Chiral symmetry restoration in monolayer graphene induced by Kekulé distortion

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We propose a chiral symmetry restoration mechanism in monolayer graphene, in analogy with the strongly coupled gauge theory. The chiral (sublattice) symmetry of graphene, which is spontaneously broken under the effectively strong Coulomb interaction, is restored by introducing the Kekulé-patterned lattice distortion externally. Such a phase transition is investigated analytically using the techniques of strong coupling expansion on the lattice gauge theory model, by preserving the original honeycomb lattice structure. We discuss the relation between the chiral phase transition and the spectral gap amplitude, and we show the modification of the dispersion relation of the quasiparticles.

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Ever since its first experimental isolation in 2004, graphene has attracted a great deal of interest in the fields of particle physics as well as materials science. One of its important features is that the electrons/holes on monolayer graphene can be effectively described as massless Dirac fermions around half filling on the triangular sublattices, leading to the generation of a mass gap. This mechanism is analogous to the dynamical mass generation mechanism of quarks in quantum chromodynamics (QCD). The techniques of lattice gauge theory have been employed on the hypothetical square lattice, to investigate the chiral symmetry breaking in graphene either numerically or analytically.

In this paper, we propose a mechanism that restores the “chiral symmetry” even under the strong Coulomb interaction. Such a phase transition is induced by the external Kekulé distortion, which is described by the alternating bond strength like the benzene molecule. The Kekulé distortion yields the asymmetry between two Dirac points and gives a finite gap in the spectrum, but does not break the chiral (sublattice) symmetry explicitly. It can be introduced externally by the effect of the substrate or the addition of atoms on the layer. The interplay between the breaking of the chiral symmetry and the Kekulé distortion at long wavelength, i.e. in the mean field, has not yet been understood in previous works.

In order to incorporate the effect of the Kekulé distortion, the effective gauge theory model with the original honeycomb lattice structure would be helpful. First we construct a U(1) lattice gauge theory model for graphene, with both the spatial and temporal directions regularized on the hexagonal-prismatic lattice. Then, we apply to this model the strong coupling expansion techniques of the lattice gauge theory, which has been employed widely in analyzing the properties of strong coupling gauge theories such as QCD. We propose the chiral symmetry restoration transition by adding the Kekulé distortion term to the model action. The interplay between the orders results in the modification of the gap size, depending on the distortion amplitude.

Noninteracting electrons on the monolayer graphene with the perfect honeycomb lattice symmetry are described by the conventional tight-binding Hamiltonian

$$H = \hbar \sum_{\mathbf{r} \in A} \sum_{i=1,2,3} \left[ a_i^\dagger(\mathbf{r}) b_i(\mathbf{r} + \mathbf{s}_i) + b_i^\dagger(\mathbf{r} + \mathbf{s}_i) a_i(\mathbf{r}) \right], \quad (1)$$

with the nearest-neighbor hopping amplitude $\hbar$. The operators $a_i^\dagger(a)$ and $b_i^\dagger(b)$ create (annihilate) a fermion on the triangular sublattices A and B, respectively. $s_i (i = 1, 2, 3)$ is the orientation vector pointing from an A-site to a neighboring B-site, with the lattice spacing $|s_i| \approx a_0 = 1.42\, \text{Å}$. This Hamiltonian yields the energy eigenvalue $E(\mathbf{k}) = \pm \hbar |\Phi(\mathbf{k})|$, where $\Phi(\mathbf{k}) \equiv \sum_{r=1,2,3} e^{i \mathbf{k} \cdot \mathbf{s}_r}$. $E(\mathbf{k})$ vanishes at two Dirac points $\mathbf{K}_\pm$ in the Brillouin zone $\Omega$ (see Fig.1). By neglecting quadratic and higher order terms in momentum, $\Phi$ can be written around the Dirac points as $\Phi(\mathbf{K}_\pm + \mathbf{k}) = (3/2) a_{\mathbf{K}_\pm} (\pm k_x + ik_y) + O(k^2)$, which we call here the “linear approximation”. Thus, the dispersion relation can be linearized around the Dirac points, with the Fermi velocity $v_F = (3/2) a_{\mathbf{K}_\pm} \hbar$ about 300 times smaller than the speed of light. An effective field theory description has been established in continuum, with a 4-component Dirac fermion $\psi = [a(\mathbf{K}_+ + \mathbf{k}), a(\mathbf{K}_- + \mathbf{k}), b(\mathbf{K}_+ + \mathbf{k}), b(\mathbf{K}_- + \mathbf{k})]^T$.

From the tight-binding Hamiltonian in Eq. (1), we can construct a Euclidean action for fermions with the original honeycomb lattice structure. As done in Ref.9, we perform a temporal scale transformation $\tau \rightarrow \tau' / v_F$, so that the effective Fermi velocity in the action can be rendered to be unity. Here we discretize the temporal direction with the lattice spacing $a\tau$, which is set to be comparable to the spatial lattice spacing $a_\mathbf{K}_\pm$. (In this
paper, we set $a_{\tau}$ equal to $a_{\text{vac}}$ for convenience of calculation.) A pair of fermion doublers are inevitably generated in the temporal direction, which we reinterpret as the spin (up/down) degrees of freedom.

In order to incorporate the interaction between the fermions and the electromagnetic field, we require the local U(1) gauge invariance, with the compact link variables $U_\tau(r, \tau') = \exp \left[ ie \int_{r'}^{r''} d\tau' A_\tau \right]$ and $U_i(r, \tau') = \exp \left[ ie \int_{r'}^{r''} d\tau \cdot A \right]$ ($e$ is the electric charge); thus we obtain a “gauged” honeycomb lattice model

$$S_F = \frac{1}{2} \sum_{r \in A, \tau'} [a^\dagger(x) U_\tau(x) a(x + a_\tau) - \text{H.c.}]$$

$$+ \frac{1}{2} \sum_{r \in B, \tau'} [b^\dagger(x) U_\tau(x) b(x + a_\tau) - \text{H.c.}]$$

$$+ \frac{2}{\nu_F} \sum_{r \in A, \tau'} \sum_{i=1}^{3} [a^\dagger(x) U_i(x) b(x + s_i) + \text{H.c.}],$$

where $x$ denotes the (2+1)-dimensional position $(r, \tau')$. Here we take $a^\dagger$ and $b^\dagger$ ($a$ and $b$) as the Grassmann fields corresponding to the creation (annihilation) operators of the fermionic quasiparticles around half-filling. Kinetic term of the gauge field, $S_G$, can also be discretized on the honeycomb lattice with the U(1) link variables. $S_G$ becomes proportional to the inverse of the effective Coulomb coupling strength, $\beta \equiv e v_F / e^2 = 4 \pi e / a_{\text{QED}}$, where $e$ is the dielectric constant of the surrounding material and $a_{\text{QED}} \approx 1/137$ is the fine-structure constant of QED.

This lattice model reproduces the “reduced QED”-like model in the continuum limit. The fermions (quasiparticles) propagate much slower than the electromagnetic field (photons) (i.e. $v_F \ll c$), so that the retardation (magnetic) effect of the electric field can safely be neglected. Therefore, the spatial link variables $U_i$ can be set to unity here, which we call the “instantaneous approximation”.

Now we can perform the strong coupling expansion by $\beta$, which is 0.037 in the vacuum-suspended graphene. (Here we take $v_F \sim c/300$ at any value of $\beta$.) In this work, we only consider the leading order $[O(\beta^0)]$ in the strong coupling expansion, which corresponds to the strong coupling limit ($\beta \to 0$) of the Coulomb interaction. The gauge term $S_G$ does not contribute in this limit, so that the partition function of this system can be written only in terms of the fermionic term $S_F$ as

$$Z = \int [da^\dagger da][db^\dagger db][dU_{\tau'}] e^{-S_F[a^\dagger, a, b^\dagger, b, U_{\tau'}]}. \quad (3)$$

First we observe the behavior of the global symmetry of the system when there is no lattice distortion. By the integration over the link variables $U_{\tau'}$, temporal kinetic terms [first two lines in Eq.(2)] are converted into 4-Fermi terms $-(1/4)n_a(x)n_a(x + a_\tau)$ and $-(1/4)n_b(x)n_b(x + a_\tau)$, which are spatially local and temporally non-local by one lattice spacing. Here the bosonic operator $n_\chi(x) \equiv \chi^\dagger(x) \chi(x)$ ($\chi = a, b$) corresponds to the local charge density. These terms can be considered as the on-site (Hubbard) interaction, in which fermions on the same position with opposite spins interact with each other. Such an interaction may lead to the spontaneous breaking of the sublattice symmetry at the tree level, as long as the spin symmetry is not broken.

Here we introduce an auxiliary field $\sigma \equiv \langle n_a - n_b \rangle$ by the Stratonovich–Hubbard transformation, which corresponds to the charge density imbalance between two sublattices. It corresponds to the “chiral condensate” $\langle \bar{\psi} \psi \rangle$, the order parameter of chiral (sublattice) symmetry breaking, in the continuum effective theory. By the mean-field approximation over $\sigma$, the effective action at zero temperature is given in the quadratic form

$$S_F^{(0)} = \sum_{r \in A; \tau'} \sum_{k \in \Omega; \tau'} \frac{\sigma^2}{4} + \sum_{k \in \Omega; \tau'} \Psi^\dagger \psi \left( \frac{\sigma}{2} \frac{\alpha \Phi(k)}{\alpha \Phi(k)} - \sigma/2 \right) \Psi \psi,$$

where $\Psi \equiv (a, b)^T$ and $\alpha \equiv a_{\tau} h / v_F$. Thus the integration over the fermions can be successfully performed, yielding the free energy per one pair of A- and B-sites in the strong coupling limit,

$$F_{\text{eff}}^{(0)}(\sigma) = \frac{1}{2} \sigma^2 - \int_{k \in \Omega} d^2 k \ln \left[ \left( \frac{\sigma}{2} \right)^2 + |\alpha \Phi(k)|^2 \right]. \quad (5)$$

$F_{\text{eff}}^{(0)}(\sigma)$ is dominated by the second term (singularity from fermion one-loop) around $\sigma = 0$, while it is dominated by the first term (tree level of the auxiliary field) at large $|\sigma|$. Therefore, the effective potential $F_{\text{eff}}^{(0)}(\sigma)$ has a minimum at finite $|\sigma| = 0.343$, which gives the charge density imbalance between two sublattices. Finite $\sigma$ breaks the sublattice symmetry of the honeycomb lattice, leading to a gap opening in the fermionic spectrum. The term $(\sigma/2)(a^\dagger a - b^\dagger b)$ in Eq.(3), which corresponds to the effective mass term $m_{\text{eff}} \bar{\psi} \psi$ in the 4-component Dirac fermion description, modifies the dispersion relation into $E(k) = \pm \sqrt{|\Phi(k)|^2 + (v_F \sigma/2a_{\tau})^2}$. 

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**FIG. 1:** A schematic picture of the Brillouin zone corresponding to the honeycomb lattice. The Brillouin zone $\Omega$ (gray rhombic region) is spanned by the reciprocal lattice vectors $\mathbf{K}_1$ and $\mathbf{K}_2$. If the Kekulé distortion pattern [Eq.(2)] is introduced, $\Omega$ is split into three hexagonal cells: $\Omega$ and $\Omega_{\pm}$, surrounding $\mathbf{k} = 0$ and $\mathbf{K}_{\pm}$ (Dirac points) respectively.
In Fig. 2 we compare the result from the honeycomb lattice formulation with that from the square lattice formulation given in Ref 3. Here, $F_{\text{eff}}$ from the square lattice formulation is given by the free energy per four square lattice sites, which corresponds to a pair of A- and B-sites on the honeycomb lattice. We also show $F_{\text{eff}}^{(0)}(\sigma)$ in Eq. (5) with the linear approximation $\Phi(K_\pm + k) \simeq (3/2)a_{\pm}(\pm k_x + i k_y)$. “Square” shows the effective potential obtained by the strong coupling expansion with the square lattice formulation, corresponding to a pair of honeycomb lattice sites.

Let us now examine the effect of an external Kekulé distortion on the sublattice symmetry; it is represented by the additional Hamiltonian

$$H_K = \sum_{r \in A} \sum_{i=1}^{3} \delta h_i(r) a^\dagger(r) b(r + s_i) + \text{H.c.}, \quad (6)$$

$$\delta h_i(r) = \frac{\Delta}{3} \left[ e^{i(K_+ \cdot s_i + G \cdot r)} + e^{i(K_- \cdot s_i - G \cdot r)} \right], \quad (7)$$

where $G \equiv K_+ - K_-$, and $\Delta$ denotes the amplitude of the external Kekulé distortion. In this paper, we consider the case in which the distortion amplitude $\Delta$ is real and uniform. Since the distortion pattern is periodic by three times the unit cell of the honeycomb lattice, the Brillouin zone $\Omega$ is split into three hexagonal regions, $\Omega$ and $\Omega_\pm$, surrounding $k = 0$ and $k = K_\pm$ respectively (see Fig. 1). For free fermions, the Kekulé distortion opens a finite gap in the dispersion relation of quasiparticles, $E_{\text{free}}(K_\pm + k; \Delta) = \sqrt{[v_e \sigma/2a_r]^2 + \Delta^2}$, while it preserves the sublattice symmetry of the honeycomb lattice. The magnitude of the gap is proportional to the distortion amplitude $\Delta$. In the Dirac fermion description, Kekulé distortion can be written as an external field $\Delta \tilde{\psi} \gamma_3 \psi$, which is invariant under the U(1) chiral transformation generated by the chirality (sublattice inversion) $\gamma_5$.

By adding the Kekulé term to the lattice effective action in Eq. (4), it is modified as

$$S_F = \sum_{r \in A,B} \sum_{s,a} \Psi^a(r,\tau)
\left(\frac{\sigma}{2}\gamma^0 I_2 + \alpha \tilde{\Phi}^a(r,\tau) \right) \tilde{\Psi}^a(r,\tau'), \quad (8)$$

where $\Psi(r) \equiv [a(k), a(K_+ + k), a(K_- + k), b(k), b(K_+ + k), b(K_- + k)]^T$, and $I_3$ is a $3 \times 3$ unit matrix. $\tilde{\Phi}$ is defined by a $3 \times 3$ matrix,

$$\tilde{\Phi}(k) \equiv \begin{pmatrix} \Phi(k) & \Delta \Phi(K_- + k) & \Delta \Phi(K_+ + k) \\ \Delta \Phi(K_- + k) & \Phi(K_+ + k) & \Delta \Phi(k) \\ \Delta \Phi(K_+ + k) & \Delta \Phi(k) & \Phi(K_- + k) \end{pmatrix}, \quad (9)$$

with the dimensionless distortion amplitude $\Delta \equiv \Delta/3h$. By integrating out the fermionic degrees of freedom, we obtain the effective potential $F_{\text{eff}}^{(0)}(\sigma)$ as a function of $\sigma$, with the external parameter $\Delta$. When there is no Kekulé distortion, it reproduces the effective potential in Eq. (5). The minimum of the effective potential $F_{\text{eff}}^{(0)}(\sigma; \Delta)$ yields the expectation value of $\sigma$ as a function of $\Delta$, as shown in Fig. 3. By diagonalizing the matrix in Eq. (8) at $k = 0$, we obtain the magnitude of the spectral gap as

$$E(K_\pm; \Delta) = \sqrt{[v_e \sigma(\Delta)/2a_r]^2 + \Delta^2}, \quad (10)$$

which is modified from the gap of the free electrons by the distortion-dependent exciton condensate $\sigma(\Delta)$.

As seen from Fig. 3, $\sigma$ grows around $|\Delta| = 0$ and decreases at large $|\Delta|$, with the critical value $|\Delta_c/3h| =$...
0.485. The reduction of $\sigma(\Delta)$ can be qualitatively understood in terms of the effective field theory with a 4-component Dirac fermion: the amplitude of the fermion propagator $(k - v + \Delta)^{-1}$ gets suppressed as $|\Delta| \to \infty$, leading to a reduction of the dominance of the fermion one-loop effect in the effective potential. The sublattice symmetry is fully restored, i.e. $\sigma$ vanishes, at the critical value $\Delta_c$, where $\sigma(\Delta)$ exhibits the mean-field critical exponent $z = 1/2$ with the definition $\sigma \propto |\Delta - \Delta_c|^z$. As a result, we find that the external Kekulé distortion can restore the sublattice symmetry of the honeycomb lattice, although the gap in the spectrum remains finite, as shown in Fig.3. On the other hand, $\sigma(\Delta)$ increases quadratically as $\sigma(\Delta) = 0.343 + 7.02|\Delta|^2 + O(\Delta^4)$ for small $|\Delta|$. It comes from the quadratic and higher order terms in momentum which are neglected in the continuum effective theory; if the linear approximation is applied to $F_{\text{eff}}^{(0)}(\sigma; \Delta)$, the resulting $\sigma(\Delta)$ decreases monotonically around $\Delta = 0$.

In this paper, we have investigated the interplay between two symmetry breaking patterns of the honeycomb lattice, in the strong coupling limit of the Coulomb interaction. Due to the on-site part of the Coulomb interaction, the sublattice symmetry is spontaneously broken if the system has the perfect honeycomb lattice symmetry. As we introduce the Kekulé distortion as an external field, the system reveals a second-order phase transition – restoration of the sublattice (chiral) symmetry. As a result, the gap amplitude of monolayer graphene in the strong coupling limit is modified from that of free fermions if the external Kekulé distortion is under the critical value, while it is not modified at large Kekulé distortion. If the “chiral symmetry broken” phase is achieved experimentally in the vacuum-suspended graphene, the modification of the gap amplitude will have an effect on gap engineering, which has recently become important for industrial applications as electronic devices.

While the Kekulé distortion is introduced as an external parameter in the present paper, it is proposed to occur spontaneously if the interaction between the nearest-neighboring (NN) or the second-NN sites is taken into account. We are currently studying such an effect in the next-to-leading order $[O(\beta^3)]$ in the strong coupling expansion, which includes the NN interaction $\sum_{j=1}^3 [a^j(x)b(x + s_j)b^j(x + s_j + a_{j'})a(x + a_{j'}) + \text{H.c.}]$. With a sufficiently strong NN interaction, our preliminary study shows a phase transition between the sublattice symmetry-broken phase and the spontaneous Kekulé distortion phase. Such a phase transition is expected to be of first order, since either the chiral condensate or the Kekulé distortion remains finite due to the logarithmic behavior in the effective potential. The effect of the phonon-mediated interaction is also of great importance; if such an interaction is taken into account, the superconducting order may also have to be considered.

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