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Giant orbital paramagnetism in toroidal carbon nanopeapods

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Abstract
The electronic structure and the magnetic response of toroidal carbon nanopeapods (TCNPs) are investigated within the sp^3 tight-binding formalism. It is found that in the presence of mirror symmetry, there exists a level crossing at the Fermi level in the energy spectrum of a TCNP, leading to giant orbital paramagnetism (GOP), in spite of the curvatures and hybridizations of the outer toroidal carbon nanotube (TCN). When the mirror symmetry is broken by rotating the inner C_{60}s, however, two level crossings appear at the Fermi level, and the GOP changes into a very small diamagnetic response. The results reveal the GOP in a filled TCN, depending on the characteristics of the filling materials and temperature.

1. Introduction

The discovery of toroidal carbon nanotubes (TCNs) [1] has attracted many workers to explore their peculiar electromagnetic properties when threaded by a flux [2–15]. Due to the particular vacant circular geometries, particularly, there exists giant orbital paramagnetism (GOP, as in [5]) in conventional TCNs (formed by hexagons only) with 'magic radii' [3], corrugated TCNs constructed by coalescing C_{60}s along the five-fold axis or by connecting the ends of Haeckelite carbon nanotubes (CNTs) [4], and polygonal TCNs [5], which offer promise for application in small electromagnetic devices. GOP also exists in TCNs when the highest occupied molecular orbital (HOMO) level is partially occupied by added electrons or holes [6].

Experimentally, the empty space of TCNs, as in CNTs [16–19], can be filled by other materials in the process of synthesis [1], and in this way new carbon composite structures may be formed. Some novel physical phenomena and properties may be expected in such toroidal composites. It has been shown that a semiconducting TCN with an encapsulated Fe, Au, or Cu ring possesses an energy gap of less than 0.1 eV, while the composite encapsulating an Fe ring is ferromagnetic [20]. Persistent currents in a carbon ring strongly depend on the outer TCN sheath [21].

A carbon nanopeapod (CNP), formed by a CNT encapsulating a fullerene molecular chain, has been observed [16]. Scanning tunneling microscope measurements and calculations show that a periodic array of C_{60} molecules gives rise to electronic band hybridization between TCNs and C_{60}s in a CNP [22], which makes C_{60}@(10, 10) CNP a metal with multi-carriers [23, 24], while charge transfer from the outer tube to C_{60}s occurs [24–26]. Some novel electromagnetic properties can be expected in a toroidal CNP (TCNP) when threaded by a flux. Of special interest is the magnetic response of the flux-induced persistent current.

It was found in previous works that due to the curvatures [9–13] and hybridizations [7, 13] of a 'metallic' TCN, an energy gap opens at the Fermi level (ϵ_F), which changes the GOP of the pure 'metallic' TCN into very small diamagnetism. For a TCNP formed by a C_{60} loop chain inside a TCN, however, the orbital hybridizations between the TCN and the C_{60} chain may modulate the electronic structure of the outer TCN, leading to partial occupation of the HOMO level, i.e. a level crossing at zero flux and ϵ_F. Therefore, the GOP effect can be expected in a filled TCN such as a TCNP. It was shown that C_{60} rotation has significant effects on the electronic and transport properties of CNPs [26–28], which may significantly affect the possible GOP in a C_{60}-filled TCN. By developing a supercell method, we explore the electronic

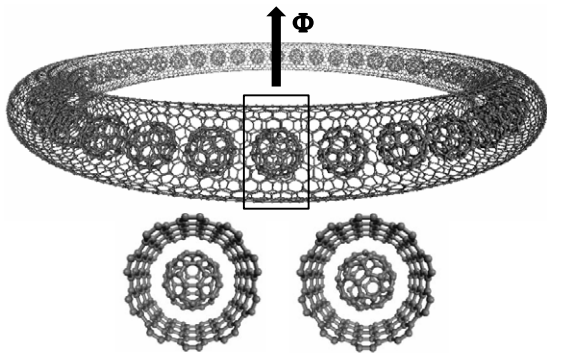

Figure 1. Schematic of a TCNP threaded by a perpendicular flux. The unit cell (denoted by the rectangle) is shown below, with or without mirror symmetry.

structure and magnetic response of TCNPs within the sp^3 tight-binding formalism. The GOP has been obtained, depending on mirror symmetry of the TCNPs and temperature.

2. Model and method

The TCNP model device is shown in figure 1. A commensurability condition between the outer TCN and inner C_{60} chain is imposed, as in straight CNPs [23–29], to satisfy the rotational symmetry. The TCNP has equidistant C_{60}s and is indexed by $(C_{60})_q@(n,m)\times p$, with q being the number of unit cells or C_{60}s and $(n,m)\times p$ the outer TCN containing p unit cells. We mainly focus on the $(C_{60})_{p/4}@(10,10)\times p$ TCNP, with a lattice parameter (or center distance of two neighboring C_{60}s along the tube axis) of $d = 0.98$ nm, similar to the experimental observations [16] and computational simulations [23] in CNPs.

An sp^3 tight-binding model, taking into account both carbon 2s and 2p orbital hybridizations, is introduced to calculate the electronic structures of TCNPs, and has been successfully applied to CNPs [28, 29], TCNs [7, 13] and C_{60} clusters [30]. The Hamiltonian of a TCNP can take the form of TCNs:

$$H = \sum_{i,\alpha}\varepsilon_\alpha c^\dagger_{i,\alpha}c_{i,\alpha} + \sum_{\substack{i,j,\alpha,\alpha'\\(j\neq i)}}\gamma_{\alpha,\alpha'}f(r_{i,j})e^{i\varphi_{i,j}}c^\dagger_{i,\alpha}c_{j,\alpha'} + \sum_{\substack{i,k,\alpha,\alpha'\\(k\neq i)}}\gamma'_{\alpha,\alpha'}f'(r_{i,k})e^{i\varphi_{i,k}}c^\dagger_{i,\alpha}c_{k,\alpha'}, \quad (1)$$

where i, j and k label the atomic sites within the full ring (i and j are the nearest-neighboring, i and k are the next-nearest-neighboring), $\alpha, \alpha' = s, p_x, p_y, p_z$ label the atomic orbital, ε_α is the orbital energy, $\gamma_{\alpha,\alpha'}$ and $\gamma'_{\alpha,\alpha'}$ are the hopping integrals between different orbitals. We adopt the parameters given in [29] to model the nearest-neighbor and the second neighbor interactions. Considering the variations of the bond length, the hopping integrals for the nearest-neighbor and the second neighbor interactions are multiplied by the modified factors $f(r_{i,j})$ and $f'(r_{i,k})$ [31]. Based on the London approximation, the hopping integrals between site i and sites j, k are modified by phase factors $\exp(i\varphi_{i,j})$ and $\exp(i\varphi_{i,k})$, with $\varphi_{i,j}$ and $\varphi_{i,k}$ the flux-induced phases. Instead of diagonalizing directly the whole Hamiltonian matrix, we adopt the Fourier-transformed Hamiltonian in a sector for fixed $\beta = l\times 2\pi/q, (l = 1, 2, \ldots, q)$ in terms of rotational symmetry [7], with β the conjugate variable to the unit-cell index l along the ring:

$$H_\beta = \sum_{i,\alpha}\varepsilon_\alpha b^\dagger_{i,\alpha,\beta}b_{i,\alpha,\beta} + \sum_{\substack{i,j,\alpha,\alpha'\\(j\neq i)}}\gamma_{\alpha,\alpha'}f(r_{i,j})e^{i(\varphi_{i,j}+\beta)}b^\dagger_{i,\alpha,\beta}b_{j,\alpha',\beta} + \text{h.c.} + \sum_{\substack{i,k,\alpha,\alpha'\\(k\neq i)}}\gamma'_{\alpha,\alpha'}f'(r_{i,k})e^{i(\varphi_{i,k}+\beta)}b^\dagger_{i,\alpha,\beta}b_{k,\alpha',\beta} + \text{h.c.}, \quad (2)$$

where i enumerates the atomic sites within each unit cell and j and k enumerate the nearest- and the second-nearest-neighbors within the same or a neighboring unit cell. For a given β, the eigenlevels can be obtained by diagonalizing H_β. When neglecting the interaction of electrons, the magnetic moment (M) of a TCNP at zero temperature is calculated by

$$M = -\sigma\sum_n\frac{\partial E_n}{\partial\Phi} = -\frac{\sigma}{\Phi_0}\sum_n\frac{\partial E_n}{\partial\phi}, \quad (3)$$

with $\phi = \Phi/\Phi_0$, $\Phi_0 = h/e$ the flux quantum, E_n the eigenlevels of the TCNP, and σ the torus area. The summation runs to the highest occupied energy level. M is a function of flux Φ with fundamental period Φ_0. At finite temperature T, M is calculated from the free energy F:

$$M = -\frac{\sigma}{\Phi_0}\frac{\partial F(\phi,T)}{\partial\phi}, \quad (4)$$

where $F = -k_BT\sum_n\ln\{1+\exp[(\mu-E_n)/k_BT]\}+N\mu$ with μ the chemical potential of the N-electron system, and k_B the Boltzmann constant.

3. Calculations and discussion

Before investigating the electronic structure of a typical example of a $(C_{60})_{72/4}@(10,10)\times 72$ TCNP, the energy spectra of the primary $(10,10)\times 72$ TCN and the primary C_{60} chain are first given, in order to serve as a reference. From figure 2(a), there appears to be an asymmetric structure of the energy spectrum of the TCN, due to the complicated misorientations and hybridizations of the 2s and 2p orbitals and variations of bond length induced by high curvatures. Two level crossings are observed at $\phi = \pm 0.38$ at the Fermi level ($\epsilon_F = -0.009$ eV). Though the HOMO dispersion is considerable, the GOP of the TCN is precluded at small flux, due to the energy gap (0.059 eV) at $\phi = 0$. For the C_{60} chain, the inter-distance between the neighboring C_{60}s is so large that the direct interaction between them is very weak. As shown in figure 2(b), the highly degenerate HOMO and lowest unoccupied molecular orbital (LUMO) states of the C_{60} chain have no dispersion, with an energy gap of 2.017 eV, similar to a C_{60} cluster [30].

For the resultant $(C_{60})_{72/4}@(10,10)\times 72$ TCNP, the orbital hybridizations between the outer TCN and the inner C_{60} chain are taken into account. As shown in figures 3(a) and (b), the Fermi level of the TCNP is shifted down to

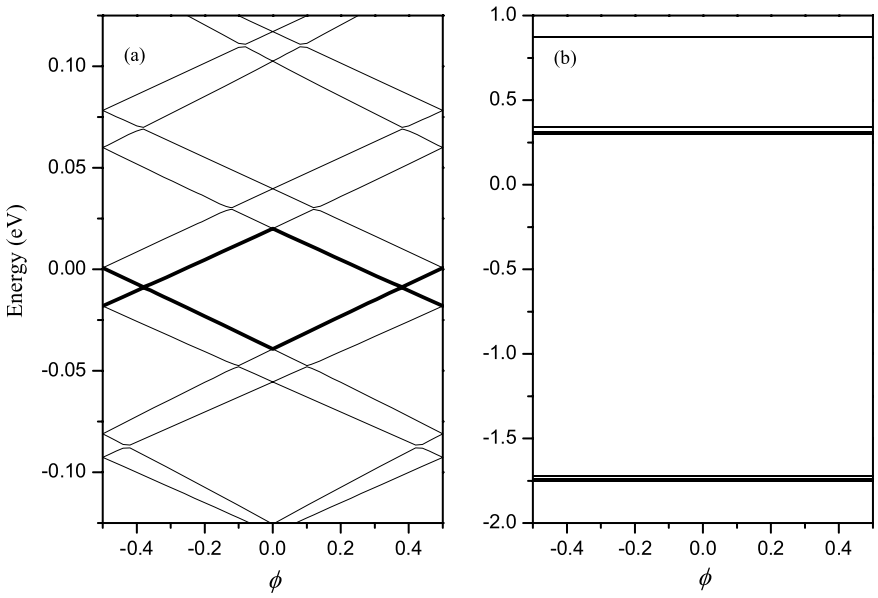

Figure 2. Energy spectra of (a) the primary (10, 10) × 72 TCN and (b) the primary C_{60} chain of the $(C_{60})_{72/4}$@(10, 10) × 72 TCNP. The bold lines in (a) denote the HOMO and LUMO states.

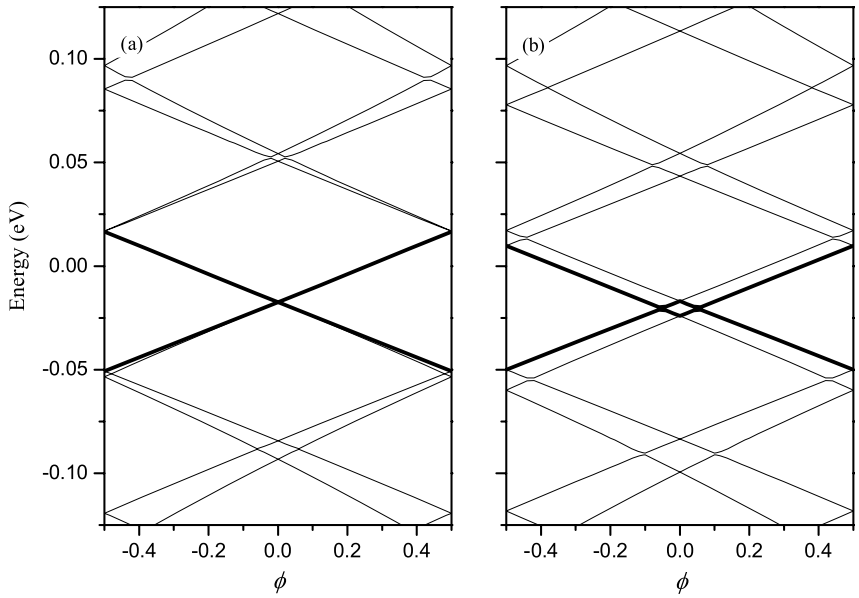

Figure 3. Energy spectra of the $(C_{60})_{72/4}$@(10, 10) × 72 TCNP in the presence (a) or absence (b) of mirror symmetry. The bold lines denote the HOMO and LUMO states.

−0.018 eV. The non-dispersive states of the C_{60} chain do not appear near ϵ_F, where the energy states come from the outer TCN, with no state mixing between the C_{60} chain and the TCN. On the other hand, the interaction between the inner C_{60} chain and the outer TCN induces perturbations on the states near ϵ_F, which can be modulated by rotating the inner C_{60}s to keep the mirror symmetry of the TCNP, or not. When the TCNP is in the presence of mirror symmetry (figure 3(a)) the two level crossings of the primary TCN are merged into one crossing at zero flux and ϵ_F, while the HOMO dispersion remains considerable. When the mirror symmetry is broken by rotating C_{60}s (figure 3(b)) the single crossing is separated into two crossings again, appearing at $\phi = \pm 0.06$. The electronic structures imply that the unusual magnetic response may be expected in the outer TCN [4, 5] of the TCNP, which depends on the C_{60} rotation.

Figure 4 shows M as a function of flux in the studied TCNP for $T = 0$. For the $(C_{60})_{72/4}$@(10, 10) × 72 TCNP with mirror symmetry, a jump structure of M is observed at $\phi = 0$, due to the single level crossing of the outer TCN. Such a jump structure may imply a GOP at small flux. It is calculated that in a magnetic field of 0.1 T, there exists a GOP of 28.38 μ_B (Bohr magneton) in the TCNP, as predicted by Terrones *et al* [4, 6]. While the curvatures and hybridizations

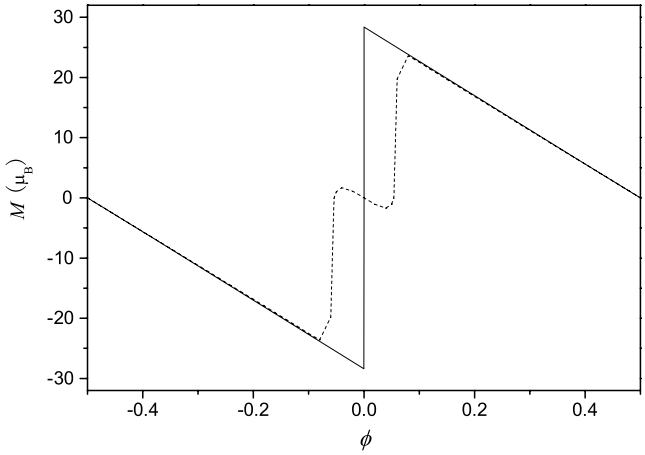

Figure 4. Magnetic moments as a function of flux in the $(C_{60})_{72/4}@(10, 10) \times 72$ TCNP in the presence (——) and in the absence (- - - -) of mirror symmetry.

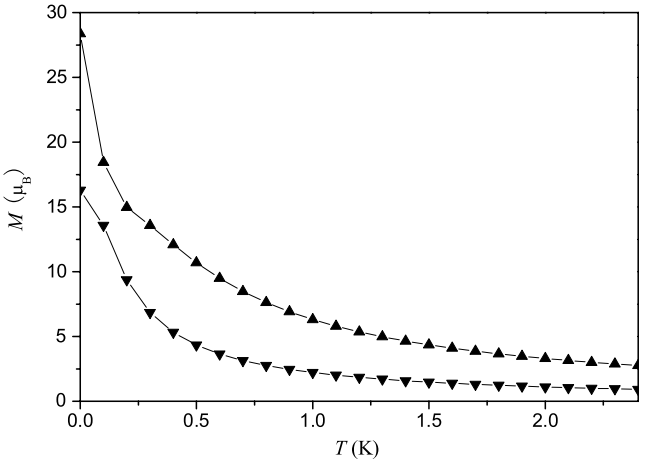

Figure 5. Magnetic moments as a function of temperature in the $(C_{60})_{p/4}(10, 10) \times p$ TCNP at $p = 60$ (–▼–) and $p = 72$ (–▲–) in the presence of mirror symmetry. The external field is 0.1 T.

of the outer TCN have been taken into account, the GOP in the primary TCN can be obtained only in the absence of curvatures and hybridizations [3]. When the mirror symmetry of the $(C_{60})_{72/4}@(10, 10)\times 72$ TCNP is broken by C_{60} rotation, two jumps appear at $\phi = \pm 0.06$, and the GOP in the TCNP changes into a very small orbital diamagnetism of $-0.033\ \mu_B$. The results show that the GOP effect can be observed in a filled TCN such as a TCNP, while the filling materials, e.g. the inner C_{60} chain of the TCNP, play an important role in determining the existence of GOP.

The temperature dependence of GOP in TCNPs is shown in figure 5. The GOP in the $(C_{60})_{60/4}@(10, 10) \times 60$ and $(C_{60})_{72/4}@(10, 10) \times 72$ TCNPs decreases exponentially with increasing temperature at low temperatures, due to the cancelation between the M produced by the states below and above ϵ_F of the TCN, as in pure TCNs [3, 4, 10]. It is found that due to the low-lying excited states carrying persistent current with the same sign as the ground states, there exists a temperature-enhanced persistent current (and thus M) in the mesoscopic ring coupled to a side structure [32]. For the TCNP, as a TCN coupled to a C_{60} chain, similarly the non-dispersive states of the primary C_{60} chain may become dispersive and lead to a temperature-enhanced M. However, the states are away from ϵ_F, and thus the thermal excitations are not possible at low T, and a temperature-enhanced GOP is not observed in the TCNPs.

4. Conclusion

We studied the electronic structure and the magnetic response in a toroidal carbon nanopeapod, a carbon composite model device formed by bending a straight carbon nanopeapod and connecting the ends of the outer toroidal carbon nanotube seamlessly. It is found that in spite of the curvatures and hybridizations of the outer toroidal carbon nanotube, giant orbital paramagnetism can be observed in a toroidal carbon nanopeapod when the mirror symmetry is maintained, and is destroyed by the symmetry breaking. The results show that a giant orbital paramagnetism can be observed in a filled toroidal carbon nanotube, depending on the characteristics of the filling materials and temperature.

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