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Variational approach to the excitonic phase transition in graphene

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We analyze the Coulomb interacting problem in undoped graphene layers by using an excitonic variational ansatz. By minimizing the energy, we derive a gap equation which reproduces and extends known results. We show that a full treatment of the exchange term, which includes the renormalization of the Fermi velocity, tends to suppress the phase transition by increasing the critical coupling at which the excitonic instability takes place.

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I. INTRODUCTION

The role of Coulomb interactions in the low-energy regime of undoped graphene layers has arisen great interest and still remains somewhat controversial. This is rooted to the poor screening properties of graphene, a peculiarity that can be traced back to the linear density of states of the low-energy theory, which vanishes at the Dirac point. An early weak-coupling analysis of the problem, based on the renormalization-group (RG) method, showed that the Coulomb interaction is marginally irrelevant, flowing to a noninteracting fixed point.[1] This picture can be rigorously justified at all couplings in the limit of a large number of electron flavors.[2] In that scenario, undoped graphene layers would behave mostly as a noninteracting system of electrons with minor traces of interactions reflected in the lifetime of quasiparticles[3] and in a logarithmic renormalization of the Fermi velocity.[1] Remarkably, this picture seems to match reasonably well with current experimental data.[4–6]

The relative strength of the Coulomb interaction measured, as compared with the kinetic energy of the electrons, is ruled by the dimensionless coupling constant $g_0 \equiv e^2/\epsilon v_F$, where e is the electron charge, v_F the Fermi velocity, and ϵ the dielectric constant of the medium in which graphene is embedded. We use the subscript 0 to denote unscreened values of the coupling, see below. For samples in vacuum, $e^2 \simeq 14.4$ eV Å, and $v_F \simeq 6.3$ eV Å, so that $g_0 \simeq 2.3$. Density-functional theory[7,8] give a value for the screened coupling in the range $g \sim 0.5-2$. This puts graphene in the intermediate coupling regime and hence the validity of the weak-coupling analysis relies on the absence of a strong-coupling fixed point in the RG transformation. Indications of such a fixed point have been found by extending the weak-coupling RG to higher orders in the coupling-constant expansion.[9] The experimental data would still be compatible with this strong-coupling scenario if current setups had graphene sufficiently isolated from the environment and could operate with perfectly neutral samples.

The possibility of phases beyond the reach of perturbative or weak-coupling renormalization-group methods in undoped graphene has been explored in the literature by using different approaches. The main candidate for a strong-coupling phase is an excitonic condensate, in which electron and holes bind together opening up a gap in the density of states and rendering the system insulating. The mechanism responsible for this phase would be the gain in exchange energy arising from the long-range Coulomb interaction. A gap equation for this transition has been derived within the Dyson-Schwinger formalism[10] and different solutions of this equation yield (unscreened) critical couplings for the phase transition around an unscreened coupling $g_{0c} \sim 1-2$.[10–12] This scheme is equivalent to the summation of a class of diagrams and can be considered an extension of weak coupling approaches. Monte Carlo calculations in the lattice have been carried out to analyze this problem,[13,14] finding an insulating phase above $g_{0c} \simeq 1.11$ and $g_{0c} \simeq 1.66$, respectively. A phase transition beyond a certain coupling can also be found for short-range interactions in the half-filled honeycomb lattice,[15] although the critical coupling takes the model beyond the regime where the approximation of the electronic bands by the Dirac equation is valid. Finally, the study of the two-body problem in graphene, with Coulomb interactions, leads to a remarkable instability of the wave function for a critical coupling $g_{0c}=1$,[16] that might underlie the eventual formation of excitons.

In this Rapid Communication, we investigate the possibility of an excitonic strong-coupling phase in undoped graphene by using a variational ansatz. The method used here can be extended in a straightforward way to finite temperatures or to finite carrier concentrations. We derive a gap equation similar to that obtained in the previous literature[10,12] but with the inclusion of a the renormalization of the Fermi velocity. By analyzing numerically and analytically the resulting gap equation, we find that the latter produces a suppression of the phase transition by increasing the critical coupling.

II. MODEL AND VARIATIONAL ANSATZ

As we have mentioned, we will address the problem of an undoped graphene sample with Coulomb interactions in the low-energy regime, where the electron motion is described by the Dirac equation. The Hamiltonian for this problem reads

$$\mathcal{H} = \sum_{\mathbf{k}s} sk n_{\mathbf{k}s} + \frac{1}{2}\sum_{\mathbf{q}} V_q n_{\mathbf{q}} n_{-\mathbf{q}}, \tag{1}$$

where $s=\pm$ refers to the upper and lower cones, respectively. In our model, the spin and valley degrees of freedom are

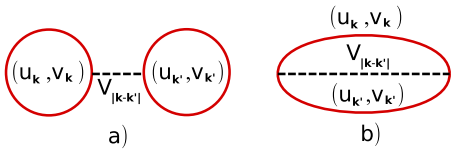

FIG. 1. (Color online) Diagrams included in the ground-state energy within the variational ansatz. (a) Hartree term, which is zero. (b) Exchange term, which is the dominant one.

considered only as extra degeneracies in the number of fermions. The Coulomb potential is given by $V_q=2\pi g/q$, where g is the dimensionless coupling constant introduced above. We assume that g includes contributions from static screening.[2,10] In the random-phase approximation (RPA), transitions between the valence and conduction bands lead to a momentum-independent dielectric constant, which can be incorporated in a straightforward into this formalism. Alternatively, one can view this approach as the leading approximation in the limit $N\to\infty$, where N is the number of fermion flavors.[17]

Our goal is to analyze the ground state of this Hamiltonian by using a variational ansatz which includes the possibility of pairing between electron and holes. Such an ansatz was proposed to study excitons formation in semiconductors[18] and is reminiscent of the ansatz used in the BCS theory of superconductivity,

$$|\Psi\rangle = \Pi_{\mathbf{k}}(u_k + v_k c^{\dagger}_{\mathbf{k}+} c_{\mathbf{k}-})|D\rangle. \tag{2}$$

The ansatz contains a coherent superposition of states with a different number of electron-hole pairs. Here $|D\rangle$ stands for the filled Dirac sea and u_k and v_k are variational parameters to be determined by minimizing the ground-state energy. Without loss of generality, they are taken real. Notice that they are not independent since the normalization of the wave function imposes the constraint $u_k^2+v_k^2=1$.

III. DERIVATION OF THE GAP EQUATION

Following the lines of a typical variational calculation, the energy of the ansatz is evaluated by projecting the Hamiltonian into this state. It has two contributions, the Hartree and the exchange one, as shown in Fig. 1. The Hartree contribution is zero, by virtue of the normal ordering of the Hamiltonian with respect to the Dirac sea, which is physically related to the neutrality of charge of the global system. The dominant contribution comes from the exchange energy, which includes terms with a momentum transfer of $\mathbf{q}=\mathbf{k}'-\mathbf{k}$. The projected Hamiltonian reads then

$$\langle\Psi|:\mathcal{H}:|\Psi\rangle = \sum_{\mathbf{k}} k(v_k^2-u_k^2) - \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}\Bigg[2u_k u_{k'} v_k v_{k'} + \cos^2\left(\frac{\theta_{\mathbf{k}'}-\theta_{\mathbf{k}}}{2}\right)(u_k^2 u_{k'}^2 + v_k^2 v_{k'}^2) + \sin^2\left(\frac{\theta_{\mathbf{k}'}-\theta_{\mathbf{k}}}{2}\right)(u_k^2 v_{k'}^2 + v_k^2 u_{k'}^2)\Bigg], \tag{3}$$

where we have used the normal-ordered Hamiltonian in order to carry out the calculation. The extreme condition must be imposed respecting the normalization constraint. The result gives the following equation:

$$\left[k + \sum_{\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}\cos(\theta_{\mathbf{k}'}-\theta_{\mathbf{k}})(u_{k'}^2 - v_{k'}^2)\right]u_k v_k = (u_k^2 - v_k^2)\sum_{\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}u_{k'}v_{k'}. \tag{4}$$

This equation can be simplified by introducing the following parameters:

$$\xi_k = k + \sum_{\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}\cos(\theta_{\mathbf{k}'}-\theta_{\mathbf{k}})(u_{k'}^2 - v_{k'}^2), \tag{5}$$

$$\Delta_k = 2\sum_{\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}u_{k'}v_{k'}, \tag{6}$$

$$E_k^2 = \xi_k^2 + \Delta_k^2. \tag{7}$$

The first equation is the self-energy insertion to the electron propagator, which adds to the linear term coming from the noninteracting dispersion relation and represents a renormalization of the Fermi velocity. The second equation introduces Δ_k, which can be identified with the gap that arises in the electronic spectrum when excitons are formed. This is clearly expressed in the third equation, which gives the dispersion relation of Bogoliubov quasiparticles in the excitonic condensate.

In terms of these new parameters, the solution to the variational problem reads: $u_k v_k = \frac{\Delta_k}{2E_k}$, $v_k^2 = \frac{1-\xi_k/E_k}{2}$, $u_k^2 = \frac{1+\xi_k/E_k}{2}$. By plugging these expressions into the equation for the gap, Eq. (6), we get a self-consistent integral equation, namely,

$$\Delta_k = \sum_{\mathbf{k}'} V_{|\mathbf{k}'-\mathbf{k}|}\frac{\Delta_{k'}}{E_{k'}}. \tag{8}$$

As we have already mentioned, a similar gap equation has been already found by using the Schwinger-Dyson formalism.[10]

Further insight can be obtained by carrying out the angular integral while keeping the lowest order terms in a Legendre-polynomial expansion of the Coulomb interaction $V_{|\mathbf{k}'-\mathbf{k}|}$. This yields a simplified integral equation in the continuum limit of the problem,

$$\Delta_k = g\int_0^{\Lambda} dk' k' \Delta_{k'} \frac{\mathcal{K}(k,k')}{\sqrt{\xi_{k'}^2 + \Delta_{k'}^2}}, \tag{9}$$

where we have introduced the following kernel:

$$\mathcal{K}(k,k') = \frac{1}{k}\theta(k-k') + \frac{1}{k'}\theta(k'-k). \tag{10}$$

The main feature of this gap equation, as compared with previous approaches, is the inclusion of the exchange correction to the free-electron dispersion relation, Eq. (5).

IV. ANALYSIS OF THE GAP EQUATION

In order to extract information from the gap equation, we make the following assumption:[10,19] the dominant contribution to the gap equation corresponds to the region $k \gg \Delta^*$, where $\Delta^* = \Delta_{k=\Delta^*}$. We neglect the contribution to the condensation energy of the modes with $k \ll \Delta^*$, as also done when analyzing one-dimensional instabilities or in the BCS theory of superconductivity. This allows us to make $E_q \simeq \xi_q$ and write Δ^* as the lower limit of the integral,

$$\Delta_k \simeq g \int_{\Delta^*}^{\Lambda} dk' k' \Delta_{k'} \frac{\mathcal{K}(k,k')}{\xi_{k'}}. \tag{11}$$

By using the same type of reasoning, an expression for the ξ_k can be derived, which only retains the leading, most divergent terms (and valid for $\xi_k > \Delta^*$),

$$\xi_k = k + \frac{g}{4} k \log\left(\frac{\Lambda}{k}\right). \tag{12}$$

This is the renormalization of the Fermi velocity that arises from a RG analysis,[1] which has been so far neglected in the literature on the excitonic condensation. We will see shortly that this logarithmic correction plays a crucial role in the analysis of the gap equation.

We take derivatives in Eq. (11). Using Eq. (10), we obtain

$$k^2 \Delta_k'' + 2k\Delta_k' + g(k)\Delta_k = 0, \tag{13}$$

which has the form of a three-dimensional radial-Schrödinger equation with a potential $g(k)$. The latter is the running coupling constant in the RG sense, which has appeared in a natural way from the exchange correction to the linear dispersion relation. It reads

$$g(k) = \frac{g}{1 + \frac{g}{4}\log\left(\frac{\Lambda}{k}\right)}. \tag{14}$$

The differential Eq. (13) must be supplemented with boundary conditions that are also derived from Eq. (11),

$$k^2 \Delta_k'|_{k=\Delta^*} = 0, \tag{15}$$

$$(k\Delta_k' + \Delta_k)|_{k=\Lambda} = 0. \tag{16}$$

The first one is the infrared condition, since it is evaluated at the gap $\Delta^* \ll \Lambda$, while the second one is the ultraviolet one, evaluated at the cutoff. Equations (13), (15), and (16) determine the function Δ_k up to a numerical constant, which is fixed by the condition $\Delta^* = \Delta_{k=\Delta^*}$.

V. ADIABATIC SOLUTION

A preliminary study of Eqs. (13)–(16) can be made by assuming that $g(k)$ varies slowly enough for an adiabatic approximation to be reasonable. Noting that the case of a constant potential $g(k)=g$ admits an exact solution of the form

$$\Delta_k = Ak^{-1/2(1+\sqrt{1-4g})} + Bk^{-1/2(1-\sqrt{1-4g})},$$

the adiabatic solution can be found to be, following Ref. 11,

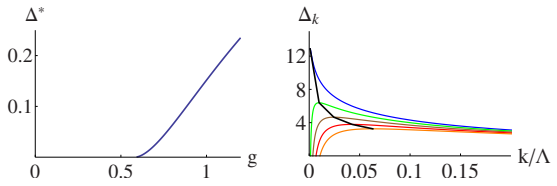

FIG. 2. (Color online) Left: dependence of Δ^* on g obtained by numerically integrating Eq. (13) with the boundary conditions in Eqs. (15) and (16). Right: dependence of Δ_k on k for $g=0.6$, 0.65, 0.7, 0.75, and 0.8 (from top to bottom). The thick black line shows the position of the maxima of Δ_k, which give the value of Δ^*, see Eq. (15). The solutions are not normalized.

$$\Delta_k^{\mathrm{ad}} = \frac{C_+ e^{i\varphi(k)} + C_- e^{-i\varphi(k)}}{\sqrt{k}\left[g(k) - \frac{1}{4}\right]^{1/4}}, \tag{17}$$

where $\varphi(k) \equiv \int_{\Delta^*}^{k} \frac{dk'}{k'} \sqrt{g(k') - \frac{1}{4}}$. Implementation of boundary conditions (15) and (16) yields the quantization rule $\varphi(\Lambda) + \delta_\Lambda + \delta_{\Delta^*} = \pi n$, where n is a positive integer and $\delta_k \equiv \arctan\sqrt{4g(k)-1}$. The goal is to solve for Δ^*, a nonzero value meaning that there is an excitonic instability. The condition $g(k) > 1/4$ for all values of k, leads to the requirement $\Delta^* > \Delta_{\min} = \Lambda e^{-8(1-1/4g)}$. We find that a nonzero, real solution of the quantization condition described above (with $n=1$) satisfying $\Delta^* > \Delta_{\min}$, exists for g greater than a critical value $g_c \simeq 0.5$, which marks the onset of the excitonic instability.

VI. NUMERICAL SOLUTION

We further check the previous analysis by numerically solving Eq. (13) with the boundary conditions (15) and (16). The results are shown in Fig. 2. We find solutions for $g \geq g_c \simeq 0.59$, in reasonable agreement with the adiabatic approximation. The asymptotic limit $\Delta_k \sim 1/\sqrt{k}$ [see Eq. (17)] is only clearly visible for $g \sim g_c$ and $k \ll \Lambda$. A detailed analysis of the region where $(g - g_c) \to 0^+$ suggests that $\Delta^* \propto (g - g_c)$, see Fig. 3. For comparison, we also show the numerical results obtained by neglecting the renormalization of the Fermi velocity. They reproduce correctly the main features found in analytical studies, namely, $g_c = 1/4$ and $\Delta^* \sim e^{-A/\sqrt{g-g_c}}$, where A is a constant.[10–12]

VII. CONCLUSIONS

We have analyzed the problem of Coulomb interactions in undoped graphene by using a variational ansatz that includes

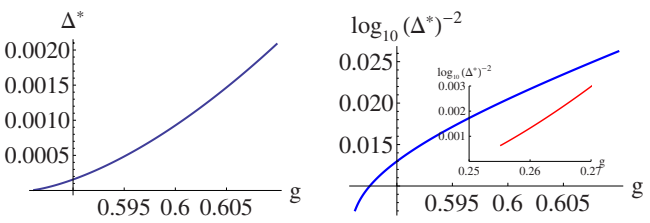

FIG. 3. (Color online) Details of the dependence of Δ^* on g near the transition. The inset on the right graph shows the results from numerically solving Eq. (13) without velocity renormalization [i.e., assuming $g(k)=g$ in Eq. (14)].

the possibility of exciton formation. Our approach can be readily extended to other two- and three-dimensional materials, as well as to finite temperatures and carrier concentrations.[20] It allows us to calculate the total free energy, which can be compared to that of other broken-symmetry phases, or to level crossings, which indicate first-order phase transitions. A first-order transition to a gapless state is likely to take place when the carrier concentration is changed, as in other low correlated materials with a low carrier concentration.[21]

Our variational analysis reproduces the main features of the excitonic transition in graphene.[10] In addition, we find that a renormalization of the Fermi velocity is a natural by-product of the variational treatment. The resulting change in one-particle energies leads to a cancellation of the leading divergences with trigger the excitonic transition. A similar effect is observed in the analysis of the excitonic transition due to short-range interactions in graphene bilayers.[22,23] Our variational analysis leads to a critical coupling $g_c \simeq 0.59$, which is about a factor two larger than the critical coupling obtained neglecting the Fermi velocity renormalization, $g_c = 1/4$.[10–12,19] The renormalization of g to two loops gives a transition at $g_c \simeq 0.83$.[9]

The unscreened coupling constant in graphene is $g_0 = e^2/v_F \approx 2.3$. Screening from a substrate reduces this value to $2g_0/(1+\epsilon_S) > g_0/\epsilon_S$. Common substrates such as SiO_2, SiC, and BNi have $\epsilon_{SiO_2} \approx 3.9$, $\epsilon_{SiC} \approx 9.7$ and $\epsilon_{BNi} \approx 4.5$. Screening makes the gapped phase less likely. In suspended graphene, we can assume that the effective value of g is modified solely by internal screening.[2,10] Using the RPA, we obtain $g = g_0/(1+N\pi g_0/8)$, where $N=4$ is the number of electron flavors and $g_0 = e^2/v_F$ is the bare coupling constant. Then, an upper bound of g is $g_{max} = \lim_{e^2/v_F \to \infty} g(e^2/v_F) = 2/\pi \simeq 0.64$, which lies slightly above the value of g_c obtained with our variational ansatz. For the realistic value of $g_0 = 2.3$ we obtain $g = 0.50$, which is below the critical value $g_c \simeq 0.59$ which we have found by solving Eq. (13) numerically.[24] Note, finally, that our mean-field ansatz does not include quantum fluctuations that would increase the value of g_c.

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[24] Monte Carlo results suggest a critical coupling in the range of expected values in suspended samples (Ref. 13), which is smaller than the value predicted by our variational ansatz. The origin of this discrepancy is unclear. It could arise from differences in the regularization of the short-range part of the interaction or in the treatment of screening at high frequencies.