The first principle calculation of two-dimensional Dirac materials

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Abstract. As the size of integrated device becoming increasingly small, from the last century, semiconductor industry is facing the enormous challenge to break the Moore's law. The development of calculation, communication and automatic control have emergent expectation of new materials at the aspect of semiconductor industrial technology and science. In spite of silicon device, searching the alternative material with outstanding electronic properties has always been a research point. As the discovery of graphene, the research of two-dimensional Dirac material starts to express new vitality. This essay studied the development calculation of 2D material's mobility and introduce some detailed information of some approximation method of the first principle calculation.

1. Introduction

Since the graphene has been successfully synthesis, 2D material got a lot of attention. The reason is that is has great potential in the fundamental science and application research. For example, as a good electro material, they can be made excellent field effect transistor.

2D Dirac material is a kind of material system established as the discovery of graphene [1]. The Dirac material has very excellent electronic properties, the most widely known material is graphene. The band structure of Dirac material contains Dirac corn, which means the dispersion relation is linear near the Dirac point. In the meanwhile, around the Fermi surface, the electrons show a behavior of massless Dirac Fermion, besides, with the effect of magnetic field, it shows half-integer and fraction hall effect [2], with high carrier mobility and other new electronic properties [3]. At present, 2D Dirac material mainly include graphene, silylene, germylene [4], borophene and specific graphdiyne [5]. Figure 1 shows Dirac material consists by different elements.
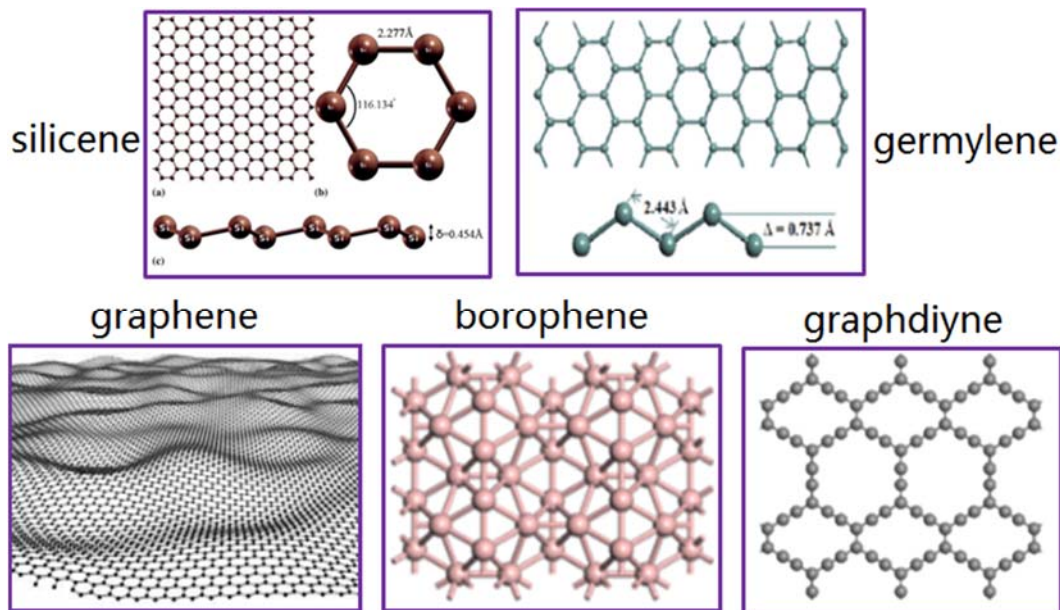
Figure 1. The 2D Dirac materials consist of different element

The physical properties in the solid depend on the electron properties around the Fermi surface in the solid to a great extent. The solid band theory was developed gradually since the foundation of quantum theory at early of the last century. At 1928, Bloch pointed out that the nature of the electron behavior is the motion in the lattice historical potential field [6]. In order to calculate the energy level of the electron, Hartree proposed self-consistent calculation method. However, the exchange-correlation potential wasn't take into consideration, therefore Fock made an amendment and it is called Hartree-Fock method which can be used to calculate the band structure of electron [7]. In 1936, Fermi came up with the concept of pseudo potential which has been applied to calculation physics, however, it is not easy to build appropriate pseudo potential. This process requires lots of theoretical and practical prove [8]. In 1937, Slater came up with another method to calculate band structure of solid called Augmented-Plane-Wave Method [9]. This method further developed to the methods we now use. After 1960, many theoretical calculation methods developed rapidly as the development of computer. The greatest process was the Density Functional Theory (DFT) proposed by Hobenberg, Kohn and Sham [10]. The innovation of DFT lies in it considers the electronic properties as the function of electron density. Now DFT has become a reliable method to calculate ground electronic properties and band structure. In 1980, DFT got great development. Including the application of the self-consistent method, the exploitation of many software based on DFT calculation. In 1986, Bednorz and Muller found the high temperature superconducting phenomenon [11]. It gives rise to many calculations related to phonons and promote the development of many more complicated calculation methods.

2. Bloch theory
In the foundation of mean field approximation, Bloch proved this theorem that the solutions of the Schrodinger equation for a periodic potential must be of a following form

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{1}$$

where $u_k(\mathbf{r})$ has the same period as the lattice $u_k(\mathbf{r}) = u_k(\mathbf{r}+\mathbf{T})$. The Bloch theorem is that the eigenfunctions of the wave equation for a periodic potential are equal to the product of a function $u_k(\mathbf{r})$ with the crystal lattice periodicity times a plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ [12]. Then I'll give a restricted proof of this theorem which is valid when ψ_k is nondegenerate. We assume N lattice points on a ring of

length Na. The potential energy is $U(x) = U(x + sa)$, where s is an integer. Then we consider the ring's symmetry, when the x is added Na, the eigenfunctions must be equal with the previous one. Then, on going once around the ring, $\psi(x + Na) = \psi(x) = C^N \psi(x)$, because $\psi(x)$ must be single-valued. In this case, $C = \exp(i2\pi s / N); s = 0, 1, 2, ..., N-1$, so as long as $u_k(x)$ has the periodicity a, so that $u_k(x) = u_k(x + a)$, then we get Bloch result $\psi_k = u_k \exp(i2\pi sx / Na)$.

3. Density Functional Theory

Density functional theory is a proposed by Kohn and Hohenberg in the 1960s. It is a method to find the Schrodinger equation that reflects the quantum behaviour of molecules and atoms which finally reflects the properties of the materials. The Density Functional Theory include two fundamental mathematical theorems [13]. The first theorem is: The ground state energy for Schrodinger's equation can be uniquely identified by the distribution of the electron density. The second theorem defines how to get this functional: The electron density which make the total energy of the functional minimum is the true electron density.

3.1. Kohn-Sham Equation

In the density functional theory, the energy functional corresponding to the terms of the single-electron wave functions can be written as

$$E\left[\{\psi_i\}\right] = E_{known}\left[\{\psi_i\}\right] + E_{XC}\left[\{\psi_i\}\right],$$

(2)

where the results have two forms, one form is $E_{known}\left[\{\psi_i\}\right]$, and the other form is, E_{XC}. The "known" terms has four part:

$$E_{known}\left[\{\psi_i\}\right] = \frac{h^2}{m}\sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(r)n(r)d^3r + \frac{e^2}{2}\int\int \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' + E_{ion}$$

(3)

The another term, $E_{XC}\left[\{\psi_i\}\right]$, is the exchange-correlation functional, and this term include all the quantum mechanical effects which are not included in the first terms[13]. By putting the energy into Schrodinger equation we have the form

$$\left[\frac{h^2}{2m}\nabla^2 + V\left(\vec{r}\right) + V_H\left(\vec{r}\right) + V_{XC}\left(\vec{r}\right)\right]\psi_i\left(\vec{r}\right) = \varepsilon_i\psi_i\left(\vec{r}\right)$$

(4)

Which is called the Kohn-Sham equations. On the left-hand side, there are three potentials, V, V_H,

$$V_H\left(\vec{r}\right) = e^2 \int \frac{n\left(\vec{r}'\right)}{|\vec{r}-\vec{r}'|}d^3r' \qquad\qquad V_{XC}\left(\vec{r}\right) = \frac{\delta E_{XC}\left(\vec{r}\right)}{\delta n\left(\vec{r}\right)}$$

and V_{XC}. Where $V_H\left(\vec{r}\right) = e^2 \int \frac{n\left(\vec{r}'\right)}{|\vec{r}-\vec{r}'|}d^3r'$ is called Hatree potential. $V_{XC}\left(\vec{r}\right) = \frac{\delta E_{XC}\left(\vec{r}\right)}{\delta n\left(\vec{r}\right)}$ is called exchange-correlation potential which is the derivation of the exchange-correlation functional.

3.2. Exchange-correlation Functional

Exchange-correlation functional is a term that defined to include all the quantum mechanical effects that are not included in the "known" terms. In fact, the true form of this term is unknown yet. However, there are some approximation of exchange-correlation functional and simplify the problem. $E_{XC}[n]$, for an arbitrary n,

$$E_{XC}[n] = \int \varepsilon_{XC}(n)\,n\,dr + \int \varepsilon_{XC}^{(2)}(n)|\nabla n|^2 \, n\,dr + \dots .$$
(5)

However, if n(r) is sufficiently varying slowly, one can show that

$$E_{XC}[n] = \int n(r)\varepsilon_{XC}(n(r))\,dr ,$$
(6)

where $\varepsilon_{XC}(n(r))$ is the exchange and correlation energy per electron of a uniform electron gas of density n. The $E_{XC}[n]$ can be also obtained a scheme which includes exchange effects exactly.

$$E_{XC}[n] = E_X[n] + \int n(r)\varepsilon_C(n(r))\,dr ,$$
(7)

where $E_X[n]$ is the exchange energy of a Hartree-Fock system of density n(r) and $\varepsilon_C(n(r))$ is the correlation energy per particle of a homogeneous electron gas.

3.3. The other approximation method of exchange-correlation functional

3.3.1. LDA and LSDA method

The approximation expression $E_{XC}^{LDA}[n] = \int n(r)\varepsilon_{XC}(n(r))\,dr$ is called LDA (Local-density Approximation) method. This approximation consider the exchange-correlation field is related only to electron density distribution in the space. LDA is the earliest method and the foundation of Generalized Gradient Approximation (GGA) method. If the spin is taken into consideration, this method can be advice to Local Spin-density Approximation,

$$E_{XC}^{LSDA}[n_\uparrow, n_\downarrow] = \int n(\vec{r})\varepsilon_{XC}(n_\uparrow, n_\downarrow)\,dr ,$$
(8)

This kind of approximation is so accurate for solids that it is used widely. In fact, the LSD method usually gives a remarkably accurate bond length but undervaluation of atomization energies.

3.3.2. GGA method

After the LSD method, the generalized gradient approximation(GGA) method had been proposed.

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int n(\vec{r})\varepsilon_{XC}^{GGA}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)\,d^3r ,$$
(9)

which introduces the density gradients $\nabla n_\uparrow$ and $\nabla n_\downarrow$ as additional local ingredients of ε_{XC}^{GGA}. The GGA method contains two main methods, the PW method and PBE method.

3.3.2.1. PW method

The PW method is a kind of approximation of GGA approximation proposed by Perdew and Wang in 1991. They argued that the gradient expansion for the hole in real space is an expansion in R (distance from the electron) as well as ∇ [14]. This method has no semiempirical parameter like the former ones and is also a more accurate description. The PW GGA-II exchange energy is

$$E_X^{PWGGA}[n_\uparrow, n_\downarrow] = \frac{1}{2}E_X^{PWGGA}[2n_\uparrow] + \frac{1}{2}E_X^{PWGGA}[2n_\downarrow] ,$$
(10)

where $E_X^{PWGGA}[n] = \int d^3r\,n\varepsilon_x(r_s,0)F(s)$, $\varepsilon_x(r_s,0) = -3k_F/4\pi$. We use atomic units

($\hbar = e^2 = m = 1$). Here, $k_F = \left(3\pi^2 n\right)^{1/3} = 1.91916 / r_s$ is the local Fermi wave vector and $s = \left|\nabla n\right| / 2k_F n$ is a scaled density gradient. The function F(s) is

$$F\left(s\right) = \frac{1 + 0.19645s \sinh^{-1}\left(7.7956s\right) + \left(0.2743 - 0.1508e^{-100s^2}\right)s^2}{1 + 0.19645s \sinh^{-1}\left(7.7956s\right) + 0.004s^4}$$

(11)

For small s,

$$F = 1 + 0.1234s^2 + O\left(s^4\right)$$

(12)

The PW GGA-II correlation energy is

$$E_c^{PWGGA}\left[n_\uparrow, n_\downarrow\right] = \int d^3 rn\left[\varepsilon_c\left(r_s, \zeta\right) + H\left(t, r_s, \zeta\right)\right],$$

(13)

where $t = \left|\nabla n\right| / 2gk_s n$ is another scaled density gradient, $g = \left[\left(1+\zeta\right)^{2/3} + \left(1-\zeta\right)^{2/3}\right]/2$ and $k_s = \left(4k_F / \pi\right)^{1/2}$ is the local screening wave vector.

3.3.2.2. PBE method
The PBE method (Perdew-Burke-Ernzerhof method) is now the most commonly used approximation in DFT theory which is proposed by Perdew, Burke and Ernzerhof in 1996. This method begin with the GGA for correlation in the form

$$E_C^{GGA}\left[n_\uparrow, n_\downarrow\right] = \int d^3 rn\left[\varepsilon_C^{unif}\left(r_s, \zeta\right) + H\left(r_s, \zeta, t\right)\right],$$

(14)

where r_s is the local Seitz radius ($n = 3/4\pi r_s^3 = k_F^3 / 3\pi^2$), $\zeta = \left(n_\uparrow - n_\downarrow\right)/n$ is the relative spin polarization[15], and $t = \left|\nabla n\right| / 2\phi k_s n$ is a dimensionless density gradient. Here $\phi\left(\zeta\right) = \left[\left(1+\zeta\right)^{2/3} + \left(1-\zeta\right)^{2/3}\right]/2$ is a spin-scaling factor, and $k_s = \sqrt{4k_F / \pi a_0}$ is the Thomas-Fermi screening wave number ($a_0 = \hbar^2 / me^2$). The gradient contribution H is constructed from three conditions:

(a)   If H is sufficiently slowly varying ($t \to 0$), H can be given by its second-order gradient expansion $H \to \left(e^2 / a_0\right)\beta\phi^3 t^2$, where $\beta \simeq 0.066725$.

(b)   If H is rapidly varying ($t \to \infty$), $H \to -\varepsilon_C^{unif}$.

(c)   Under uniform scaling to the high-density limit, $H \to \left(e^2 / a_0\right)\gamma\phi^3 \ln t^2$.

Then the form of the exchange energy have another four restrictions:

(d)   We must have

$$E_X^{GGA} = \int d^3 rn\varepsilon_X^{unif}\left(n\right)F_X\left(s\right),$$

(15)

where $\varepsilon_X^{unif} = -3e^2 k_F / 4\pi$.

(e)   The exchange energy follows the spin-scaling relationship

$$E_X\left[n_\uparrow, n_\downarrow\right] = \left(E_X\left[2n_\uparrow\right] + E_X\left[2n_\downarrow\right]\right)/2,$$

(16)

(f)   It should have (as $s \to 0$) $F_X\left(s\right) \to 1 + \mu s^2$, where $\mu = \beta\left(\pi^2/3\right) \simeq 0.21951$.

(g)   The Lieb-Oxford bound

$$E_X\left[n_\uparrow,n_\downarrow\right]\geq E_{XC}\left[n_\uparrow,n_\downarrow\right]\geq -1.679e^2\int d^3rn^{4/3} \quad , \tag{17}$$

will be satisfied if the spin-polarized enhancement factor

$$F_X\left(s\right)=1+\kappa-\kappa/\left(1+\mu s^2/\kappa\right) \quad , \tag{18}$$

where $\kappa=0.804$. Then the exchange-correlation energy can be constructed as the following form

$$E_{XC}^{GGA}\left[n_\uparrow,n_\downarrow\right]=\int d^3rn\varepsilon_X^{unif}\left(n\right)F_{XC}\left(r_s,\zeta,s\right) \quad , \tag{19}$$

3.4. First principle calculation

First principle calculation (or the ab initio calculation) is to find the geometric construction, electronic structure, thermodynamic properties, optical properties and so on by solving Schodinger equations with self-consistent based on the atomic components. The basic idea is to comprehend the multi-atom system as the multi-particle system consists of nuclears and electrons and dealing with the problems with non-empirical to the utmost extent.

The first principle calculation just need five basic physical constants. (m,e,h,c,k) and the electron structure of different elements. Then we can reasonably predict many physical properties. The difference between the cell size resulted from calculation and experiment is only several percentage points, other properties are almost the same with experimental results. These show the veracity of this theory.

The first principle calculation have three basic hypothesis to simplify the problems:

(1)   Using Born-Oppenheimer adiabatic approximation to transform the multi-particle problem to multi-electron problem.

(2)   Using single-electron approximation to simplify the solution of Schodinger equation.

(3)   Using self-consistent calculation to find the ground state properties.

4.   Tight-binding Model

In solid state physics, the tight-binding model is a method to use the superposition of the wave functions for isolated atoms as the approximation of the wave functions to calculate the electronic band structure. In some case, the electron can be considered to be tied around the atom, then the wave function can be constructed as the sum of atom orbital wave functions $\phi_a\left(\vec{r}-\vec{l}\right)$. Because of the Bloch Theory, the wave function has the form $\phi_{\vec{k}}\left(\vec{r}\right)=\sum_l e^{i\vec{k}\cdot\vec{l}}\phi_a\left(\vec{r}-\vec{l}\right)$. There exists a method called the LCAO method (linear combination of atomic orbitals method) used to help solve this problem. Tight-binding models are applied wildly in physics. The model is accurate in many cases, even when it fails, it can be combined with other methods to give better results [12].

5.   Deformation Potential Theory

The deformation potential theory bring in an additional Hamiltonian term $H\left(\overline{\varepsilon}\right)$, which is the result from the strain that exerted on the material and its effects on the band structure. This Hamiltonian is based on first order perturbation theory. It's matrix elements have the form $\left\{H\left(\overline{\varepsilon}\right)\right\}_{ij}=\sum_{\alpha,\beta=1}^{3}D_{ij}^{\alpha\beta}\varepsilon_{\alpha\beta}$, where $D^{\alpha\beta}$ denotes the deformation potential operator which transforms under symmetry operations as second rank tensor and $\varepsilon_{\alpha\beta}$ describes the $\left(\alpha\beta\right)$ strain tensor component. The subscripts $\left(ij\right)$ in $D^{\alpha\beta}$ represent the matrix element of the operator $D^{\alpha\beta}$. Because of the strain tensor is symmetric as

regards to α and β, and the deformation potential operator also have the symmetry that $D^{\alpha\beta} = D^{\beta\alpha}$ and therefore makes the number of independent deformation potential operators to be six.

6. Conclusion

In recent years, the carrier mobility of 2D system has been paid more and more attention. This essay introduces Bloch theory, the density functional theory and its application in first principle calculation. In addition, we have a discussion about some approximation of exchange correlation potential which is important in Kohn-Sham equation, like LDA, LSDA, GGA includes PW and PBE method. The advantage and disadvantage of each method is summarized as well. Finally, we discussed about the tight-binding model and deformation potential theory for the calculation of the carrier mobility of 2D materials. Hopefully, this paper could give an instruction to the two-dimensional Dirac materials researchers.

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