Orbital magnetism of Dirac systems

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Abstract. Orbital magnetic susceptibility is calculated for massive Dirac systems, such as graphene with a band gap, and bismuth. Gap opening allows us to relate the singular orbital magnetism of massless Dirac system to the usual magnetism of conventional metal. In gapped graphene, we show that the valley degree of freedom produces Zeeman splitting as a real spin does, and causes Pauli paramagnetism which dominates over Landau diamagnetism. Singular susceptibility of intrinsic graphene can be understood as divergence of those contributions in zero-mass limit. A similar analysis is applied to three-dimensional Dirac systems to explain the strong diamagnetism of bismuth.

1. Introduction
In condensed matter systems, the orbital magnetism sensitively depends on the detail of the electronic band structure, and sometimes largely deviates from the conventional Landau diamagnetism. Particularly, narrow gap materials such as graphite [1, 2, 3] or bismuth [4, 5, 6] exhibit a singular behavior in the orbital susceptibility near the energy gap. Graphene monolayer [7, 8, 9] is a zero-gap system in which the conduction and valance bands stick touch at \( K \) and \( K' \) points in the Brillouin zone, called valleys, and the low-energy physics is characterized by chiral quasiparticles analogous to massless Dirac fermions. [1, 10, 11, 12, 13, 14, 15, 16, 17] At the Dirac point where two bands cross each other, the magnetic susceptibility has a singularity expressed as a delta function in Fermi energy \( \varepsilon_F \), i.e., the susceptibility is negative infinite at \( \varepsilon_F = 0 \), while vanishes when \( \varepsilon_F \) enters the conduction or valence band. [1, 18, 19, 20, 21, 22, 23, 24, 25] The orbital magnetism was also studied for related materials, such as graphite intercalation compounds,[26, 27, 28, 29] carbon nanotube,[30, 31, 32, 33] few-layer graphenes,[34, 35, 36] and organic compounds having Dirac-like spectrum.[37]

In this paper, we calculate the orbital magnetism of massive Dirac systems having an energy gap, to understand a singular diamagnetism of massless Dirac system as a zero-mass (i.e., zero-gap) limit of a conventional system. In Sec. 2, we calculate the susceptibility of a gapped monolayer graphene. We find that the pseudo-spin degree of freedom associated with valleys produces Zeeman splitting as a real spin does, and gives rise to Pauli paramagnetism in analogous way to the usual system. In zero-gap graphene, the singular susceptibility change in varying \( \varepsilon_F \) i.e., disappearance of the diamagnetism off the Dirac point, is understood as a contribution of valley Pauli paramagnetism give by band electrons. In Sec. 3 we extend the analysis to a three-dimensional Dirac system which models bismuth.
2. Monolayer graphene

Electronic states of graphene in the vicinity of $K$ and $K'$ points in the Brillouin zone are well described by the effective mass approximation.\cite{1, 10} Let $|A\rangle$ and $|B\rangle$ be the Bloch functions at the $K$ point, corresponding to $A$ and $B$ sublattices, respectively. In a basis ($|A\rangle, |B\rangle$), the Hamiltonian for the monolayer graphene around the $K$ point becomes

$$\mathcal{H}^K = \left( \frac{\Delta}{\nu \pi_+} \nu \pi_+ - \Delta \right),$$

where $v \approx 1 \times 10^6$ m/s is the band velocity \cite{8, 9}, $\pi_\pm = \pi_x \pm i\pi_y$, and $\pi = -i\hbar \nabla + (e/c)A$ with vector potential $A$ giving external magnetic field $B = \nabla \times A$. In the following, we neglect the spin Zeeman energy because the spin splitting is much smaller than Landau-level separations.

The diagonal terms $\pm \Delta$ represent the potential asymmetry between $A$ and $B$ sites, which opens an energy gap at the Dirac point. This can arise in graphene placed on a certain substrate material, where the interaction between the graphene and the substrate lattice produces different potentials between $A$ and $B$. Indeed, a band gap of the order of 0.1eV has been observed in graphene epitaxially grown on a SiC substrate. \cite{38, 39} From a theoretical point of view, the singular behavior in ideal graphene with vanishing gap is better understood by taking the limit $\Delta \to 0$, as will be shown below. We can safely assume $\Delta \geq 0$ without loss of generality. In a magnetic field, the eigenenergy becomes

$$\varepsilon^K_n = \text{sgn}_-(n) \sqrt{(\hbar \omega_B)^2 |n| + \Delta^2},$$

$$\varepsilon^K_{n'} = \text{sgn}_+(n) \sqrt{(\hbar \omega_B)^2 |n| + \Delta^2}$$

with $n = 0, \pm 1, \pm 2, \cdots$, $\hbar \omega_B = \sqrt{2\hbar v/l_B}$, $l_B = \sqrt{\hbar/eB}$, and

$$\text{sgn}_\pm(n) = \begin{cases} +1 & (n > 0); \\ \pm 1 & (n = 0); \\ -1 & (n < 0). \end{cases}$$

The Landau levels of $n \neq 0$ are doubly degenerate between the $K$ and $K'$ valleys, while those of $n = 0$ are not. Figure 2(a) shows an example of energy levels at $\hbar \omega_B = 2\Delta$.

The thermodynamical potential at temperature $T$ then becomes

$$\Omega = -\frac{1}{\beta} \frac{g_v g_s}{2 \pi l_B^2} \sum_{s = \pm} \sum_{n = 0}^\infty \varphi[\varepsilon_s((\hbar \omega_B)^2 n)] \left( 1 - \frac{\delta_{n0}}{2} \right),$$

where $\beta = 1/k_B T$, $\varepsilon_s(x) = s\sqrt{x + \Delta^2}$, $\varphi(\varepsilon) = \log \left[ 1 + e^{-\beta(\varepsilon - \zeta)} \right]$ with $\zeta$ being the chemical potential, and $g_s = 2$ and $g_v = 2$ represent the degrees of freedom associated with spin and valley, respectively. The magnetic susceptibility is defined by

$$\chi = -\left( \frac{\partial^2 \Omega}{\partial B^2} \right)|_{B=0}.$$

In weak magnetic field, using the Euler-Maclaurin formula, the summation in $n$ in Eq. (4) can be written as an integral in continuous variable $x$ and a residual term proportional to $B^2$. At zero temperature, we have \cite{25}

$$\chi(\varepsilon_F) = -\frac{g_v g_s}{6 \pi c^2} \frac{e^2 v^2}{2|\Delta|} \theta(|\Delta| - |\varepsilon_F|).$$
In the limit of $\Delta \rightarrow 0$, the susceptibility approaches a delta function

$$\chi(\varepsilon_F) = -g_s g_\ast \frac{e^2 v^2}{8\pi c^2} \delta(\varepsilon_F),$$

(7)

in agreement with the previous result.[1, 26, 21] The susceptibility Eq. (6) and the density of states are shown in Fig. 2 (b). The susceptibility is not zero in the gap, because the completely filled valence band gives a constant diamagnetic susceptibility. When the Fermi energy enters the conduction band, the susceptibility jumps down to zero, resulting in zero total magnetism.

Because the Hamiltonian is equivalent to that of a Dirac electron with a nonzero mass, the magnetic susceptibility around the band edge should correspond to that of a conventional electron. This is clearly illustrated by the effective Hamiltonian expanded in the vicinity of $\mathbf{k} = 0$. For the conduction band, the effective Hamiltonian for the A site near the band bottom ($\varepsilon = \Delta$) is written apart from the constant energy as [25]

$$\mathcal{H}^{K} \approx \frac{v^2}{2\Delta} \pi_+ - \pi_+ = \frac{\pi^2}{2m^*} + \frac{1}{2} g^* \mu_B B,$$

(8)

$$\mathcal{H}^{K'} \approx \frac{v^2}{2\Delta} \pi_+ - \pi_+ = \frac{\pi^2}{2m^*} - \frac{1}{2} g^* \mu_B B,$$

(9)

where $\mu_B = e\hbar/(2mc)$ is the Bohr magneton with $m$ being the free electron mass, and we defined $m^* = \Delta/v^2$. For instance, the $g$ factor is estimated at $g^* \approx 60$ at $\Delta = 0.1$ eV, and diverges as $\propto \Delta^{-1}$ as the gap decreases. The last term in each Hamiltonian can be regarded as the pseudo-spin Zeeman term, where the different valleys $K$ and $K'$ serve as pseudo-spin up ($\xi = +1$) and down ($\xi = -1$), respectively. This agrees with the Zeeman energy expected for an intrinsic magnetic moment, that originates from the self-rotation of the wave packet in Bloch electron. [40, 41]

Obviously, the pseudo-spin Zeeman term gives the Pauli paramagnetism and the first term containing $\pi^2$ gives the Landau diamagnetism in the usual form as

$$\chi_P(\varepsilon) = \left(\frac{g^*}{2}\right)^2 \mu_B^2 D(\varepsilon),$$

(10)

$$\chi_L(\varepsilon) = -\frac{1}{3} \left(\frac{m^*}{m}\right)^2 \mu_B^2 D(\varepsilon),$$

(11)

with density of states $D(\varepsilon) = g_s g_\ast m^*/(2\pi \hbar^2) \theta(\varepsilon)$. The total susceptibility $\chi_P + \chi_L$ actually agrees with the amount of the jump at the conduction band bottom in $\chi$ of Eq. (6). Because $g = 2m/m^*$ in the present case, we have $\chi_L = -\chi_P/3 \propto 1/m^*$ as in the free electron, giving the paramagnetic susceptibility in total. Therefore the susceptibility exhibits a discrete jump toward the paramagnetic direction when the Fermi energy moves off the Dirac point.

In the original Hamiltonian, the Landau-level energies in Eq. (2) can be rewritten as

$$\varepsilon_{\xi,s,n'} = s\sqrt{(\hbar \omega_B)^2 \left(n' + \frac{1}{2} + \frac{\xi s}{2}\right) + \Delta^2} + \Delta = \Delta \left(n' = 0, 1, 2, \cdots\right).$$

(12)

Figure 2(a) shows energy levels for $\hbar \omega_B = 2\Delta$ and the relationship between the different labeling schemes of Eqs. (2) and (12). For the conduction band, the levels of the same $n'$ with opposite pseudo-spins $\xi = \pm 1$ share the same Landau level function labeled by $n'$ on the A site, on which the states near the conduction-band bottom ($\varepsilon = \Delta$) have most of the amplitude. For the valence band, similarly, $n'$ describes the index of the Landau-level function at the $B$ site.
The density of states at zero magnetic field is

\[
D(\varepsilon) = \frac{g_v g_s}{\pi^2 h^3 v_F^3} |\varepsilon| \sqrt{\varepsilon^2 - \Delta^2} \theta(\varepsilon^2 - \Delta^2),
\]

where \( g_v \) is the valley degeneracy allowing the presence of different \( k \) points described by the above Hamiltonian in the first Brillouin zone. The Landau levels in a uniform magnetic field in \( z \) direction are given by [25]

\[
\varepsilon_{s,n,\sigma} = s \sqrt{(\hbar \omega_B)^2 (n + \frac{1}{2} + \frac{\sigma}{2}) + v^2 p_z^2 + \Delta^2},
\]

with \( \hbar \omega_B = \sqrt{2 \hbar v_F / l_B} \), \( s = \pm 1 \), and \( \sigma = \pm 1 \). This is equivalent to the two-dimensional Dirac system, Eq. (12), when the term \( \Delta^2 \) is replaced with \( \Delta^2 + v^2 p_z^2 \). The susceptibility \( \chi(\varepsilon) \) is
calculated by integrating Eq. (6) in $p_z$ as

$$\chi(\varepsilon) = -\frac{g_s g_v \epsilon^2 v^2}{6 \pi e^2} \int \frac{dp_z}{2 \pi \hbar} \frac{\theta(\Delta^2 + v^2 p_z^2 - \varepsilon^2)}{2 \sqrt{\Delta^2 + v^2 p_z^2}}$$

$$= -\frac{g_s g_v \epsilon^2 v^2}{12 \pi^2 \hbar c^2} \left\{ \begin{array}{ll}
\log \frac{2 \varepsilon_c}{|\Delta|} & (|\varepsilon| < |\Delta|); \\
\log \frac{2 \varepsilon_c}{|\varepsilon| + \sqrt{\varepsilon^2 - \Delta^2}} & (|\varepsilon| > |\Delta|),
\end{array} \right. \quad (16)$$

where $\varepsilon_c$ is a cut-off energy. In the limit of $\Delta \to 0$, the susceptibility at zero energy logarithmically diverges.

At an energy $\varepsilon$ just above the band bottom $|\Delta|$, we obtain the paramagnetic contribution

$$\chi(\varepsilon) - \chi(0) \approx \frac{2}{3} \left( \frac{m^*}{m^*} \right)^2 D(\varepsilon) \mu_B^2, \quad (17)$$

where $D(\varepsilon) = (g_s g_v / 4 \pi^2) (2m^*/\hbar^2)^{3/2} \sqrt{\varepsilon}$ with $m^* = \Delta / v^2$. This is nothing but the magnetic susceptibility, dominated by the Pauli paramagnetism, of a three-dimensional metal with mass $m^*$ and $g$ factor $g^* = 2m / m^*$. Figure 2 shows the susceptibility and the density of states in the present system. The singular decrease of the susceptibility at the band edges is understood in terms of the appearance of the dominant spin paramagnetism inside the band.

We note that in bismuth the index $\sigma$ in Eq. (15) represents real spin, while it was valley pseudo-spin in Eq. (12) for graphene. The Pauli component included in Eq. (17) thus describes the real spin paramagnetism enhanced by the strong spin-orbit coupling, apart from the bare electron paramagnetism.

4. Conclusion

We have calculated the orbital magnetism of massive Dirac systems. In an analogous way to conventional metal, the susceptibility near the band edge can be expressed by the Landau diamagnetism and the Pauli paramagnetism associated with pseudo-spin, such as valleys in graphene. The diverging magnetism of zero-gap graphene can be intuitively interpreted as a
result of vanishing the effective mass. The similar analysis is also applied to three dimensional Dirac systems which models bismuth. In any cases, the susceptibility near the energy gap is typically of the order of $(m/m^*)^2 \mu_B^2 D(\varepsilon)$, and overwhelms the real-spin Pauli paramagnetism of bare electrons, owing to small effective mass $m^*$. We expect that the singular susceptibility in graphene is observed by employing the experimental techniques used for two-dimensional electron systems on semiconductor. [43, 44]

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