Semiconducting carbon nanotube quantum dots: calculation of the interacting electron states by exact diagonalisation

MERVYN ROY¹ and P. A. MAKSYM¹

¹ *Department of Physics and Astronomy, University of Leicester, University Road, Leicester LE1 7RH.*

PACS 73.63.Fg – Nanotubes

PACS 73.21.La – Quantum dots

PACS 73.23.H – Coulomb blockade; single-electron tunneling

Abstract. – In semiconducting carbon nanotube quantum dots that contain a few interacting electrons the electron-electron correlation is always important. The states of up to 6 interacting electrons in such a dot are calculated by exact diagonalisation of a 2-band, effective mass Hamiltonian. The addition energy and the few electron density are investigated for a wide range of dots with different physical properties and, in a large proportion of these dots, the electrons are found to form Wigner molecules.

Introduction. – It is now possible to form one dimensional quantum dots from high quality semiconducting carbon nanotubes [1]. Quantum dots are tunable artificial atoms that provide an ideal laboratory for exploring the physics of atoms and molecules and have many potential applications, for example in quantum computing. As dots can be used to controllably confine small numbers of charge carriers they have stimulated much interest in the quantum states of a few interacting electrons. One dimensional nanotube (NT) dots are, however, very different to the 2D semiconductor dots that have been used to study effects such as the formation of all electron (Wigner) molecules [2, 3] and electronic shell filling analogous to that observed in atoms [4]. The reduced dimensionality of NT dots alters the form of the effective Coulomb interaction [5], it affects the allowed symmetries of the states [6] and the types of confinement that can be engineered.

In particular, NT dots can be used to fabricate room temperature single electron transistors because of the large single particle level spacings which can be engineered [7]. They are promising candidates for spin qubits [8] and also exhibit interesting shell filling effects due to the approximately degenerate [8] K, K' sub-bands. This has been examined in detail in metallic NT dots [9, 10] but, only recently has it been possible to accurately measure the addition energy [1] or the differential conductance [11] of semiconducting NT dots.

In the Coulomb blockade [4] regime the occupancy of all types of NT dot can be controlled to the level of a single electron. Importantly, however, semiconductor NT

dots can be completely emptied of electrons [1]. In marked contrast to metallic NT dots, semiconductor NT dots can therefore contain just a few interacting particles. To understand this technologically important system it is necessary to add detailed modelling of the electronic states to the existing experimental measurements, and the work described here is motivated by this.

In this Letter we develop a 2-band effective mass Hamiltonian H with a modified coulomb interaction that describes the interacting electrons in a semiconducting NT dot. We write H in dimensionless form, diagonalise it exactly for up to 6 electrons and investigate the interacting electron states over all of the physically accessible region of the dimensionless parameter space. We find that electron-electron correlation is always important in semiconducting NT dots and this has implications for the interpretation of experimental addition energy data [1]. Almost nowhere are the electrons sufficiently weakly correlated for the Hartree-Fock theory to be accurate. Instead we see evidence for the formation of quasi-1D all electron molecules over a surprisingly large proportion of the parameter space. Unlike most inorganic semiconductor dots, it should therefore be possible to fabricate an NT dot in the 1D strongly correlated limit. And, unlike semiconductor nanowire dots [12] (which might also be fabricated in this limit) the physics of the NT dot is not complicated by edge effects. At present, NT dots are perhaps the only semiconductor dots in which quasi-1D Wigner molecules can both be accurately modelled and experimentally probed.

Dot Model. — Our dot model is based on the gated semiconductor NT dot device in ref. [1]. In this type of dot the confinement potential is electrostatic and soft walled [1, 13]. The details depend on the exact specifications of the device but, near to the centre of the NT, the potential varies quadratically with a gate voltage dependent energy zero, and we use a 1D harmonic confinement potential in our model. Typically, the dot length scales are of the order of a few tens of nanometres and the dot energy scales are a few, to a few tens, of meV. We consider NTs with a band gap E_g much larger than this energy scale and a unit cell length much smaller than this length scale. This type of dot can be described with an effective mass Hamiltonian. However, there are new features that arise from the NT bandstructure and these can be understood by considering the electronic structure of graphene.

Theory. — NTs are rolled up graphene sheets and the NT states near to the conduction band (CB) minima are formed from the states of graphene near to the K and K' points. However, care must be taken when deriving the NT states because of the unusual nature of the graphene bandstructure near to K and K' : first, the K and K' points are equivalent and this leads to two equivalent CBs in all semiconducting NTs (we neglect the very small spin orbit splitting [8]); second, the dispersion near to each of the graphene K and K' points is linear. To derive the NT dot states we follow a procedure similar to refs. [14, 15] and use the two component Bloch wavefunctions of graphene as basis states. This introduces new features into our effective mass theory for interacting electrons in a NT quantum dot. The net result is a one dimensional 2-band effective mass Hamiltonian with a modified Coulomb interaction,

$$H = \sum_{i=1}^N \left[\frac{-\hbar^2}{2m^*} \frac{d^2}{dz_i^2} + \frac{m^*\omega^2}{2} z_i^2 \right] + \frac{\rho/R}{2\epsilon_r} \sum_{i \neq j} U(z_i - z_j, R). \quad (1)$$

Here N is the number of electrons, ω is the harmonic confinement frequency, R is the NT radius, ϵ_r the dielectric constant and $\rho = e^2/(4\pi\epsilon_o)$. The effective mass m^* is calculated from a 4-orbital tight binding calculation with the parameterisation of Porezag *et al.* [16]. $\rho U/\epsilon_r$ is the effective intraband Coulomb interaction. This effective interaction includes the effect of both the NT band structure and the cylindrical geometry of the tube. Here, we neglect the interband Coulomb scattering because its effect on the N -particle ground state energy is small [5]. In this case the band index acts simply as an extra label by which states can be distinguished (a 'pseudospin').

To derive our expressions for H and U we first consider the single particle NT effective mass equations starting from the Hamiltonian of a graphene sheet. In two component form the graphene states are $(\phi_{A\mathbf{k}} + (-1)^\mu e^{i\theta_{\mathbf{k}}} \phi_{B\mathbf{k}})/\sqrt{2}$ where $\mu = 1, 0$ for the valence or conduction band, $\phi_{A\mathbf{k}}$ and $\phi_{B\mathbf{k}}$ are the Bloch functions of the A, B sub-lattices of graphene and $\mathbf{k}$ is measured from

the K or K' point. The co-ordinate axes have been rotated so that the NT chiral vector points along y , and z is the direction of the tube. Then, the phase factor $\theta_{\mathbf{k}}$ is the sum of the chiral angle θ and the polar angle $\phi_{\mathbf{k}}$ of $\mathbf{k}$. In a NT $\mathbf{k}$ is quantised and the product of the envelope function and the Bloch function is periodic [15]: $k_y R = n - \nu/3$ where $\nu = \pm 1$ and n is an integer. In an external potential v , the NT states, written as a superposition of the Bloch states at K , are then $\psi(y, z) = \sum_{n\mu k_z} a_{n\mu k_z} e^{i\mathbf{k} \cdot \mathbf{r}} (\phi_{A\mathbf{K}} + (-1)^\mu e^{i\theta_{\mathbf{k}}} \phi_{B\mathbf{K}})/\sqrt{2}$, and there is an equivalent expression for states near K' .

The key steps to develop our theory are as follows. First, because our confinement potential is 1 dimensional the coupling between NT bands of different k_y vanishes. Second, $E_g \gg \hbar\omega$, so we neglect the coupling between conduction and valence bands. It is physically reasonable that this cross gap perturbation is small: our confinement potential binds electrons and repels holes and so the overlap between these states is small. To first order, the coupling is zero and, we have estimated the second order correction and it is small ($\approx 10^{-3}$ meV).

We now have an uncoupled Schrödinger equation for each n, μ band, $\epsilon_{k_z} a_{k_z} + \sum_{k'_z} (1 + e^{i(\theta_{\mathbf{k}'} - \theta_{\mathbf{k}})}) v_{k_z - k'_z} a_{k'_z} = E a_{k_z}$. This is similar to the momentum space effective mass equation of motion in a parabolic band, except it contains a term involving the phase factor, $\theta_{\mathbf{k}} = \theta + \arctan(k_z/k_y)$. For the $n = 0, \mu = 0$ CB, $k_y = 1/(3R)$ and, as the NT dot length scale is much larger than R , we can expand the phase dependent term in powers of k_z/k_y . For any real symmetric potential, the effect of the phase term on the single particle energy is zero to first order. To second order the correction for a harmonic potential is a constant energy shift of < 0.1 meV which we neglect. However, although the phase has negligible effect on the single particle energy, it introduces an offset between the envelope functions F that multiply the A and B sub-lattice Bloch states: the total wavefunction is $\psi(y, z) = e^{ik_y y} (F(z) \phi_{A\mathbf{K}} + e^{i\theta} F(z + 3R) \phi_{B\mathbf{K}}) / (2\sqrt{2}\pi R)$. The interaction potential U is found by taking matrix elements of the Coulomb interaction between these states. So, assuming the Coulomb interaction is slowly varying on the length scale of the graphene cell,

$$U(z, R) = \frac{1}{4} (2u(z, R) + u(z - 3R, R) + u(z + 3R, R))$$

$$u(z, R) = \frac{2R}{\pi \sqrt{z^2 + 4R^2}} \mathbf{K} \left(\frac{2R}{\sqrt{z^2 + 4R^2}} \right), \quad (2)$$

where $z = z_i - z_j$ and $\mathbf{K}$ is an elliptic integral of the first kind. In Eq. 2, $u(z, R)$ is derived from the standard form of the interaction between charged particles on the surface of a cylinder and diverges like $\log(R/z)$ as $z \rightarrow 0$. The terms $u(z - 3R, R)$ and $u(z + 3R, R)$ in the effective interaction arise from the phase difference between Bloch states on the A and B sub-lattices of graphene. This form of the interaction does not occur in traditional semiconductor quantum dots. It is a consequence of the form of the nanotube band structure which, in turn comes from

the physical lattice structure of graphene and the fact that the graphene is rolled up to form the tube.

So far we have considered the CB constructed from states near K but we can also write down equivalent equations for states near K' . The K and K' CBs are coupled by the Coulomb interaction, but the effective interband interaction is small [5] and we neglect it. Our Hamiltonian is block diagonal in the total spin. As we ignore the interband interaction it is also block diagonal in the total pseudospin and, interestingly, the 2-electron spin 1 and spin 0 ground states are degenerate [5].

Calculation. – To calculate the few electron states we first write H in dimensionless form by choosing the unit of energy as $E_u = [\rho^2 m^* \omega^2 / \epsilon_r^2]^{1/3}$ and the unit of length as $\lambda = [\rho / (\epsilon_r m^* \omega^2)]^{1/3}$. Then, with $x = z/\lambda$, and dimensionless parameters, $\alpha^3 = [\rho^2 m^* / (\hbar^3 \epsilon_r^2 \omega)]^2$ and $\beta = R/\lambda$,

$$H' = \sum_{i=1}^N \left[\frac{-1}{2\alpha} \frac{d^2}{dx_i^2} + \frac{1}{2} x_i^2 \right] + \frac{1}{2} \sum_{i \neq j} U(x_i - x_j, \beta). \quad (3)$$

We diagonalise H' in a basis of determinantal harmonic oscillator functions to an accuracy of 0.1%. Within our approximations, H' describes the interacting electron states for a parabolic dot in any NT, with any confinement frequency and any dielectric constant in terms of α and β . Here, we consider only the region of the parameter space in which $\hbar\omega$ and ϵ_r take physically reasonable values for the range of NTs with $0.2 < R < 1.7$ nm ($1 < \hbar\omega < 50$ meV and $1 < \epsilon_r < 7$).

Results. – By examining the electron density (fig. 1) we identify different regimes of behaviour: in the strongly correlated regime (solid line) the Coulomb interaction dominates the single particle confinement, the electrons are pushed apart and tend to form Wigner crystal-like states with well defined peaks in the charge density for each electron. These states are similar to those studied in ref. [6] in a general 1D dot. In the 'weakly' correlated regime (dashed line) the interaction energy is slightly weaker than the single particle confinement energy and the electrons are forced together in the centre of the dot. There is also an intermediate regime (dotted line).

The transition between these regimes is primarily controlled by α which is analogous to a mass in H' . Physically, increasing α at fixed m^* and ϵ_r corresponds to reducing the confinement $\hbar\omega$. If α is large the electrons localise at the lowest energy minima in the potential landscape defined by the Coulomb repulsion and harmonic confinement; it is energetically favourable for the electrons to form Wigner crystal-like states. If α is small however, the kinetic energy is large and the electrons can no longer localise at the Wigner lattice points. They are then confined near the centre of the dot by the harmonic potential. The effect of β is less important. Physically, reducing β at fixed

Fig. 1: Electron density for 2 (a) and 4 (b) electrons.

$\hbar\omega$, m^* and ϵ_r corresponds to reducing R . β controls the rate of divergence of $u(x_i - x_j, \beta)$ as $x_i \rightarrow x_j$, and the density is relatively insensitive to this. However, because we constrain the parameter space by limiting $\hbar\omega$ and ϵ_r , the range of allowed α depends on β and the different α regimes are only accessible at different β .

The physics in the different regimes of behaviour can be studied quantitatively by comparing the exact calculated 2-electron ground state energy E_2 with the energies obtained with two different physical models. In the first (molecular) model we assume the electrons are strictly localised at Wigner crystal lattice sites. This approximation should be good in the strongly correlated limit where the tunnelling between sites is small. In the second physical model, which should be most accurate in the weakly correlated limit, we calculate the ground state within the Hartree-Fock (HF) approximation with a harmonic oscillator single particle basis.

To calculate the 2-electron ground state energy within the molecular approximation we write H' in centre of mass (CM) and relative motion (RM), $x' = (x_1 - x_2)/\sqrt{2}$, coordinates. The 2-electron Hamiltonian is then separable and the ground state eigenvalue of the CM part of H' is $1/(2\sqrt{\alpha})$. We expand the RM potential to 2nd order in x about its global minima, $V_{RM}(x') = x'^2/2 + U(\sqrt{2}x', \beta) \approx V_{RM}(x'_o) + \alpha\omega_{RM}^2(x' - x'_o)^2/2$. The RM ground state energy is then $V_{RM}(x'_o) + \omega_{RM}/2$.

In fig. 2 (b) we see that the ground state energy increases as α is reduced and the kinetic energy term in H' grows larger. We can also see that the HF method gives a poor approximation to E_2 . Even in the 'weakly' correlated regime (small α) the interaction is too strong for the HF approximation to be accurate. A common measure of the interaction strength [1] is $\langle U \rangle / (\hbar\omega)$ where $\langle U \rangle$ is the expectation value of $U(z, R)$. At best $\langle U \rangle / (\hbar\omega) = 0.8$ and the HF energy is still larger than E_2 by 4%.

Fig. 2 (a) shows the difference between exact and molecular calculations. As expected the molecular model is best at large α , but it is reasonably accurate over a surpris-

Fig. 2: (a) Difference of E_2 and the 2-electron ground state energy calculated with the molecular model. (b) Solid lines: exact E_2 . Dotted lines: HF energy (when $\beta = 0.231$ the HF energy is $> E_2$ by at least 4%). The symbols which label each line are plotted at every fifth data point.

ingly large proportion of the parameter space. For all $\alpha \geq 2$ it is accurate to within 2% and the electron states are Wigner molecule-like. In the Wigner molecule regime $\langle U \rangle / (\hbar\omega) > 1.17$. Here, the approximation underestimates E_2 because we have ignored the non-parabolicity of the potential at the global minima in V_{RM} . In this region the approximation is more accurate for high β : increasing β softens the walls of the barrier between minima in V_{RM} and hence reduces the higher order terms in the expansion of V_{RM} . Although the molecular model captures the essence of the physics, it ignores the possibility of tunnelling between minima. However if $\alpha \geq 2$, the exact splitting is always small ($< 0.025E_2$) and the tunnelling probability P is negligible: with the WKB approximation we find $P < 0.01$.

The Addition Energy. — To make the connection to experiment we have also calculated the addition energy, $E_A(N) = E_{N+1} - 2E_N + E_{N-1}$. Jarillo-Herrero *et al* [1] recently measured E_A for a dot formed by gating a (35,0) semiconducting NT. They found a 2-electron periodicity in E_A with oscillations of a few meV. The magnitude of the measured E_A decreased smoothly with N from roughly 45 meV at $N=1$.

We have calculated E_A throughout the dimensionless space (fig. 3 (a)). At small α , we see evidence for the expected 4-electron periodicity that is a consequence of the K, K' sub-band degeneracy and is often seen in NT dots [10, 11]. As α increases the oscillations in E_A get smaller, but at large α it is difficult to converge the ground state energies for $N \geq 5$ [17].

It is known that deformations or imperfections in the NT can split the two equivalent conduction bands [18] and, to obtain the 2-electron periodicity seen in ref. [1], we must introduce such a splitting. In fig. 3 (c) we show the qualitative consequences of adding a splitting δ into

Fig. 3: Dimensionless addition energy, E_A , calculated with 2 bands (a) and 1 band (b). Solid line: $\alpha = 36.29, \beta = 0.025$. Dotted: $\alpha = 1.68, \beta = 0.128$. Dashed: $\alpha = 0.88, \beta = 0.170$. E_A is not plotted if energies are not converged to within 0.1%. (c) E_A at different values of the band splitting δ . $\delta = 0.0$: open circles with solid line, $\delta = 0.1E_u$: crosses with dashed line, $\delta = 0.5E_u$: filled circles with thick dotted line, $\delta \rightarrow \infty$: open squares with solid line.

our model. If δ is small, then typically (but not always) increasing δ increases the strength of the oscillations. If δ is large ($> 0.6E_u$) we can neglect the highest energy CB and the calculation simplifies to a 1-band form (fig. 3 (b)). In this case we clearly see the different regimes of behaviour: in the strongly correlated regime (solid line) E_A is featureless, oscillations begin to appear in the intermediate regime (dotted line) and become more pronounced when α is small (dashed line).

To link these results to experiment we must set the energy unit from the effective mass, confinement energy and dielectric constant of the experimental NT dot ($m^* = 0.034$ in a (35,0) NT). We assume that the confinement potential is fixed by the design of the device and that the applied gate voltage, which controls N , alters only the energy zero of the potential. As the data in ref. [1] shows a 2-electron periodicity we focus on the 1-band results, we assume a relatively large δ introduced by some imperfection or deformation [18] of the particular NT studied in ref. [1].

In ref. [1] the NT dot confinement energy was deduced to be $\hbar\omega = 4.3$ meV with a constant interaction model that is accurate in the weakly correlated limit. With this value in the calculation, we must set ϵ_r to be unphysically low ($\epsilon_r \approx 1$) to reproduce the experimental energies. Also, with $\hbar\omega = 4.3$ meV and $\epsilon_r = 1$ ($E_u = 25.9$ meV) the calculated E_A (fig. 3 (b), solid line) is featureless: it clearly does not have the oscillations of a few meV that were seen in the measurements. The problem lies with the constant interaction model. This model does not work for NT dots because the effect of the Coulomb interaction is so large. If a (35,0) NT dot device were fabricated with $\hbar\omega = 4.3$ meV, its quantum states would be extremely strongly correlated and the N-electron density Wigner molecule-like (fig. 1: solid line) [19].

The electronic correlation is significant even in the 'weakly' correlated regime at small α . To match the oscillations observed in the experiment $\hbar\omega$ must be much larger than the 4.3 meV reported in ref. [1]. For example, with a more physically reasonable value of the dielectric constant ($\epsilon_r = 6$) and with $\hbar\omega = 31.8$ meV (giving $E_u = 29.8$ meV) we obtain an addition energy curve (fig. 3 (b), dashed line) qualitatively similar to the experiment data. except that the calculated E_A falls slightly too quickly with N . However, in a real device $\hbar\omega$ will increase with increasing gate voltage (or N) and this will reduce the slope in E_A with N .

Conclusion. — In summary, we have developed a new effective mass theory of the interacting electron states in semiconducting NT dots, and we have performed exact diagonalisation calculations to examine the physics of the interacting system in detail. In this letter we have shown that correlation effects are important for almost all physically reasonable semiconducting NT dots. Our calculated addition energies for $N < 6$ are qualitatively similar to experiment and, by investigating the 2-electron states in detail we find evidence of Wigner crystallisation in a large portion of the parameter space. NT dot devices operated in this regime would be ideal systems in which to observe quasi-1D Wigner molecules.

* * *

It is a pleasure to acknowledge useful discussions with Dr Y. Kawano and support from the UK Engineering and Physical Sciences Research Council. This work was performed using the University of Leicester Mathematical Modelling Centre's Supercomputer.

REFERENCES

- [1] JARILLO-HERRERO P., SAPMAZ S., DEKKER C., KOUWENHOVEN L. P. and VAN DER ZANT H. S. J., *Nature*, **429** (2004) 389.
- [2] YANNOULEAS C. and LANDMAN U., *Rep. Prog. Phys.*, **70** (2007) 2067

- [3] MAKSYM P. A., IMAMURA H., MALLON G. P. and AOKI H., *J. Phys.: Condens. Matter*, **12** (2000) R299.
- [4] KOUWENHOVEN L. P., AUSTING D. G. and TARUCHA S., *Rep. Prog. Phys.*, **64** (2001) 701.
- [5] ROY M. and MAKSYM P. A., *Physica E*, **40** (2008) 1616.
- [6] SZAFRAN B., PEETERS F. M., BEDNAREK S., CHWIEJ T. and ADAMOWSKI J., *Phys. Rev. B*, **70** (2004) 035401.
- [7] POSTMA H. W. C., TEEPEN T., YAO Z., GRIFONI M. and DEKKER C., *Science*, **293** (2001) 76.
- [8] KUEMMETH F., ILANI S., RALPH D. C. and MCEUEN P. L., *Nature*, **452** (2008) 448.
- [9] COBDEN D. H. and NYGARD J., *Phys. Rev. Lett.*, **89** (2002) 046803.
- [10] MORIYAMA S., FUSE T., SUZUKI M., AOYAGI Y. and ISHIBASHI K., *Phys. Rev. Lett.*, **94** (2005) 186806.
- [11] MAKAROVSKI A., LIU J. and FINKELSTEIN G., *Phys. Rev. Lett.*, **99** (2007) 066801.
- [12] ZHONG Z., FANG Y., LU W., LEIBER C. M., *Nano Lett.*, **5** (2005) 1143.
- [13] ROY M. and MAKSYM P. A., *Phys. Stat. Sol. (c)*, **3** (2006) 3959.
- [14] DiVINCENZO D. P. and MELE E. J., *Phys. Rev. B*, **29** (1984) 1685.
- [15] ANDO T., *J. Phys. Soc. Japan*, **74** (2005) 777.
- [16] POREZAG D., FRAUENHEIM T., KÖHLER T. H., SEIFERT G. and KASCHNER R., *Phys. Rev. B*, **51** (1995) 12947.
- [17] E_5 is accurate to $\approx 1\%$ with $> 3.5 \times 10^5$ Slater determinants in the expansion.
- [18] KE S. H., BARANGER H. U. and YANG W., *Phys. Rev. Lett.*, **91** (2003) 116803.
- [19] The N-electron density is relatively insensitive to δ .