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Electronic orbital angular momentum and magnetism of graphene

Ji Luo

Department of Physics and Institute for Functional Nanomaterials, University of Puerto Rico at Mayagüez, Mayagüez, PR 00681, USA

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ABSTRACT

Orbital angular momentum (OAM) of graphene electrons in a perpendicular magnetic field is calculated and corresponding magnetic moment is used to investigate the magnetism of perfect graphene. Variation in magnetization demonstrates its decrease with carrier-doping, plateaus in a large field, and de Haas–van Alphen oscillation. Regulation of graphene's magnetism by a parallel electric field is presented. The OAM originates from atomic-scale electronic motion in graphene lattice, and vector hopping interaction between carbon atomic orbitals is the building element. A comparison between OAM of graphene electrons, OAM of Dirac fermions, and total angular momentum of the latter demonstrates their different roles in graphene's magnetism. Applicability and relation to experiments of the results are discussed.

1. Introduction

The magnetism of graphene is rather intriguing. It is believed that carrier-undoped graphene has a very large diamagnetic susceptibility and the susceptibility decreases rapidly with the increasing carrier-doping of either electrons or holes [1–3]. Theoretically, the susceptibility was derived according to quasi-continuous Landau levels (LLs) of graphene in a weak magnetic field, and the thermal potential energy constructed from LLs plays the central role [3,4]. This anomalous susceptibility is interesting and attempts have been made to interpret its origin [3].

In addition, many factors have been found to contribute to graphene's magnetism, such as vacancies [5–8], substituting atoms [8], absorbed atoms [8–10], edge structures and edge states [11–13], finite size of graphene [14,15], electron–electron interaction [2], substrates [16], and strain [17]. Magnetism-related properties of gapped graphene were also studied [18,19]. Although diamagnetism was observed in experiments, the magnetization was measured for graphene crystallites with nanometer size [20]. For a new material, the elimination of uncontrollable disturbances is necessary for both applications and the revelation of underlying physics, and graphene is expected to be made more and more perfect. Theoretically, wave functions of graphene electrons in a perpendicular magnetic field are obtainable [21,22]. Along with LLs, these wave functions may provide more insight into graphene's magnetic properties.

In this work, orbital angular momentum (OAM) of graphene electrons in a perpendicular magnetic field is calculated according to the electronic wave functions. The corresponding orbital magnetic moment (OMM) is found paramagnetic for negative LLs and diamagnetic for positive LLs. As a result, carrier-undoped graphene could be paramagnetic and the magnetization decreases with the increasing carrier-doping of either electrons or holes. For a fixed magnetic field, the magnetization variation with the carrier-doping is obtained as a function of temperature and Fermi energy. It presents plateaus similar to those in quantum Hall effect as Fermi energy varies in a large magnetic field. As the magnetic field varies, the magnetization demonstrates de Haas–van Alphen oscillation. A parallel electric field can change the electronic states and regulate graphene's magnetism. The derivation of OAM of graphene electrons manifests that their OMM originates from their atomic-scale motion in graphene lattice. The vector hopping interaction of carbon atomic orbitals constitutes building element of the OAM. Its honeycomb-like distribution in graphene lattice and its magnitude result in the unique form of the OAM operator, and its modulation by the two-component electronic wave function generates the OAM for a specific state. The OAM of a graphene electron is different from that of the Dirac fermion, although they are described by the same two-component wave function. The superposition of degenerate states may result in diversity of graphene's magnetization. This superposition, the deep states with energies far below the zero, and the small size of graphene crystallites may be the origin of experimentally observed diamagnetism.

2. Electronic orbital angular momentum, electronic orbital magnetism moment, and magnetization variation of graphene

The graphene is taken as xy-plane with x-axis parallel to one set of C–C bonds. Unit vectors of the axes are denoted by $\vec{x}$, $\vec{y}$,

E-mail address: ji.luo@upr.edu

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and $\vec{z}$. A three-dimensional vector is denoted by $\vec{r}=x\vec{x}+y\vec{y}+z\vec{z}$ and its two-dimensional projection in the graphene plane with $z=0$ by $\vec{\rho}=x\vec{x}+y\vec{y}$. Two kinds of Dirac points $\vec{k}_F=(2\pi/3\sqrt{3}a_0)(\sqrt{3}\vec{x}+\tau\vec{y})$ are distinguished by $\tau=\pm1$, with a_0 the C–C bond length. A graphene electron is described by a two-component wave function $\Psi=(\psi_1 \quad \psi_2)^T$ which, in an orthogonal electromagnetic field with scalar potential $\varphi(\vec{\rho})$ and vector potential $\vec{A}(\vec{\rho})$, is determined by the Dirac-like Hamiltonian

$$\hat{H}=v_F\vec{\sigma}\cdot(-i\hbar\nabla_2+e\vec{A})-e\varphi I_2, \tag{1}$$

where $v_F\approx10^6$ ms^{-1} is the Fermi velocity, $\nabla_2=\vec{x}\partial/\partial x+\vec{y}\partial/\partial y$, I_2 is the 2×2 unit matrix, and $\vec{\sigma}=\sigma_x\vec{x}+\tau\sigma_y\vec{y}$ with $\sigma_{x,y}$ the first two Pauli matrixes. Because of this $\hat{H}$, Ψ is regarded as describing a virtual massless Dirac fermion.

For a graphene electron described by Ψ, its velocity operator and OAM operator with respect to a point $\vec{\rho}_0$ are [23]

$$\hat{\vec{v}}=v_F\vec{\sigma},\quad \hat{\vec{l}}_e=(\vec{\rho}-\vec{\rho}_0)\times m_e\hat{\vec{v}}, \tag{2}$$

with m_e the mass of an electron. Electronic states are usually not eigen-states of $\hat{\vec{l}}_e$. However, for a localized and normalized state Ψ, the expectation value $\vec{l}_e=\int_\infty\Psi^+\hat{\vec{l}}_e\Psi d^2\vec{\rho}$ plays the real role, like the expectation value of $\hat{\vec{v}}$ in graphene's quantum Hall effect [24]. For a graphene electron, the usual relation between the OMM and the OAM still holds. In fact, the state Ψ has the current density $\vec{j}=\Psi^+\hat{\vec{v}}\Psi$ [2,23]. Therefore the OMM is [25]

$$\vec{\mu}=\frac{1}{2}\int_\infty(\vec{\rho}-\vec{\rho}_0)\times(-e\vec{j})d^2\vec{\rho}=-\frac{e}{2m_e}\vec{l}_e. \tag{3}$$

Graphene's electronic states can be calculated for $\tau=+1$ only, since OAM is the same for $\tau=\pm1$. Suppose

$$L_B=\sqrt{\frac{\hbar}{eB}},\quad \varepsilon_B=v_F\sqrt{\hbar eB} \tag{4}$$

respectively denote magnetic length and energy quantum. One chooses an arbitrary point $(x_0,\ y_0)$. By adopting symmetric potential gauge $\vec{A}=(B/2)[-(y-y_0)\vec{x}+(x-x_0)\vec{y}]$, $\varphi=0$ and using polar coordinates $x=x_0+\rho\cos\theta$, $y=y_0+\rho\sin\theta$ one has the eigen-energies (LLs) and eigen-states of $\hat{H}$

$$\varepsilon=\pm\sqrt{2n}\varepsilon_B, \tag{5}$$

$$\begin{cases}\psi_1=\pm\sqrt{\frac{2}{n}}CL_Be^{i(m-1)\theta}e^{-\rho^2/4L_B^2}\rho^{|m|-1}\\ \qquad\times[nL(n_\rho,|m|,\rho^2/2L_B^2)-(n_\rho+|m|)L(n_\rho-1,|m|,\rho^2/2L_B^2)],\\ \psi_2=iCe^{im\theta}e^{-\rho^2/4L_B^2}\rho^{|m|}L(n_\rho,|m|,\rho^2/2L_B^2)\end{cases} \tag{6}$$

where $n_\rho=0,1,2,\ldots$, $m=0,\pm1,\pm2,\ldots$, $n=n_\rho+(|m|+m)/2=0,1,2,\ldots$, $L(n,m,x)=\sum_{k=0}^{n}(n+m)![k!(n-k)!(m+k)!]^{-1}(-x)^k$ is a generalized Laguerre polynomial with $L(-1,m,x)=0$, and the normalization constant $C=L_B^{-|m|-1}\sqrt{2^{-|m|-2}n_\rho!/\pi(n_\rho+|m|)!}$. States (6) with $m\geq0$ were presented in Ref. [22].

An LL (5) is degenerate since it is independent of m and $(x_0,\ y_0)$. As a result real electronic states could be superposition of states (6) with the same n. A possible case can be obtained according to graphene's electronic distribution. Electronic density of each state (6) $|\psi_1|^2+|\psi_2|^2$ roughly occupies a circular area with radius $\sqrt{2}L_B$ and center $(x_0,\ y_0)$. For a finite (large) graphene with an area S, with spin degeneracy and valley degeneracy not included the number of states N for each LL with a fixed n is that of the magnetic-flux quantum h/e which has the area $h/eB=2\pi L_B^2$ [26], that is,

$$N=\frac{S}{2\pi L_B^2}. \tag{7}$$

Since $2\pi L_B^2$ is also the area of a state (6), it is supposed that each real state is the superposition of states (6) with the same n and $(x_0,\ y_0)$ but different m. For each LL the N centers of states are regarded as uniformly dispersed in the graphene plane so that the circular areas all together fully cover the plane. This distribution lowers the energy of Coulomb interaction between electrons.

The expectation values of the OAM operator and corresponding OMM for a state (6) are calculated out to be

$$\vec{l}_e=\pm\sqrt{2n}m_ev_FL_B\vec{z},\quad \vec{\mu}=\mp\sqrt{\frac{n}{2}}ev_FL_B\vec{z}. \tag{8}$$

Results for the superposed states are also (8), as long as n and $(x_0,\ y_0)$ are fixed. Therefore states (6) with $\varepsilon<0$ have paramagnetic moment and those with $\varepsilon>0$ have diamagnetic one. The OMM (8) is much larger than Bohr magneton $\mu_B=\hbar e/2m_e$, as is found in carbon nanotubes [27]. For instance, for $n=1$ and $B=10$ T, one has $l_e\approx50\hbar$ and $\mu\approx50\mu_B$. Graphene's magnetism is thus mainly determined by its electrons' OMM. As a result, carrier-undoped graphene could have large para-magnetization, since at temperature $T=0$ K and for Fermi energy $\varepsilon_F=0$, states (6) with $\varepsilon<0$ are occupied and those with $\varepsilon>0$ are empty. Nevertheless, graphene's magnetization cannot be calculated by summing the OMM in Eq. (8), because LLs (5) and wave-functions (6) may not well represent deep states whose energy is far below zero. Instead one can calculate the magnetization variation with carrier-doping. Graphene's magnetization variation can be explains as follows: When the graphene is increasingly doped with electrons, more and more states with $\varepsilon>0$ are occupied, and this brings about more and more electrons with diamagnetic moment; when the graphene is increasingly doped with holes, more and more states with $\varepsilon<0$ are empty, and this brings about less and less electrons with paramagnetic moment. In both cases, the magnetization is decreased with the increasing carrier-doping.

Suppose the magnetization for $T=0$ K and $\varepsilon_F=0$ is $M_0\vec{z}$ and that for $T>0$ K and $\varepsilon_F\neq0$ is $M\vec{z}$. With spin degeneracy and valley degeneracy included, both the occupied nth LL (doped with electrons) and the empty $-n$th LL (doped with holes) contribute to the magnetization by the dia-magnetization $-4N\sqrt{n/2}v_FeL_B\vec{z}/S=(-\sqrt{2n}v_Fe/\pi L_B)\vec{z}$. The magnetization variation $\Delta M\vec{z}=(M-M_0)\vec{z}$ can be calculated by

$$\Delta M=-\frac{ev_F}{\pi L_B}\sum_{n=1}^{+\infty}\sqrt{2n}[1-f(-\sqrt{2n}\varepsilon_B)+f(\sqrt{2n}\varepsilon_B)], \tag{9}$$

where $f(\varepsilon)=1/\{1+\exp[(\varepsilon-\varepsilon_F)/k_BT]\}$ is the Fermi–Dirac distribution function with k_B the Boltzmann constant. Usually the carrier-doping involves only LLs with small n, and terms in Eq. (9) with very large n actually do not contribute to the result.

In general the $\Delta M\sim\varepsilon_F$ curve for fixed B and T resembles a parabola. For $\varepsilon_{B,F}\ll k_BT$, by calculating Eq. (9) as an integral one obtains

$$\Delta M=-\frac{2e}{h\varepsilon_B^2}[3\zeta(3)(k_BT)^3+2\ln2\times k_BT\varepsilon_F^2], \tag{10}$$

with $\zeta(3)=\sum_{k=1}^{+\infty}k^{-3}\approx1.202$, indicating $|\Delta M|\propto T^3$ for $\varepsilon_F=0$. For a large magnetic field, the $\Delta M\sim\varepsilon_F$ curve presents plateaus like those in quantum Hall effect [28]. Suppose LLs up to n are filled with electrons or LLs above from $-n$ are filled with holes. In both cases the corresponding ΔM plateau is

$$\Delta M=-\frac{ev_F}{\pi L_B}\sum_{k=1}^{n}\sqrt{2k}. \tag{11}$$