Electronic shell and supershell structure in graphene flakes

M. Manninen, H. P. Heiskanen, and J. Akola

NanoScience Center, Department of Physics, FI-40014 University of Jyväskylä, Finland

October 14, 2008

Abstract. We use a simple tight-binding (TB) model to study electronic properties of free graphene flakes. Valence electrons of triangular graphene flakes show a shell and supershell structure which follows an analytical expression derived from the solution of the wave equation for triangular cavity. However, the solution has different selection rules for triangles with armchair and zigzag edges, and roughly 40000 atoms are needed to see clearly the first supershell oscillation. In the case of spherical flakes, the edge states of the zigzag regions dominate the shell structure which is thus sensitive to the flake diameter and center. A potential well that is made with external gates cannot have true bound states in graphene due to the zero energy band gap. However, it can cause strong resonances in the conduction band.

PACS. 73.21.La Quantum dots – 81.05.Uw Carbon, diamond, graphite – 61.48.De Structure of carbon nanotubes, boron nanotubes, and closely related graphitelike systems – 81.05.Uw Carbon, diamond, graphite

1 Introduction

Electrons confined in a finite cluster of atoms with spherical symmetry exhibit a shell structure [1,2]. In large enough clusters, the shells representing different classical periodic orbits can interfere forming a supershell structure [3,4] that has been observed in large alkali metal clusters [5]. The supershell structure is especially visible in a two-dimensional triangular cavity which has only two classical periodic orbits [6]. The triangular cavity is interesting also due to the fact that the Schrödinger equation and the wave equation are exactly solvable in that system [7,8,9], and it has been shown that triangular shapes are preferred in two-dimensional nearly free electron systems [10,11,12].

Recently, experiments have shown that single layer graphene flakes can be prepared on inert surfaces where the graphene-surface interaction is weak [13,14,15,16,17,18]. Since the manipulation of graphene on different substrates is still a fast developing area, it is not out of question that graphene flakes with accurate shape and size can be eventually processed on a substrate where the interaction is so weak that it does not affect the graphene electronic levels close to the Fermi point. Hence, we study ideal free graphene flakes neglecting the interaction with the substrate. The experiments have inspired a wealth of theoretical studies of graphene [19,20,21,22,23,24,25,26,27,28,29,30,31,32] but according to our knowledge the shell and supershell structure of large graphene flakes has not been addressed except in our recent work [33].

Electronic structure calculations based on the density functional theory (DFT) have shown that the energy levels close to the Fermi level, which consists of discrete points in graphene, are determined by the p electrons perpendicular to the graphene plane (for a review see [34]). A simple tight-binding (TB) model with only one electron per site and only the nearest-neighbour hopping describes well the electronic structure close to the Fermi points as suggested by Wallace already in 1947 [35]. The TB Hamiltonian used is then the simple Hückel model

$$H_{ij} = \begin{cases} -t, & \text{if } i, j \text{ nearest neighbours} \\ 0, & \text{otherwise} \end{cases}$$

(1)

where the hopping parameter t (resonance integral) determines the width of the bands and the on-site energy is chosen to be $\epsilon_F = 0$. We present our results in units $t = 1$ which in real graphene corresponds to $\sim 2.6$ eV. In reality, the flake edges are either passivated (e.g. with hydrogen) or reconstructed in order to remove dangling bonds. The passivation is not expected to affect the perpendicular p-states, and we can simply neglect the existence of such atoms. This has been also validated by our recent DFT calculations [33]. At the bottom of the valence band the TB model results in free-electron-like states with nearly constant density of states (DOS). This allows us to compare these “normal” free-electron states with those of the “massless electrons” at the bottom of the conduction band calculated for the exactly same geometry.

The paper is organized as follows: In Section 2 we discuss the shell and supershell structure in triangular graphene flakes, in Section 3 we show how the edge geometry dominates the shell structure in circular flakes, and in Section 4 we describe quantum dots that have been made with external potentials in an infinite graphene sheet. Section 5 gives the conclusions.
2 Shell structure of triangular graphene flakes

In a triangular cavity with hard walls and a constant potential inside, the two-dimensional Schrödinger equation has an exact solution \[ \epsilon_{n,m} = \epsilon_0(n^2 + m^2 - nm), \] (2)

where \( \epsilon_0 \) depends on the particle mass and the size of the cavity, and \( m \) and \( n \) are integers with \( n \geq 2m \geq 1 \). Figure 1 shows the density of states calculated with the TB model (TB-DOS) for a large graphene triangle of 44097 atoms which has a zigzag edge. In such a large triangle, DOS is similar to that of an infinite graphene sheet except for the appearance of the edge states which appear as a sharp peak at zero energy. A detailed study of the energy levels at the bottom of the valence band reveals that the level structure is nearly exactly described with the analytical formula of Eq. (2). TB-DOS and Eq. (2) produce the same curve shown in the lower left corner of the figure. Note that TB-DOS is plotted here as a function of the wave number defined as \( Q = \sqrt{\epsilon + 3t} \) (The bottom of the band is \(-3t\)). The regular oscillation as a function of \( Q \) corresponds to the shell structure and the peak amplitude variation (breathing) marks the supershell structure [9]. Triangles with an armchair edge show a similar supershell structure at the bottom of the band [33].

![Fig. 1. Upper panel: TB-DOS (p_z electrons) of a graphene triangle with 44097 atoms and zigzag edges. The discrete energy levels have been smoothened with Gaussians. The peak at zero energy corresponds to the edge states. The lower panels show TB-DOS as a function of the wave number at the bottom of the band (left) and above the Fermi level (right). The dashed line shows the analytical result of Eq. (3). The wave numbers are: \( Q = \sqrt{\epsilon + 3} \) and \( q = \epsilon \), where \( \epsilon \) is the energy in units of \( t = 1 \). The Gaussian widths have been adjusted in the lower panels in order to show the individual energy levels.](image)

At the bottom of the conduction band, close to \( \epsilon = 0 \), the dispersion relation of the electron energy is linear, \( \epsilon(k) = c\hbar k \), where \( c \) is the electron velocity. This means that the electrons behave as massless particles. If we consider the conduction electrons as free particles, we cannot solve the energy eigenvalues from the Schrödinger equation but should use the relativistic Dirac equation [31]. However, we choose here a simpler approach and make an ansatz that the energy eigenvalues are solutions of the Klein-Gordon wave equation with positive energy eigenvalues. This immediately gives

\[ \epsilon_{n,m} = \epsilon_1 \sqrt{n^2 + m^2 - nm}, \] (3)

which is the same as for normal electrons apart of the square root dependence of the quantum numbers and a different prefactor. The numerical solutions of the TB problem for triangles with a zigzag edge, indeed, show that the energy eigenvalues become more-and-more accurately described with those of Eq. (3) when the triangle size increases. Figure 1 (lower right panel) compares the result of the ansatz of Eq. (3) with the full TB calculation for the large triangle. The agreement is nearly perfect up to \( \epsilon = 0.1 \) (corresponding to 0.25 eV), and the discrepancy at larger energies is due to the increasing nonlinearity and anisotropy of the energy bands.

The results suggest that the supershell structure of the triangular cavity appears in zigzag-edged triangular graphene flakes, but the flake should have at least ca. 40000 atoms (i.e., \( L \geq 40 \) nm) before the first supershell oscillation becomes clearly visible. We remark that in the case of armchair edge, Eq. (3) is still valid, but also indices with \( m = n \) are allowed [33]. More detailed results for smaller triangles are described in Ref. [36], where we also show that the shell structure is quite robust against edge roughness in the close vicinity of the Fermi level.

3 Shell structure in circular graphene flakes

In the case of a two-dimensional cavity with circular symmetry, the energy levels of the Schrödinger equation are determined by the zeroes of the Bessel functions \( B_j \) with integer values \( j \). The TB model gives corresponding results at the bottom of the valence band, because the electrons are well represented by nearly free electrons. Following the ideas presented for the triangles one would expect that the energy levels close to the bottom of the conduction band could be determined similarly. However, in this case, the detailed geometry of the edge (perimeter) has a dominant role in determining the energy levels above the Fermi level, and the energy spectrum is very sensitive to the number of atoms in the circular dot, as shown in figure 2. The circular flakes have been obtained by cutting a circle out of an infinite graphene sheet. Note, that the actual edge geometry depends not only on the radius but also on the site of the center.

The reason for the size-sensitivity can be traced back to the edge states which are present in graphene constructions with zigzag edges. In circular dots, the perimeter has short regions of zigzag segments that are mixed with other motifs (especially armchair). This roughness causes edge states with different energies, which is in sharp contrast...
to the zigzag triangles where all the edge states have exactly zero energy in the TB model. Figure 2 shows the electron density of one such state with density maxima at the surface.

Usually, the shell structure is determined by the overall shape of the confining potential in metallic and semiconductor quantum dots, and the detailed atomic structure does not play any role due to the fact that the electron wave length is much larger than the interatomic spacing. This is not the case in the circular graphene flakes. Although the wavelength of the "Dirac electron" is still much larger than the interatomic spacing, the tendency for localization of electrons close to the zigzag edges destroys the simple shell structure, and different circular flakes result in qualitatively different electron levels as shown in Fig. 2.

4 Quantum dots prepared with external potential

So far, we have studied free graphene flakes where the electron confinement is determined by the flake edges. In semiconductor heterostructures, quantum dots are usually prepared by confining the delocalized conduction electrons in a small region with external gates (for a review see [37]). It is expected that a similar technique can be applied in the future also for the two-dimensional gas of "Dirac electrons" in graphene. External gates form nearly harmonic confinement close to the center of the quantum dot. Another possibility for supported graphene flakes could be to modify the atomic structure of the substrate so that different regions would comprise different elements, and, consequently, cause different interaction with the adsorbate. In this case, the resulting potential well could be more of the square-well-type than harmonic.

The situation is different for an external confinement (infinite graphene sheet) than for a finite flake with edges. Since there is no band gap in graphene, an external potential well cannot bind an electron as demonstrated in Fig. 3. In addition, this differs considerably from the quantum dots manufactured from semiconductor heterostructures, where bound electronic states can exist inside the band gap of the semiconductor in question.

We have studied the effect of an external confinement by using a large hexagonal graphene flake with 4902 atoms. An external potential was added at the center of the flake. We considered three different external potentials: A circular well, a square-shaped well, and a smooth Gaussian potential with circular symmetry. Surprisingly, the results are qualitatively similar irrespective of the type of the attractive potential. Bound states appear at the bottom of the valence band where the electrons act as normal free electrons. In the more interesting region close to the Fermi level, no bound states can be observed. However, above the Fermi level all the potentials result in strong resonances with a large enhancement of the wave function amplitude within the potential well region. Figure 4 shows the densities of the wave functions for two such resonances. The wave functions do not decay to zero outside the potential well but reach a small and uniform amplitude that goes all the way to the flake edge (the small amplitude is not visible Figure 3).
For a potential barrier, the penetration of a wave function inside an apparently forbidden region is often referred to as the Klein paradox, which has its origin in the Dirac theory of massless fermions. As Figure 3 shows for the TB (band structure) model, the wave function penetration inside the “forbidden region” is a natural consequence of the missing band gap: An electron that appears on the conduction band on one side of the step continues as a valence electron on the other side.

5 Conclusions

We have studied the possibility of observing electronic shell and supershell structure in free graphene flakes. For this purpose, we have used a simple tight-binding model with one electron per atomic site ($p_z$ electrons). Despite its simplicity, the TB model describes the key features of the graphene band structure close to the Fermi points.

In large triangular flakes with zigzag edges, the shell structure of the “Dirac electrons” in the conduction band is the same as for free electrons in a triangular cavity. The analytical expression gives the energy levels accurately up to $\sim 0.25$ eV above the Fermi energy, and the number of shells within this region depends on the number of atoms in the triangle. A triangle of ca. 40000 atoms ($L \gtrsim 40$ nm) shows already the first supershell oscillation.

In the case of circular graphene flakes, the shell structure above the Fermi level is dominated by the states that are localized close to the zigzag regions of the edges. This makes the shell structure very sensitive, not only to the radius of the circular flake (number of atoms) but also to the location of the center.

Potential wells which are created on an infinite graphene sheet with external potentials (e.g. external gates, inhomogeneous substrate) cannot localize electrons. This is a consequence of the missing band gap in the graphene band structure. However, such potential wells cause resonance states above the Fermi level, which can strongly affect the conductance of narrow graphene strips.

Acknowledgments This work has been supported by the Academy of Finland.

References

1. J.L. Martins, R. Car, and J. Buttet, Surf. Sci. 106, 265 (1981).
2. W.A. de Heer WA, Rev. Mod. Phys. 64, 677 (1993).
3. R. Balian and C. Bloch, Ann. of Phys. 60, 401 (1970).
4. H. Nishioka, K. Hansen, and B. Mottelson, Phys. Rev. B 42, 9377 (1990).
5. J. Pedersen, S. Bjornholm, J. Borggreen, K. Hansen, T.P. Martin, and H.D. Rasmussen, Nature 353, 733 (1991).
6. M. Brack, J. Balschke, S.C. Greah, A.G. Magner, P. Meier, and S.M. Reimann, Z. Phys. D 40, 276 (1997).
7. M.G. Lame, Leçons sur le Théorie Mathématique d’Elasticité des Coves Solides (Bachelier, Paris 1852).
8. H.R. Krishnamurthy, H.S. Mani, and H.C. Verma, J. Phys. A: Math. Gen. 15 2131 (1982).
9. M.A. Doncheski, S. Hepplemann, R.W. Robinet, and D.C. Tseusy, Am. J. Phys. 71, 541 (2003).
10. S.M. Reimann, M. Koskinen, H. Häkkinen, P.E. Lindelof, and M. Manninen, Phys. Rev. B 56, 12147 (1997).
11. J. Kolehmainen, H. Häkkinen, and M. Manninen, Z. Phys. D 40, 306 (1997).
12. S.M. Reimann, M. Koskinen, J. Helgesson, P.E. Lindelof, and M. Manninen, Phys. Rev. B 58, 8111 (1998).
13. C. Berger, Z.M. Song, T.B. Li, X.B. Li, A.Y. Ogbagghi, R. Feng, Z.T. Dai, A.N. Marchenkov, E.H. Conrad, P.N. First, and W.A. De Heer, J. Phys. Chem. 108, 19912 (2004).
14. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, and A.A. Firsov, Science 306, 666 (2004).
15. C. Berger, Z.M. Song, X.B. Li, X.S. Wu, N. Brown, C. Naud, D. Mayo, T.B. Li, J. Hass, A.N. Marchenkov, E.H. Conrad, P.N. First, and W.A. De Heer, Science 312, 1191 (2007).
16. K.S. Novoselov, Z. Jiang, Y. Zhang, S.V. Morozov, H.L. Stormer, U. Zeitler, J.C. Maan, G.S. Boebinger, P. Kim, and A.K. Geim, Science 315, 1379 (2007).
17. A.K. Geim and K.S. Novoselov, Nature Materials 6, 183 (2007).
18. G. Li and E.A. Andrei, Nature Phys. 3, 623 (2007).
19. J. Alicea and M.P.A. Fisher, Phys. Rev. B 74, 75422 (2005).
20. V.P. Gusynin and S.G. Sharapov, Phys. Rev. Lett. 95, 146801 (2005).
21. J. Tworzydlo, B. Trauzettel, M. Titov, A. Rycerz, and C.W.J. Beenakker, Phys. Rev. Lett. 96, 246802 (2006).
22. V.P. Gusynin, S.G. Sharapov, and J.P. Carbotte, Phys. Rev. Lett. 96, 256802 (2006).
23. S.Y. Zhou, G.H. Gweon, J. Graf, A.V. Fedorov, C.D. Spataru, R.D. Diehl, Y. Kopelevich, D.H. Lee, S.G. Louie, and A. Lanzara, Nature Phys. 2, 595 (2006).
24. T. Yamamoto, T. Noguchi, and K. Watanabe, Phys. Rev. B 74, 121409 (2006).
25. K. Nomura and A.H. MacDonald, Phys. Rev. Lett. 98, 76602 (2007).
26. Y.W. Son, M.L. Cohen, and S.G. Louie, Phys. Rev. Lett. 97, 126803 (2007).
27. D.A. Areshkin, D. Gunlycke, and C.T. White, Nano Lett. 7, 204 (2007).
28. J. Fernández-Rossier and J. J. Palacios, Phys. Rev. Lett. 99, 177204 (2007).
29. J.-H. Chen, C. Jiang, S. Xiao, M. Ishigami, and M.S. Fuhrer, Nature Nanotech 3, 206 (2008).
30. E.V. Castro, N.M.R. Peres, J.M.B. Lobes dos Santos, A.H. Castro Neto, and F. Guinea, Phys. Rev. Lett. 100, 026802 (2008).
31. R.R. Akhmerov and C.W.J. Beenakker, Phys. Rev. B 77, 085423 (2008).
32. Z.Z. Zhang, K. Chang, and F.M. Peeters, Phys. Rev. B 77, 235411 (2008).
33. J. Akola, H.P. Heiskanen, and M. Manninen, Phys. Rev. B 77, 193410 (2008).
34. A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, and A.K. Geim, arXiv:0709.1163v2.
35. P.R. Wallace, Phys. Rev. Lett. 71, 622 (1947).
36. H.P. Heiskanen, J. Akola, and M. Manninen, Submitted for publication (2008).
37. S.M. Reimann and M. Manninen, Rev. Mod. Phys. 74, 1283 (2002).