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Dirac electrons in solids

Hidetoshi Fukuyama [a,*], Yuki Fuseya [b], Masao Ogata [c], Akito Kobayashi [d], Yoshikazu Suzumura [d]

[a] Department of Applied Physics and Research Institute for Science and Technology, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
[b] Department of Materials Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[c] Department of Physics, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[d] Department of Physics, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

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ABSTRACT

Electronic band structures in solids sometimes have features similar to Dirac electrons in vacuum. Well-known examples are bismuth and graphite; 4×4 original Dirac matrix in three dimension (3d) in the former with strong spin–orbit interaction, while 2×2 massless Dirac in two dimension (2d) with weak inter-layer coupling described essentially by Weyl equation in the latter. Recently one layer of graphite, graphene, is realized and studied both extensively and intensively. Other recent examples include a molecular solid, α-(BEDT-TTF)$_2$I$_3$, which has a layered structure with electronic states described by tilted-Weyl equation, and Fe-pnictides. There is also a theoretical proposal that one of inverse perovskites, Ca_3PbO, can be a candidate in 3d with strong spin–orbit interaction similar to bismuth. The particular feature of Dirac electrons in solids is a small, or even vanishing, band gap and then thermodynamic or transport properties are affected by inter-band coupling of electronic states. Typical ones are responses to external magnetic field. Actually, it has long been known that orbital susceptibility of these Dirac electrons has very particular features resulting from inter-band effects of magnetic field. It is of interest to see such inter-band effects on Hall effects to be compared with orbital susceptibility, which will be introduced in this paper, together with possible consequences of mutual interaction between valleys triggered by tilting in molecular solids.

Contents

1. Introduction

Relativistic quantum theory of electrons by Dirac leads to the well-known energy spectrum with respect to wave-number, $\boldsymbol{k}$,

$$E(\boldsymbol{k}) = \pm\sqrt{E_0^2 + c^2k^2}, \tag{1a}$$

$$E_0 = mc^2. \tag{1b}$$

Here $\hbar=1$, $k=|\boldsymbol{k}|$, and m and c are electron rest mass and the velocity of light, respectively. In Eq. (1a), $+$ refers to electrons while $-$ to positrons. Electronic states having $E(\boldsymbol{k})$ are doubly degenerate because of spins as is deduced from the Dirac equation represented by 4×4 matrix. For wave vector satisfying $(ck)^2 \gg E_0^2$, $E(\boldsymbol{k}) \sim \pm ck$. In the special case of vanishing rest mass, $m=0$, $E(\boldsymbol{k}) = \pm ck$ for any $\boldsymbol{k}$, which is described by 2×2 Weyl equation and expected to apply to neutrinos except possible small masses. The k-linear dependences of $E(\boldsymbol{k})$ are particular features of Dirac electrons. In solids, the motion of electrons are represented by the band structures with wave number defined within the

* Corresponding author.
E-mail addresses: fukuyama@rs.kagu.tus.ac.jp (H. Fukuyama), fuseya@mp.es.osaka-u.ac.jp (Y. Fuseya), ogata@phys.s.u-tokyo.ac.jp (M. Ogata), akito@slab.phys.nagoya-u.ac.jp (A. Kobayashi), suzumura@s.phys.nagoya-u.ac.jp (Y. Suzumura).

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Brillouin zones. There are cases where the band structure happens to have similar features to Eq. (1) for some region of $\boldsymbol{k}$-space. If these regions of $\boldsymbol{k}$ of some particular bands are located near the Fermi energy, characteristics of Dirac electrons are reflected in the properties of macroscopic solids. Examples include bismuth [1–3] and graphite [4,5], whose fascinating electronic properties have been studied about half a century ago. The essence of electronic states of the former is the same as that of Dirac electrons, whereas in the latter the Weyl equation. Recently there is growing interest in such Dirac electrons including graphene [6], a single layer of graphite, and some kinds of molecular solids [7]. Moreover there have been indications of existence of Dirac electrons for FePn superconductors [8–11] and inverse perovskite such as Ca_3PbO [12].

In this paper, origin of such Dirac electrons is discussed on general grounds, and results of recent studies on Bi and molecular solids are introduced.

2. Origin of Dirac electrons in solids

In solids, as is well known, electronic motions are under the influence of periodic potential and the energy eigenvalues and eigenfunctions are given by the energy bands, $\varepsilon_n(\boldsymbol{k})$ and Bloch functions $\Psi_{n\boldsymbol{k}}(\boldsymbol{r})=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$, where $u_{n\boldsymbol{k}}(\boldsymbol{r})$ is a periodic function with respect to lattice and depends on both band index, n, and wave vector, $\boldsymbol{k}$. It is to be noted that the $\boldsymbol{k}$-dependences of $u_{n\boldsymbol{k}}(\boldsymbol{r})$ is very complicated in general and then very hard to determine explicitly. This fact indicates that the detailed understanding of the electronic states, especially scattering processes between electrons and by impurities, and responses to external field, is very difficult if based on the Bloch representation. This fact has been taken seriously in 1950s because of the strong need to understand semiconductors. The difficulty has been overcome by Luttinger and Kohn [13] by their discovery of a particular representation of electronic states, now called LK representation, which is orthonormal and complete. In this representation, the basis functions are $\chi_{n\boldsymbol{k}}(\boldsymbol{r})=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}_0}(\boldsymbol{r})$, where the wave vector of the periodic function is fixed to a particular value, $\boldsymbol{k}_0$, which is in principle taken anywhere in the Brillouin zone but in practice at a particular point corresponding to the band gap. The merit of this LK representation lies in the fact that the $\boldsymbol{k}$-dependence is only in the phase factor $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ same as in free electrons and then the changes of the wave vector of electrons in the scattering processes are easily described. As compensation to this great advantage, the Hamiltonian is no longer diagonal in LK representation in contrast to Bloch representation and become a matrix with respect the band indices. This Hamiltonian matrix has a following form in general

$$\mathcal{H}_{nn'}=[\varepsilon_n(\boldsymbol{k}_0)+k^2/2m]\delta_{n,n'}+k_\alpha p^\alpha_{nn'}/m, \tag{2}$$

where $\boldsymbol{k}$ is measured relative to $\boldsymbol{k}_0$. The off-diagonal components of the Hamiltonian matrix, $p^\alpha_{nn'}$, in Eq. (2) are all well-defined and called kp Hamiltonian. This is exact and not an approximation. The "kp perturbation" results once the off-diagonal terms are treated perturbatively to diagonalize the Hamiltonian leading to effective masses and g-factors of conduction and valence bands, respectively. Through these procedures very detailed understanding of electronic states of semiconductors has become possible, which can be considered to be the scientific foundation of present semiconductor technology. This procedures will be explicitly seen by considering the following simple two bands separated by the band gap E_g at $\boldsymbol{k}_0$, assumed to be at symmetry point,

$$\mathcal{H}=\begin{pmatrix} E_g/2+k^2/2m & (k_xp_x+ik_yp_y)/m \\ (k_xp_x-ik_yp_y)/m & -E_g/2+k^2/2m \end{pmatrix}. \tag{3}$$

The eigenvalues of this Hamiltonian are given as $E_\pm=k^2/2m\pm\sqrt{(E_g/2)^2+(kp/m)^2}$ with $(kp)^2\equiv(k_xp_x)^2+(k_yp_y)^2$. For wave vector satisfying $(E_g/2)^2\gg(kp/m)^2$, these eigenvalues are approximated as $E_\pm=E_g/2+k^2/2m^*_\pm$ with the effective mass given by $1/2m^*_\pm=1/2m\pm p^2/m^2E_G$. This is called effective mass approximation. On the other hand for $(E_g/2)^2\ll(kp/m)^2$, $E_\pm\sim\pm|kp|/m$ similar to Dirac electrons. This implies that, if the two bands separated by a small (or vanishing) band gap happen to be near the Fermi energy, solids will reflect interesting characteristics of Dirac electrons. In such cases the inter-band matrix elements represented by p in Eqs. (2) and (3) in the Hamiltonian can result in important consequences in various electronic responses, both in thermodynamic and transport properties.

3. Dirac electrons under magnetic field and susceptibility

Inter-band effects of magnetic field have been seriously taken in 1950s and 1960s, especially in the context of responses of Bloch electrons to external magnetic field, in particular weak field orbital susceptibility [14–17]. This is because the large diamagnetism of bismuth experimentally first observed in early 1930's [18] remained the mystery. The difficulty of the single band approach to the orbital susceptibility was clear. This is because the Landau–Peierls formula based on the single band approximation is given as [19]

$$\chi_{\mathrm{LP}}=\frac{e^2}{48\pi^3c^2}\sum_n\int d\boldsymbol{k}\left\{\frac{\partial^2\varepsilon_n}{\partial k_x^2}\frac{\partial^2\varepsilon_n}{\partial k_y^2}-\left(\frac{\partial^2\varepsilon_n}{\partial k_x\partial k_y}\right)^2\right\}\frac{\partial f(\varepsilon_n)}{\partial\varepsilon_n}, \tag{4}$$

where $f(\varepsilon)$ is the Fermi distribution function and ε_n is the energy of the n-th band. It predicts vanishing contribution at absolute zero when the Fermi energy is tuned (by alloying with Sb) to be located in the band gap because of the factor $\partial f(\varepsilon_n)/\partial\varepsilon_n$ in Eq. (4). On the other hand, experimentally, the magnetic susceptibility, which is negative, i.e. diamagnetic, takes large absolute value in this situation [20]. This fact has stimulated many theoretical studies on orbital susceptibility. However, the resultant formulas in one form or another turn out to be very complicated and it was not easy to extract physical implications therefrom. The mystery of bismuth was finally resolved theoretically based on the detailed calculations for the effective model for bismuth by taking inter-band effects of magnetic field into account first with help of the Wigner representation [21]. The effective model focuses on two bands separated by small band gap with full consideration of strong spin–orbit interaction. Such a model had been proposed by Cohen and Blount [1] and later put into an elegant form by Wolff [2] essentially same as the 4×4 Dirac equation but with apparent complication resulting from spatial anisotropy intrinsic to solids. The fact that the essence of anomalously large diamagnetism is in the 4×4 Dirac electrons is seen by considering the electronic energy spectrum in uniform magnetic field whose effects are correctly taken into account by the replacement of $\boldsymbol{k}$ to $\boldsymbol{k}+e\boldsymbol{A}/c$, with $-e$ and $\boldsymbol{A}$ being the electronic charge and the vector potential, respectively, in the LK representation. The results are given as follows for the simplified model ignoring the anisotropy (this may be called isotropic Wolff model, which is similar to Dirac equations in vacuum, but for solids here with cut-off in large momentum in view of the limited region in Brillouin zone for the validity of the effective model),

$$E_{n,\sigma}(\boldsymbol{k})=\sqrt{\left(\frac{E_G}{2}\right)^2+E_G\left\{\omega_c\left(n+\frac{1}{2}+\frac{\sigma}{2}\right)+\frac{k_z^2}{2m_z}\right\}}. \tag{5}$$