepsilon, \varepsilon]} \frac{1}{|x|} \cdot \overline{\phi(x)} \psi(x) dx. \end{aligned} \quad (2.12)$$

Then adding (2.11) with (2.12), using (2.10) and letting  $\varepsilon$  tend to zero (see [CDR] for technical details) we have:

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} t_C(\phi, \psi) &= (\phi, E\psi) \\ &+ 2 \lim_{\varepsilon \rightarrow 0} \overline{\phi(0)} \left[ \frac{\psi'(-\varepsilon) - \psi'(\varepsilon)}{2} + 2 \ln\left(\frac{r}{2}\right) \psi(0) - \ln(\varepsilon) (2\psi(0)) \right]. \end{aligned}$$

Now using (2.8) and the eigenvalue equation  $H_C\psi = E\psi$  we get the boundary condition:

$$\lim_{\varepsilon \rightarrow 0} \overline{\phi(0)} \left[ \frac{\psi'(-\varepsilon) - \psi'(\varepsilon)}{2} + 2 \ln\left(\frac{r}{2}\right) \psi(0) - 2 \ln(\varepsilon) \psi(0) \right] = 0, \quad (2.13)$$

which holds true for all complex numbers  $\phi(0)$ .

## 2.4 Eigenvalues and eigenfunctions

We now have to solve the equation

$$-\partial_x^2 \psi - \frac{2}{|x|} \psi = E\psi, \quad x \neq 0, \quad (2.14)$$

with the boundary condition (2.13). Similarly to Loudon in [L], we introduce a dimensionless quantity  $\alpha$  and the change of variables

$$E = -\frac{1}{\alpha^2} \text{ and } x = \frac{\alpha}{2} z, \quad (2.15)$$

then we obtain

$$\frac{d^2}{dz^2} \tilde{\psi} - \frac{1}{4} \tilde{\psi} + \frac{\alpha}{|z|} \tilde{\psi} = 0, \quad z \neq 0. \quad (2.16)$$

The solutions are known for  $z > 0$  and  $z < 0$ , see [AS, chap. 13] for example. The second thing is to see what condition at  $z = 0$  should the eigenfunctions  $\tilde{\psi}$  obey. If we scale (2.13),

$$\lim_{\varepsilon \rightarrow 0} \left[ \frac{\tilde{\psi}'(-\varepsilon) - \tilde{\psi}'(\varepsilon)}{2} + \alpha(\ln r - \ln(\alpha\varepsilon)) \tilde{\psi}(0) \right] = 0. \quad (2.17)$$

We only give here the results. Details of calculations can be found in [CDR]. If we take the only square integrable solution, we have two cases: If  $\alpha = N$  is a positive integer, then the eigenstates are the odd functions  $\tilde{\psi}_{n_{\alpha}p}$  with associated eigenvalues  $E_{n_{\alpha}p}$ , where  $n_{\alpha} = N + 1$ ,

$$\tilde{\psi}_{n_{\alpha}p}(z) = e^{-\frac{1}{2}|z|} z \frac{1}{\sqrt{2N}} L_{N-1}^1(|z|), \quad E_{n_{\alpha}p} = -\frac{1}{N^2},$$

where  $L_{N-1}^1$  is an associated Laguerre polynomial. Notice that these energies are independent of the radius of the tube. If  $\alpha$  is not an integer, the eigenstates are the even functions  $\tilde{\psi}_{n_{\alpha}s}$  with associated eigenvalues  $E_{n_{\alpha}s}$ , where  $n_{\alpha}$  is the smallest integer larger than  $\alpha$  and:

$$\tilde{\psi}_{n_{\alpha}s} = C_{\alpha} W_{\alpha, \frac{1}{2}}(|z|) = C_{\alpha} |z| e^{-\frac{1}{2}|z|} U(1 - \alpha, 2, |z|) \quad E_{n_{\alpha}s} = -\frac{1}{\alpha^2},$$

where  $C_{\alpha}$  is a normalizing constant,  $W$  is the Whittaker function and  $U$  is the confluent hypergeometric function or Kummer function of the second kind. We denote with  $\Gamma(z)$  and  $\Psi(z) = \Gamma'(z)/\Gamma(z)$  the usual gamma and digamma functions, and we get from (2.17) that for even solutions  $\alpha$  must satisfy the relation:

$$\Psi(1 - \alpha) + 2\gamma + \frac{1}{2\alpha} - \ln \alpha + \ln r = 0. \quad (2.18)$$

From this relation, which contains an implicit expression for  $\alpha(r)$ , one can deduce several important facts. For all integers  $N$  and for  $\alpha$  in between  $N$  and  $N + 1$ , there is only one solution of (2.16) satisfying the boundary condition. Furthermore, the energies associated with the non integer  $\alpha$  tend to their closest lower integer when  $r$  tends to zero. A special case is the one of the ground state  $E_{1s}$  of the exciton which tends to minus infinity as the radius tends to zero. The behaviour for small  $r$  is

$$E_{1s} \stackrel{r \rightarrow 0}{\simeq} -4(\ln r)^2.$$

Notice that equation (2.18) is exactly what one gets by explicitly calculating the condition requiring the derivative of even states to vanish at the origin, relation (3.22) in Loudon's paper, and replacing his parameter  $a$  by  $r \cdot a_0/2$ , for small  $r$ . We can also compare with the result from [PRB87] where Banyai et al. found numerically  $a = 0.3a_0 \cdot r$  for the exciton problem in a quantum wire of radius  $r$ . The energies associated to the exciton are drawn on figure 1 and we calculated numerically the lowest four eigenvalues with respect to the radius on figure 3, along with a comparison of the ground state given by the variational method of [P1]. On figure 4 a zoom was made around the first and second excited states.

One can notice that the odd states possess a constant energy, independent of the radius. This is due to the fact that the odd states vanish at zero where there is the singularity of the potential. Indeed, the potential becomes, for an odd function  $f$ :

$$\langle f, V_{\text{eff}}^r f \rangle \simeq C_0(f, f),$$

which is independent of  $r$ .



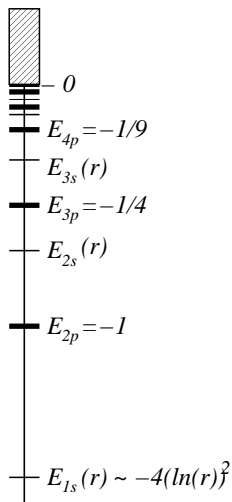


Figure 1: Energy of the bound states of the exciton. Energies are expressed in multiples of the effective Rydberg of the exciton.

### 3 Variational approach and comparison

The variational method operates by minimising the energy of a trial function and is therefore usually applied to approximate the ground state. However, by restricting the trial function to forms that are orthogonal to the ground state, low lying excited states can be obtained variationally as well. In Ref. [P1], the variational method was applied to the ground state and in Ref. [P3] a similar approach was applied to calculate the  $2p$  oscillator strength of interest for two-photon absorption. The  $2p$  state is especially important because this state is used for excitation in two-photon fluorescence measurements [Sc05]. By recording the energy of photons emitted from the lowest ( $1s$ ) exciton, a direct measure of the  $2p - 1s$  energy difference is obtained. In turn, the  $1s$  exciton binding energy (i.e the  $1s$  excitation energy measured relative to the band gap) can be derived if a reliable model for the exciton energy spectrum is invoked.

In the present work, we wish to compare results of the relatively complicated variational approach to the straight-forward and analytical Coulomb model. Hence, in the following we briefly explain the reasoning behind our variational estimate of the lowest excited ( $2p$ ) state. In practical applications, the trial function must be sufficiently simple that calculation of the energy is manageable. This implies that relatively few adjustable parameters should be considered. At the same time, a certain flexibility is required to provide reasonable accuracy. A useful strategy consists in constructing trial functions so that they correctly accommodate the known solutions in limiting cases of the general problem. Thus, we are guided by the analytical solution for the plane, i.e. for nanotube radii much larger than the effective Bohr radius. In our units, this state is simply  $\varphi_{2p} \propto x \exp\{-2/3(x^2 + y^2)^{1/2}\}$ . On the other hand, in the extreme 1D limit we expect  $\varphi_{2p} \propto x \exp\{-|x|\}$ . To accommodate both limits, we consequently suggest the (un-normalized) trial form

$$\varphi_{2p}(x, y) = x \exp\{-(x^2/k^2 + y^2/q^2)^{1/2}\}, \quad (3.1)$$

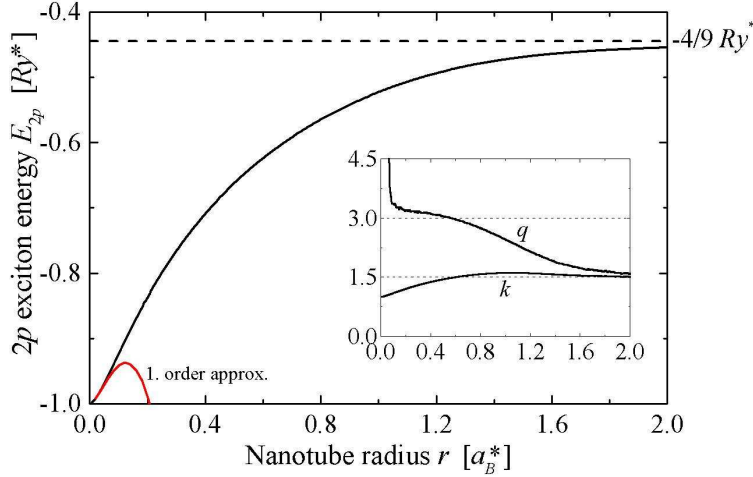


Figure 2: Variational  $2p$  state energy as a function of nanotube radius. Inset: the  $r$ -dependence of decay lengths  $k$  and  $q$  of the trial wave function.

where  $q$  and  $k$  are variational parameters to be determined by minimizing the expectation value of the energy. This expectation value is found as  $E_{2p} = (K - V)/N$ , where  $K$ ,  $V$  and  $N$  are the kinetic energy, potential energy and normalization constant, respectively. The integrations are quite cumbersome and only  $K$  and  $N$  can be obtained in closed form in terms of Struve and modified Bessel functions. The potential energy  $V$  is evaluated numerically using Gaussian quadrature.

The minimized energy as a function of radius  $r$  is illustrated in Fig. 2. The limiting values are  $E_{2p} = -1$  and  $E_{2p} = -4/9$  for small and large  $r$ , respectively, in agreement with the analytic solutions in these limits. In between these limits, the curve interpolates smoothly between the limiting values and the dominant correction at small  $r$  is  $-8(1 + \gamma + \ln(r))r^2$ .

In order to judge the usefulness of the different approaches used in the present work it is essential to determine the appropriate nanotube radius  $r$  in excitonic units, i.e. in units of  $a_B^*$ . An important point in this respect is that, in fact,  $a_B^*$  varies between different nanotubes. The relation needed for conversion is  $a_B^* = 0.529 \text{ \AA} \varepsilon / \mu$ , where  $\varepsilon$  is the dielectric constant screening the Coulomb interaction and  $\mu$  is the reduced effective mass. Whereas  $\varepsilon$  may be assumed the same for all nanotubes,  $\mu$  must be derived from the curvature of the band structure and, hence, depends on both radius and chirality of the nanotube. However, detailed studies [P2] show that  $a_B^*$  is roughly proportional to the nanotube diameter and as a consequence  $r$  (in units of  $a_B^*$ ) is nearly constant and given by  $r \approx 0.1 a_B^*$  if  $\varepsilon \approx 3.5$ . It should be noted, though, that in media with little screening a larger  $r/a_B^*$  is expected. The smallness of  $r$  means that approximations based on expansion around  $r = 0$  are expected to be accurate.

In figure 3 and 4, a comparison of variational energies and the results of the Coulomb model is given. In both the  $1s$  and  $2p$  cases, reasonable agreement between the two approaches is found around  $r \approx 0.1 a_B^*$ . Also, in both cases, the

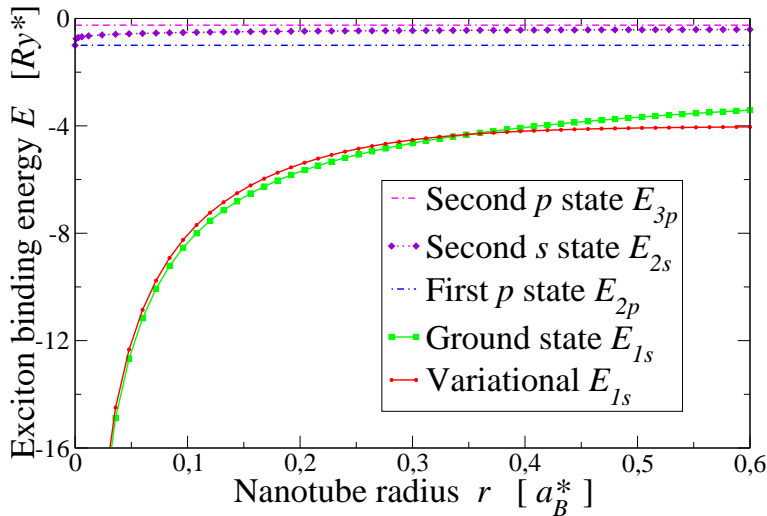


Figure 3: Energy of the four lowest bound states of the exciton with respect to the radius. Even states were calculated numerically using (2.18). Notice that the energy of the second  $s$  state is equal to the one of the first  $p$  state at zero. In red: graph of the ground state computed with the variational method on the cylinder from [P1].

variational result lies slightly higher than the Coulomb model. The ground state has deviated by more than 100% from the plane value for radii around  $0.1a_B^*$ . An error of less than 5% is seen between the curves at this point. Note that if the curve from the Coulomb model is lower in energy than the variational one, this does not mean that the approximation is better. Although in the variational approach the lower is the better since the exact solution is always below the variational result, in the Coulomb model the exact value is somewhere around the approximation, bounded by an error bound. In this work the error bound was not calculated because, unfortunately, the compromises made to get a simple formula implied a difficult calculus to optimize on the bound, even by numerical computations. For the first excited state, the Coulomb model approximation for the energy is independent of the radius of the tube. This must be a good approximation for very small radii. However, this approximation becomes increasingly inaccurate as the radius increases, as the exact value should tend to the energy of the problem on the plane with energy equal to  $-4/9a_B^*$  as do the variational curve.

## 4 Conclusion

In conclusion, the Coulomb model applied to excitons in carbon nanotubes demonstrates that the energy associated with each even state decreases to the energy of its closest odd state as the radius tends to zero. Since each odd state energy is independent of the size of the tube in this approach, all energies associated to excited states stay in the range  $(-1, 0)$  (in effective Rydberg energy units). So only the ground state diverges when the radius gets smaller. This

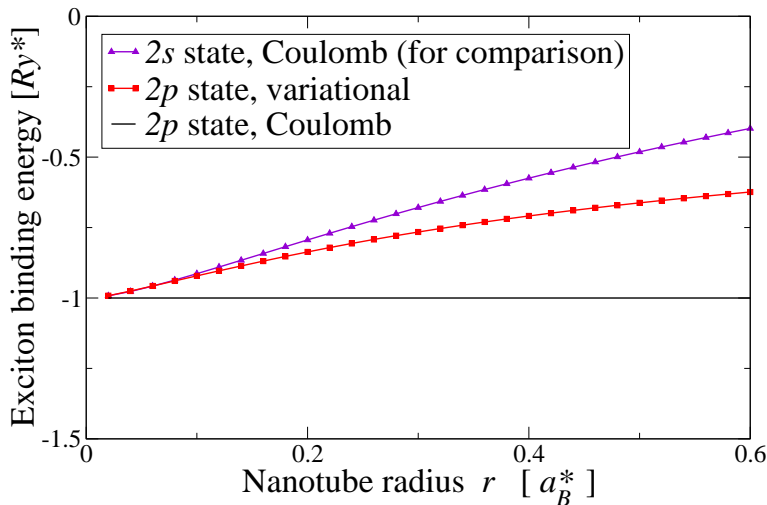


Figure 4: Zoom around the energy of the  $2p$  state showing both variational and Coulomb model results. In addition, the  $2s$  state obtained with Coulomb model is included for comparison.

is confirmed by the behaviour of variational first excited state which converges to  $-1$ . The simple exciton model proposed in this paper and studied both by means of rigorous perturbation theory and by a variational approach is a good starting point for attacking the difficult problem of electron-electron interactions in low dimensional structures such as carbon nanotubes.

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