Long-range adsorbate interactions mediated by two-dimensional Dirac fermions

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We provide here an analytical formalism to describe the indirect interaction between adsorbed atom or molecule pairs mediated by two-dimensional (2D) Dirac fermions. We show that in contrast to the case of traditional 2D electron gas, in the 2D Dirac system, the long-range interaction behaves as $1/r^3$ decaying Friedel oscillation. This analytical formalism is fully consistent with a tight-binding numerical calculation of honeycomb lattices. Our formalism is suitable for the realistic 2D Dirac materials, such as graphene and surface states of three-dimensional topological insulators.

Keywords: graphene, Green's function, Dirac fermions

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1. Introduction

A topic of fundamental importance in condensed matter physics is how the presence of defects induces strong modifications on the local electronic properties of crystalline solids. These modifications, with the stunning development of scanning tunneling microscopy (STM), have been extensively investigated on metal surfaces where they are well known as Friedel oscillations and manifested as standing waves in the local electronic density spanning regions up to $\sim$ 10 nm from the defects on the metal surfaces. These electronic density standing waves behave as conducting medium to produce indirect long-range interactions between atoms/molecules adsorbed on surfaces, leading to the adsorbate overlayer structures showing the same periodicity as the oscillations. One kind of particularly suitable prototypes that has been used in a large amount of STM measurements to study the long-range interaction between the adsorbates and the formation of adsorbate superstructure is the (111) surfaces of noble metals, on which the surface-state electrons form a two-dimensional (2D) nearly free-electron gas. These Shockley-type surface states are dispersed as $\varepsilon = \hbar^2 k^2/2m_e$ (measured relative to the bottom of the surface-state band) and localized in narrow band gaps in the center of the first Brillouin zone of the (111)-projected bulk band structure. Thus they have extremely small Fermi wave vectors $k_F = \sqrt{2m_e\varepsilon_F}/\hbar$ and consequently the Friedel oscillations of the surface state have a significantly larger wavelength than those of the bulk states. Taking a remarkable comparison as an example is that for Ag(111) surface, $k_F = 0.083$ Å^{-1},[1] while that for bulk Ag is $k_F = 1.2$ Å^{-1}.[2] A theoretical model for the description of the long-range adsorbate–adsorbate (with distance r) interaction energy ΔE_{int} mediated by the 2D electrons on such (111) surfaces of noble metals has been developed by Hyldgaard and Person.[3] This theory links ΔE_{int} and the scattering properties of the 2D electrons by adsorbate, giving rise to an asymptotic expression, $\Delta E_{int} \simeq -\varepsilon_F (2\sin\delta_F/\pi)^2 \sin(k_F r + 2\delta_F)/(k_F r)^2$ for large r, where δ_F denotes adsorbate-induced scattering phase shift of the surface-state electrons at the Fermi level. By tuning phase shift δ_F that manifests in STM-measured variation in Fermi-level electronic density, the Hyldgaard–Person theory turns to work well in explaining adsorbate superstructures formed on Cu(111),[4–8] Ag(111),[9–11] Rh(111).[12]

Recently, unconventional 2D Dirac materials, such as graphene, silicene, and 2D surface states of topological insulators, have attracted researchers to take tremendous experimental and theoretical studies.[13–18] Unlike (111) surface of noble metals, a peculiar characteristic of 2D Dirac materials is the presence of unique Dirac cone of band structure, which is described at low energies by a 2D massless-Dirac wave equation. Because of the Dirac spectrum, the impurity scattering effect in 2D Dirac materials is naturally expected to display novel behavior, which may differ from the conventional semi-

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conductor or metal-surface 2D electron gases. Many experimental and theoretical efforts have been paid towards this issue. Anomalous Friedel oscillations in the vicinity of a single localized impurity,[19,20] as well as the identification of the nature and the precise location of impurities on graphene,[21–26] surface of three-dimensional (3D) topological insulator,[27–32] and Weyl semimetals[33–37] using STM, have been variously discussed. However, the issue of the long-range interactions between the adsorbates mediated by the 2D Dirac electrons still remains open. Because of its importance to basic point of interest and to Dirac electrons based chemical catalysis and electronics, in this work we address this issue by presenting an attempt at theoretical evaluation of the adsorbate–adsorbate indirect interaction allowed by the long-range density standing wave of the massless Dirac electrons.

2. Model and method

It is known that the interaction between atoms or molecules adsorbed on the surface of the material has several different origins, which can be divided according to the distance between the adsorbates. When the distance is large, the interaction between the adsorbates is mainly indirect, and is mainly regulated by the following three ways: the first way is the electrostatic interaction, such as dipole–dipole interaction, which arises owing to the exchange of photons and surface plasmons; the second one is the elastic-type interaction, such as the interaction caused by the deformation of the substrate lattice, which arises owing to the exchange of phonons. These two types of long-range indirect interactions are generally non-oscillating and decay monotonically with the distance between the adsorbates. While the third one is the way of mediation, that is, the oscillatory interaction generated by electrons in the material, which is also the mutual concern of this work.

The Hamiltonian of the system we considered is given by $H = H_0 + V$, where

$$H_0 = \sum_{\boldsymbol{k}\lambda} \varepsilon_{\boldsymbol{k}\lambda} c^{\dagger}_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda} + \sum_{i=1}^{N} \varepsilon_i d^{\dagger}_i d_i \tag{1}$$

is the free part of the Hamiltonian. Here, $c^{\dagger}_{\boldsymbol{k}\lambda}$ ($c_{\boldsymbol{k}\lambda}$) is a creation (annihilation) operator for a Dirac electron with wave vector $\boldsymbol{k}$ and band index λ, and $\varepsilon_{\boldsymbol{k}\lambda}$ is the corresponding dispersion relation for band λ. ε_i is the energy level of adsorbates $i = 1, 2$, and d_i ($d^{\dagger}_i$) annihilates (creates) an electron in the local adsorbate energy level. For simplicity and keeping the generality, a single level in each adsorbate is assumed. N is the total number of adsorbates considered in our model. The interaction between Dirac electrons and adsorbates are simply modeled by

$$V = \sum_{\boldsymbol{k},\lambda,i} v_{i\lambda} c^{\dagger}_{\boldsymbol{k}\lambda} d_i + v^{*}_{i\lambda} d^{\dagger}_i c_{\boldsymbol{k}\lambda}, \tag{2}$$

where $v_{i\lambda}$ is the coupling strength. The adsorbate–adsorbate pair interaction in a one-electron framework can be expressed in terms of the associated change in density of states (DOS) $\Delta\rho(\varepsilon)$ as follows:

$$\Delta W = 2\int_{-\infty}^{\varepsilon_{\mathrm{F}}} (\varepsilon - \varepsilon_{\mathrm{F}})\, \Delta\rho(\varepsilon)\, \mathrm{d}\varepsilon, \tag{3}$$

where the factor of 2 accounts for electron spin degeneracy, and $(\varepsilon - \varepsilon_{\mathrm{F}})$ indicates that the number of electrons is fixed.[38] The DOS connects to the one-electron Green's function by the following relation:

$$\Delta\rho = -\frac{1}{\pi} \mathrm{Im} \frac{\partial}{\partial\varepsilon} \ln\det(1 - G_0 V), \tag{4}$$

where $G_0 = (\varepsilon - H_0 + \mathrm{i}\delta)^{-1}$ is the unperturbed retarded Green's function. Substituting Eq. (4) into Eq. (3) and integrating by parts, we have

$$\Delta W = -\frac{2}{\pi} \int_{-\infty}^{\varepsilon_{\mathrm{F}}} \mathrm{Im} \ln\det(1 - G_0 V)\, \mathrm{d}\varepsilon. \tag{5}$$

In order to obtain the determinant in Eq. (4), matrices form for Green's function G_0 and perturbation V need to be specified. Equation (5) could be applicable to any number of randomly arranged impurities, which may be modeled by a single energy level or multiple energy levels. In the following text, by using this formula, the long-range indirect interaction between double impurities adsorbed on the surfaces of monolayer graphene as well as bilayer graphene will be studied.

Taking the honeycomb lattice (monolayer graphene) as an example, the low-energy (near the Fermi level) tight-binding dispersion relations contain double bands

$$\varepsilon_{\boldsymbol{k}\lambda} = \lambda\, |f(\boldsymbol{k})|, \tag{6}$$

where $\lambda = \pm$ with the plus sign applying to the upper and the minus sign the lower band,[13] and

$$f(\boldsymbol{k}) = -t \sum_{j=1}^{3} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{a}_j)$$

with $\boldsymbol{a}_1 = a_0(0, -1)$, $\boldsymbol{a}_2 = (a_0/2)(\sqrt{3}, 1)$, and $\boldsymbol{a}_3 = (a_0/2)(-\sqrt{3}, 1)$, t denoting the nearest-neighbor hopping energy, and a_0 being the lattice constant. In the following calculations, t and a_0 are taken as a unity. Here, the representation with the eigenstates of H_0 is chosen as the basis vector, so that for double-adsorbate denoted by i and j, G_0 is a 6×6 matrix, which may written as

$$G_0 = \begin{bmatrix} G_+(\varepsilon, r_{ii}) & 0 & 0 & G_+(\varepsilon, r_{ij}) & 0 & 0 \\ 0 & G_-(\varepsilon, r_{ii}) & 0 & 0 & G_-(\varepsilon, r_{ij}) & 0 \\ 0 & 0 & G_i(\varepsilon, r_{ii}) & 0 & 0 & 0 \\ G_+(\varepsilon, r_{ji}) & 0 & 0 & G_+(\varepsilon, r_{jj}) & 0 & 0 \\ 0 & G_-(\varepsilon, r_{ji}) & 0 & 0 & G_-(\varepsilon, r_{jj}) & 0 \\ 0 & 0 & 0 & 0 & 0 & G_j(\varepsilon, r_{jj}) \end{bmatrix}, \tag{7}$$

where $G_{i/j} = \left[\varepsilon - \varepsilon_{i/j} + i\delta\right]^{-1}$, $G_\lambda(\varepsilon, r_{ii}) = \sum_{\boldsymbol{k}} G_\lambda(\varepsilon, \boldsymbol{k})$ with $G_\lambda(\varepsilon, \boldsymbol{k}) = 1/(\varepsilon - \varepsilon_{\boldsymbol{k}\pm} + \mathrm{i}\delta)$, $G_\lambda(\varepsilon, r_{ij}) = \sum_{\boldsymbol{k}} G_\lambda(\varepsilon, \boldsymbol{k})\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}}$ with $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. Here, $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ are the positions of the double adsorbates. Correspondingly, the perturbation matrix V is given by

$$V = \begin{bmatrix} 0 & 0 & v_{i+} & 0 & 0 & 0 \\ 0 & 0 & v_{i-} & 0 & 0 & 0 \\ v_{i+}^* & v_{i-}^* & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & v_{j+} \\ 0 & 0 & 0 & 0 & 0 & v_{j-} \\ 0 & 0 & 0 & v_{j+}^* & v_{j-}^* & 0 \end{bmatrix}, \tag{8}$$

Here and following we assume $v_{i\lambda} = v$ is a real number. Thereby, after some simple algebraic operations, we have

$$\Delta W_{\text{pair}} = -\frac{2}{\pi}\int_{-\infty}^{\varepsilon_{\text{F}}} \mathrm{d}\varepsilon\, \mathrm{Im}\ln\left\{1 - T_1(\varepsilon)\left[\sum_\lambda G_\lambda(\varepsilon, r_{12})\right]^2 T_2(\varepsilon)\right\}, \tag{9}$$

where $T_i(\varepsilon) = v^2/(\varepsilon - \varepsilon_i - v^2\sum_\lambda G_\lambda(\varepsilon, r_{ii}))$ is the T-matrix characterizing the electron scattering at adsorbates $i = 1, 2$. This formalism can be easily generalized to the case of multiple adsorbates.

It is difficult to confirm the oscillating periodicity and decaying type just via the numerical simulations of tight-binding lattice model. However, an analytical estimation of indirect interaction as a function of position at low energy could be worked out by considering the linear Dirac dispersion of monolayer graphene, which is presented as

$$\varepsilon_{k\lambda} = \lambda v_{\text{F}} k \tag{10}$$

about the Dirac cones with $v_{\text{F}} = 3a_0 t/2$ being the Fermi velocity. The Green's function of pure monolayer graphene is explicitly given by the following equation:

$$G_\lambda(\varepsilon, r) = \frac{\lambda}{2\pi v_{\text{F}} r} + \frac{\varepsilon}{4v_{\text{F}}^2}\left[\mathrm{Y}_0(z) + \lambda \mathrm{H}_0^{(1)}(z)\right] + (1-\lambda)\frac{\mathrm{i}\varepsilon}{4v_{\text{F}}^2}\mathrm{J}_0(z), \tag{11}$$

where $\lambda = \pm$, and $\mathrm{J}_0(z)$, $\mathrm{Y}_0(z)$, and $\mathrm{H}_0^{(1)}(z)$ are Bessel function of the first kind, Bessel function of the second kind, and Hankel function of the first kind, respectively. Here, $z = \varepsilon r/v_{\text{F}}$. By employing the asymptotic expressions of $\mathrm{J}_0(z)$, $\mathrm{Y}_0(z)$, and $\mathrm{H}_0^{(1)}(z)$ at large r, *i.e.*, $\mathrm{J}_0(z\to\infty) \approx \sqrt{2/\pi z}\cos(z + \pi/4)$, $\mathrm{Y}_0(z\to\infty) \approx \sqrt{2/\pi z}\cos(z - \pi/4)$, and $\mathrm{H}_0^{(1)}(z\to\infty) \approx 2/\pi z + \sqrt{2/\pi z}\cos(z - \pi/4)$, the long-range indirect interaction energy ΔW_{pair} between adsorbed pairs on monolayer graphene is dominated by the electrons or holes near the Fermi energy ε_{F}, may be approximatively expressed as

$$\Delta W_{\text{pair}}(r) \approx -\frac{\varepsilon_{\text{F}} v^4}{2\pi v_{\text{F}}^4}\frac{\sin\left[2q_{\text{F}} r + \phi(\varepsilon, \varepsilon_1, \varepsilon_2)\right]}{(q_{\text{F}} r)^3}, \tag{12}$$

where $q_{\text{F}} = \varepsilon_{\text{F}}/v_{\text{F}}$ is the Fermi wave vector of Dirac electrons, and ϕ denotes adsorbate-induced scattering phase shift of the Dirac electrons at the Fermi level. This is a typical Friedel oscillation with an oscillating periodicity $\pi/q_{\text{F}} = \pi v_{\text{F}}/\varepsilon_{\text{F}}$, and the position of the first minimum value in the oscillations is determined and mediated by the phase shift ϕ, which could be mediated and measured by low-temperature STM technique. Equation (12) suggests that the indirect adsorbate-adsorbate interaction is also proportional to v^4. In fact, such a result is only proper in the limit of weak coupling. For strong coupling, the v-dependence in T-matrices eventually cancels the leading v^4, which is out of our discussions here since the bulk contributions of the substrate must be considered in this case.

More importantly, the main contribution to the decaying of the oscillation on the graphene layer is proportional to $1/r^3$. However, it is well known to us that the indirect interaction between adatoms adsorbed on metallic surfaces holding parabolic bands varies as $1/r^2$ decaying Friedel oscillation in the adsorbate–metal system.[3] Additionally, we also carefully derived the indirect interaction between adatoms adsorbed on bilayer graphene (BG),[39–41] which holds parabolic bands $\varepsilon_{\text{BG}} = \lambda(v_{\text{F}}^2/t_\perp)k^2$ with $t_\perp$ the inter-layer hopping en-

ergy, and found that

$$\Delta W_{\rm pair}^{\rm BG}(r) \propto -\frac{\varepsilon_{\rm F} t_{\perp}^2}{v_{\rm F}^4} \frac{\sin(2q_{\rm F}r+\phi)}{(q_{\rm F}r)^2},$$

which behaves as $1/r^2$ decaying Friedel oscillation and is the same to the case of normal metal surface. We will not show the details of the BG-case out of briefness. Therefore, we could carefully predict that the long range indirect interaction between a pair of adsorbates mediated by massless Dirac electrons may decay faster by a factor of $1/r^3$ than that on the surfaces of metals.

One should notice from Eq. (12) that the numerators of the Friedel oscillation and corresponding energy change of indirect interaction between two adsorbed atoms appears as a sine function. This form looks like different from the theoretical result of the change of LDOS induced by a single impurity,[42] which appears as a cosine function, *i.e.*,

$$\Delta\rho_{\rm single}(r) \sim -\frac{2\sin(\delta)}{q_{\rm F}} \frac{\cos(2q_{\rm F}r+\delta)}{\pi^2 r^3}. \tag{13}$$

This difference is reasonable since our formula of $\Delta W_{\rm pair}$ is a simple integral function of the LDOS, see Eq. (3). Recently, the long-range interactions of bismuth growth on monolayer epitaxial graphene have been experimental observed, and the experimentally derived potential energy is well overlaid with the theoretical prediction of $\Delta\rho_{\rm single}(r)$ within a phase shift factor $\delta = \pi/2$.[43] And thereby, our result of $\Delta W_{\rm pair}$ shown in Eq. (12) is actually consistent with the experimental observation. In addition, cosine-type behavior also observed in the RKKY interaction of magnetic impurities in nodal-line semimetals,[44] which differs from the sine-type behavior of the indirect interaction between double nonmagnetic adatoms considered here. This difference may be due to the coupling effect between magnetic impurities and Dirac electrons is different from that between nonmagnetic impurities and Dirac electrons.

Furthermore, The influence of finite temperature on the Friedel oscillation can be easily considered by introducing the Fermi–Dirac distribution function

$$n_{\rm F}(\varepsilon) = \{1+\exp[\beta(\varepsilon-\varepsilon_{\rm F})]\}^{-1}, \tag{14}$$

is the inverse temperature with $k_{\rm B}$ the Boltzmann constant, into the formula of adsorbate–adsorbate pair interaction. Namely, equation (3) shown above may be generalized as

$$\Delta W = -\int_{-\infty}^{\varepsilon_{\rm F}} (\varepsilon-\varepsilon_{\rm F}) n_{\rm F}(\varepsilon) \Delta\rho(\varepsilon) {\rm d}\varepsilon. \tag{15}$$

By this way, we point out that the result represented by Eq. (12), which holds an oscillating period $\pi R_{\rm F}$ with $R_{\rm F} = v_{\rm F}/\varepsilon_{\rm F}$ being the Fermi wavelength, and an envelope decreasing pattern $1/r^3$ when $r < R_{\rm T}$ with $R_{\rm T} = \beta v_{\rm F}$ being the thermal length, is valid at the limit of zero temperature. At finite temperature and $0 < T < T_{\rm F}$ with $T_{\rm F} = 2\varepsilon_{\rm F}/3k_{\rm B}$ being the Fermi temperature, for long range beyond the thermal length ($r > R_{\rm T}$), the Friedel oscillation may decay exponentially, *i.e.*,

$$\Delta W_{\rm pair}(T \neq 0) \sim -\frac{\exp(-2\pi r\beta v_{\rm F})}{\pi\beta\varepsilon_{\rm F}} \Delta W_{\rm pair}(T=0). \tag{16}$$

However, if the distance is shorter than the thermal length ($r < R_{\rm T}$), the Friedel oscillation keeps unchanged from the zero temperature result. Additionally, for much higher temperature, *i.e.*, $T \gg T_{\rm F}$, the Friedel oscillations may be destroyed due to the electron–phonon coupling effect and disorder effect. Therefore, in order to observe the long-range Friedel oscillations, the conditions of $T < T_{\rm F}$ and $r < R_{\rm T}$ should be warranted in the related experiments.

3. Results and discussion

In order to check the reasonability and correctness of the above analytical formalism (12), we turn our attention to the numerical simulations of tight-binding honeycomb lattice of monolayer graphene. It is supposed that adatoms atop adsorbed on the carbon atoms, one of which sits at the origin of coordinates $\boldsymbol{r}_1 = (0,0)$ while another one at position

$$\boldsymbol{r}_2 = \frac{\sqrt{3}}{2} a_0 \left[(m+l), \sqrt{3}(m-l)\right],$$

with m and l are integer numbers. From Eqs. (6)–(9), we can clearly find that the indirect interaction between adsorbate pairs is mediated by three parameters, namely, the scattering potential v between adsorbates and Dirac fermions in monolayer graphene, the energy level ε_i of adsorbates, and the Fermi energy $\varepsilon_{\rm F}$ of graphene. The Fermi energy of graphene can be modulated either by an external gate voltage or by the doping with impurities. As a result, Fermi energy can be shifted into the conduction or valence bands, and then the adsorbates interact with each other via Dirac fermions. In our adsorbate–graphene system, one adsorbate exchanges electron with the nearest carbon-atom induces a change of DOS in graphene plane propagated by Dirac fermions to another adsorbate. Subsequently, this adsorbate exchanges electron with graphene, and then reverses back to the original adsorbate. It is conceivable that the farther the distance between double adsorbed atoms is, the weaker the indirect interaction between them is. In other words, the interaction decays as Friedel oscillation with increasing the spacing of the adsorbed atoms.

In the numerical simulations, we choose $v = 2t$ and $\varepsilon_1 = \varepsilon_2$ for simplicity. The results of the indirect interaction energy

$\Delta W_{\rm pair}$ as a function of interatomic separation $r = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ are shown by red dots in Fig. 1. The corresponding analytical results of Eq. (12) are also plotted by blue lines in Fig. 1. Consequently, the analytical approximation results in the continuum limit are well consistent with the numerical calculations of the tight-binding model. It is obvious that the interactions between adsorbates display Friedel oscillating mode with the increasing of separation in real space, which means that adsorbates repulse ($\Delta W_{\rm pair} > 0$) each other at some distances and attract ($\Delta W_{\rm pair} < 0$) at other positions. Similar to the adsorbates on the conventional metallic surfaces or doped semiconductors, the oscillation period of indirect long-range interaction between atoms/molecules adsorbed on graphene should be also dependent on the Fermi energy $\varepsilon_{\rm F}$. Indeed, as mentioned above, comparing Fig. 1(a) with Fig. 1(b), in which the Fermi energy $\varepsilon_{\rm F}$ was chosen as $\varepsilon_{\rm F} = 0.3t$, and $\varepsilon_{\rm F} = 0.5t$, respectively, we found that the period of oscillation significantly changes when we change the Fermi energy. In addition, in Figs. 1(c) and 1(d) we chose $\varepsilon_1 = 2.0$ and $\varepsilon_1 = 1.0$ within the same Fermi energy $\varepsilon_{\rm F} = -0.5t$. We can see from Figs. 1(c) and 1(d) that the parameter ε_1 just introduces a small phase shift in the Friedel interaction. The first minimal value of the interaction energy appears in the vicinity of $r \approx 16a_0 = 3.272$ nm when $\varepsilon_{\rm F} = 0.3t$, as shown in Fig. 1(a). While the indirect interaction energy reaches a minimal value at $r \approx 10a_0 = 1.42$ nm when the Fermi energy $\varepsilon_{\rm F} = 0.5t$ or $-0.5t$, which could be observed in Figs. 1(b)–1(d).

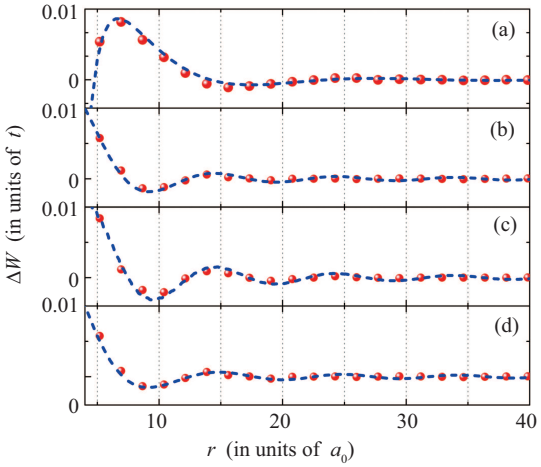


Fig. 1. The pair-indirect-interaction energy $\Delta W_{\rm pair}(r)$ between adsorbates on a monolayer graphene as a function of r (in units of a_0) with potential $v = 2t$. The red balls are the numerical results which calculated by Eq. (3), and the blue lines in figures are the results from the approximate analytical expressions, *i.e.*, Eq. (12). In the calculations, the parameters were chosen as $a_0 = 1.0$, $t = 1.0$: (a) for $\varepsilon_{\rm F} = 0.3$, $\varepsilon_1 = -1.0$; (b) for $\varepsilon_{\rm F} = 0.5$, $\varepsilon_1 = -1.0$; (c) for $\varepsilon_{\rm F} = -0.5$, $\varepsilon_1 = -2.0$; and (d) for $\varepsilon_{\rm F} = -0.5$, $\varepsilon_1 = 1.0$.

The first negative minimum of interaction energy is an important point because the attractive interactions may bring on the creation of stable adsorbate-structures in graphene and should have the significant effect on the physical properties of the system. Therefore, the larger the attractive adsorbate–adsorbate interactions is, the more stable the adsorbate–graphene system is. On the other side, however, the repulsive interaction may have a strong effect on the diffusion kinetics for this type of adsorbate–graphene system.

In the above discussion, the effect of spin–orbital coupling (SOC) in graphene is ignored since it is extremely weak. However, due to the large atomic number of Si element, the corresponding magnitude of SOC in silicene becomes noticeable and significantly modifies the energy dispersions, leading to a finite SOC gap. Therefore, it is necessary to briefly discuss the role of SOC on the long-range adsorbate interactions. The low-energy effective Hamiltonian of silicene around the Dirac K point is given by[45]

$$H_K = \left(\varepsilon_1 - \lambda_{\rm so}^{\rm 2nd}\right) I_4 + \begin{pmatrix} h_{11} & v_{\rm F}k_+ \\ v_{\rm F}k_- & -h_{11} \end{pmatrix}, \tag{17}$$

where $k_\pm = k_x \pm {\rm i}k_y$, $h_{11} = -\lambda_{\rm so}\sigma_z - a\lambda_{\rm R}(k_y\sigma_x - k_x\sigma_y)$ with $\lambda_{\rm so} = \lambda_{\rm so}^{\rm 1st} + \lambda_{\rm so}^{\rm 2nd}$ being the summation of first-order and second-order SOCs induced by low-buckled symmetry of silicene, $\lambda_{\rm R}$ being the intrinsic Rashba SOC, and a being the lattice constant. Differing from the linear Dirac spectrum of graphene, the spectrum of H_K is derived as

$$\tilde{\varepsilon}_{\boldsymbol{k}\pm} = \pm\sqrt{(v_{\rm F}^2 + \lambda_{\rm R}^2)^2 + \lambda_{\rm so}^2} \tag{18}$$

with an energy gap of $2\lambda_{\rm so}$ at the Dirac point. If the SOC is weak, the energy spectrum $\tilde{\varepsilon}_{\boldsymbol{k}\pm}$ can be approximated as $\tilde{\varepsilon}_{\boldsymbol{k}\pm} \approx \pm v_{\rm F}k + \lambda_{\rm so}^2/v_{\rm F}k$. For this case, the role of SOC on the long-range adsorbate interactions can be ignored since the energy spectrum $\tilde{\varepsilon}_{\boldsymbol{k}\pm}$ is dominated by the linear term $v_{\rm F}k$. However, if the strength of SOC is strong enough the long-range adsorbate interactions may be significantly modified. The intrinsic SOC $\lambda_{\rm so}$ is about 3.9 meV in silicene, which is much larger than that in graphene. Furthermore, from the expression of $\tilde{\varepsilon}_{\boldsymbol{k}\pm}$ one can easily find that the SOC gap $2\lambda_{\rm so}$ will not be affected by the intrinsic Rashba SOC $\lambda_{\rm R}$, but the spin of electrons in silicene may be tuned by the intrinsic Rashba SOC. As a result, the decaying law of Friedel oscillation of long-range indirect interaction energy between adsorbed pairs on the silicene may depart from $1/r^3$ due to the presence of SOC effect, so that its measurement can be used as a tool to test the strength of SOC. Unfortunately, it is difficult to derive an analytical expression of $\Delta W_{\rm pair}$ by employing the energy spectrum of silicene $\tilde{\varepsilon}_{\boldsymbol{k}\pm}$ taken into account the SOC. For this reason, more detailed numerical simulations are needed to clarify this issue, which is out of the scale of the present work and will be intensively studied in the near future.

Our formulae derived above are also suitable for the topological surface states of 3D topological insulators, in which the

spin of Dirac fermions is locked with the momentum. The effective low-energy Hamiltonian of topological surface states reads[15,16]

$$H = v_{\rm F}(k_y\sigma_x - k_x\sigma_y) + \frac{\lambda_{\rm w}}{2}(k_+^3 + k_-^3)\sigma_z, \tag{19}$$

and the corresponding surface band dispersion is

$$\varepsilon_{k\pm} = \sqrt{(v_{\rm F}k)^2 + \lambda_{\rm w}^2 k^6 \cos(3\theta)}, \tag{20}$$

where $\lambda_{\rm w}$ (~ 180 meV·nm^3 for Bi_2Se_3 and ~ 250 meV·nm^3 for Bi_2Te_3) is the warping parameter due to the C_3 symmetry, and θ is the angle between wave vector $\boldsymbol{k}$ and the k_x axis. When the Fermi level is close to the Dirac point, the warping term can be ignored, and then the long-range indirect interaction energy between adsorbed pairs on the surface of 3D topological insulator still obeys the $1/r^3$ decaying law of Friedel oscillation. However, when the Fermi level is far away from the Dirac point, the warping term would become non-negligible (especially for the Bi_2Te_3 with strongly warping surface band), and the interference patterns of DOS are dominated by surface states at the extremal points on the constant energy contour. In the presence of strong warping ($\lambda_{\rm w} \gg 0$), an analytical expression in closed form of the Green's function cannot be derived strictly. Instead, an asymptotic approximation for the Green's function in the limit of small warping ($\lambda_{\rm w} \to 0$) can be obtained as

$$\begin{aligned} G_{\rm TI}(\varepsilon, \boldsymbol{r}) = \frac{\varepsilon}{4v_{\rm F}^2}[&{\rm i}\,{\rm H}_0^{(1)}(z) \\ &-{\rm i}(\sigma_+ {\rm e}^{-{\rm i}\theta} - \sigma_- {\rm e}^{{\rm i}\theta}){\rm H}_1^{(1)}(z) \\ &+\frac{\varepsilon^2}{v_{\rm F}^3}\lambda_{\rm w}\cos(3\theta){\rm H}_3^{(1)}(z)\sigma_z] + O(\lambda_{\rm w}^2), \end{aligned} \tag{21}$$

where $\sigma_\pm = \sigma_x \pm {\rm i}\sigma_y$. One can see that the third term in $G_{\rm TI}(\varepsilon, \boldsymbol{r})$ is contributed from the warping term in the effective Hamiltonian.

It is expected that the long-range Friedel oscillation of indirect interaction energy between adsorbed pairs $\Delta W_{\rm pair}$ will be greatly modified by the warping effect. Importantly, substituting this asymptotic representation of $G_{\rm TI}(\varepsilon, \boldsymbol{r})$ into Eq. (5), the warping effect may bring about an anisotropic contribution in $\Delta W_{\rm pair}$ due to the presence of a factor of $\cos(3\theta)$. Explicitly, in the directions $\theta = (\pi/6)(2n+1)$, the contribution from warping effect switches off and the long-range Friedel oscillation contains only the $1/r^3$ contribution from the Dirac linear term. While in other directions, the contribution from warping effect may be remarkable and observable, leading to a departure from the $1/r^3$ decaying law of Friedel oscillation of $\Delta W_{\rm pair}$. However, after some long and tedious derivations, we find that it is still difficult to obtain an analytical expression of $\Delta W_{\rm pair}$ by using the asymptotic representation of $G_{\rm TI}(\varepsilon, \boldsymbol{r})$ shown above. For briefness, we will not provide detailed numerical calculations on this issue in the present work.

In order to better understand the influence of warping effect on the long-range Friedel oscillation caused by impurity scattering on the surface of topological insulator, we turn to briefly discuss the case of a single impurity. By employing $G_{\rm TI}(\varepsilon, \boldsymbol{r})$ shown above, it is easy to get that the long-range Friedel oscillation of LDOS induced by a single impurity, which is written as

$$\Delta\rho \approx -\frac{v_{\rm F}}{4\pi^2\varepsilon_{\rm F} r^3}\cos(2q_{\rm F}r) - \frac{\lambda_{\rm w}^2\varepsilon_{\rm F}^4\cos^2(3\theta)}{4\pi^2 v_{\rm F}^6 r^2}\cos(2q_{\rm F}r). \tag{22}$$

It is clear to us that, on the one hand, the warping effect provides a $1/r^2$ long-range decaying Friedel oscillation of topological surface states, which is identical to the one of a 2D normal metal, and it dominates the a $1/r^3$ contribution from the Dirac linear term. On the other hand, the contribution from the warping effect in $\Delta\rho$ is anisotropic because of the presence of $\cos^2(3\theta)$ factor. Furthermore, it has been experimentally demonstrated that[46] the long-range decaying law of Friedel oscillation induced by the step edge on the surface of Bi_2Te_3 within strong warping effect critically depends on the energy of topological surface states, and varies from $1/r^{3/2}$ to $1/r^{1/2}$ and finally to $1/r$ as increasing the energy. While the Friedel oscillation induced by the step edge on the surface of Bi_2Se_3 keeps the decaying law of $1/r^{3/2}$ as the energy increases since the warping effect is weak therein.

When the distance between the adsorbates is very small, the orbitals between the adsorbates may overlap, and then the direct interaction becomes significant and local chemical bonds are formed. Taking the direct interaction in the Hamiltonian model employed above into account, the total effective Hamiltonian is written as

$$\widetilde{H} = H + \sum_{i\neq j} v_{ij} d_i^\dagger d_j + v_{ij}^* d_j^\dagger d_i, \tag{23}$$

where v_{ij} is the overlap integral of orbitals of adsorbates i and j. In order to illustrate the problem more intuitively, we still consider only two adsorbates, and we could obtain the change in DOS as

$$\Delta\rho(\varepsilon) = -\frac{1}{\pi}{\rm Im}\frac{\partial}{\partial\varepsilon}\ln\left[\frac{\det[G_1]}{\det[G_2]}\right], \tag{24}$$

where $G_2 = 1/(\varepsilon I - \widetilde{H} + {\rm i}\delta)$ and $G_1 = 1/(\varepsilon I - H_1 + {\rm i}\delta)$ with H_1 being the Hamiltonian for only one atom is absorbed on the graphene. Explicitly, H_1 is given by a matrix that

$$H_1 = \begin{bmatrix} \varepsilon_1 & v_{1+} & v_{1-} \\ v_{1+}^* & \varepsilon_+ & 0 \\ v_{1-}^* & 0 & \varepsilon_- \end{bmatrix}. \tag{25}$$

In the absence of direct interaction term, equation (24) is conveniently reduced to Eq. (4). Substituting Eq. (24) into Eq. (3), the pair interaction energy including the direct interaction is easily obtained. In contrast to the indirect inter action, the adsorbate–adsorbate direct interaction may weakly depend on the substrate, but strongly depends on the orbital-type of adsorbate. For example, five d-orbitals may be needed for the transition metal adatoms, while only one s-orbital is needed for the hydrogen adatom. Since the direct interaction between adsorbates is very short-range, it decays exponentially with the distance, *i.e.*, $\Delta W_{\rm pair}(r) \sim -{\rm e}^{-\kappa r}$ with κ^{-1} can be the order of the size of the adsorbate. It can be seen that the direct interaction energy will not significantly modify the long-range Friedel oscillation decaying law of the adsorbate–adsorbate indirect interaction mediated by the Dirac electrons in graphene. In addition, in order to obtain more accurate direct interaction energy, correlation effect should also be considered. This can be achieved by employing the first-principles calculation method based on the density functional theory.

Although the findings in this work may be expected, we believe our results are interesting and useful for understanding the novel properties of massless Dirac electrons in graphene. In particular, the analytical results and numerical calculations in this work reveal that the decaying law of $\Delta W_{\rm pair}$ in monolayer graphene is different from that of traditional 2D electron gas or of even bilayer graphene. This work reveals the novel properties of Dirac electrons in graphene, which may be confirmed by STM experiments.

4. Conclusion

In conclusion, we have numerically and analytically studied the indirect interaction between adsorbates mediated by Dirac fermions by using the Green's function method. The analytical expression of the long range indirect interaction in the continuum limit is consistent with the numerical calculations for the tight-binding model of monolayer graphene. We have found that the adsorbate pairs on 2D Dirac materials interact via a long-range Friedel oscillation, decaying faster with a factor of $1/r^3$ than the Friedel type interactions in the normal 2D electron gases. We have also found that the indirect interaction energy reached a minimal value at different separations corresponding to the oscillation period $\pi v_{\rm F}/\varepsilon_{\rm F}$. A phase shift ϕ, which determines the position of the first extremum value in the oscillations of density of states and the indirect interactions, has been introduced into our analytical estimate. Furthermore, our analytical Friedel oscillation formalism can be easily generalized not only to the 2D Weyl semimetals and/or the 3D Weyl and Dirac semimetals, but also to multiple adsorbates. We expect that the present results of long-range adsorbate interactions mediated by a graphene like 2D Dirac electrons can be experimentally confirmed in the future low temperature STM studies.

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