Excitons in Graphene and the Influence of the Dielectric Environment

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The exciton Wannier equation for graphene is solved for different background dielectric constants. It is shown that freestanding graphene features strong Coulomb effects with a very large exciton binding energy exceeding 3 eV. A second-order transition to a weak Coulomb regime is found if the effective background dielectric constant exceeds a critical value. All bound-state solutions vanish for epitaxial graphene on a substrate with large background permittivity, such as SiC.

Graphene is an effectively two-dimensional (2D) system with unusual electronic and optical characteristics. It is widely believed that the electronic properties result from the $sp^2$ hybridization between one $s$ and two $p$ orbitals of the constituting carbon atoms, leading to the typical planar honeycomb lattice. The remaining $p$ orbital forms a half-filled $π$ band responsible for the electronic and optical properties [1–3]. Using the tight binding (TB) approximation with nearest neighbor hopping only, it was first shown by Wallace [1] that the hexagonal symmetry of the honeycomb lattice leads to the formation of symmetric electron and hole bands that touch each other at two nodes. In the vicinity of these so-called Dirac points, the dispersion is linear and the density of states vanishes. According to this picture, which is supported by many experiments [4–9], graphene behaves as a semimetal whose massless Dirac electrons have a Fermi velocity $v_F \approx 10^6 m/s$.

Whereas the existence of quasi-relativistic electrons is generally accepted, much less agreement exists concerning the role and the consequences of Coulomb interaction effects in graphene [10–25]. Studies based on a renormalization-group analysis predict a stable semimetallic ground state [10–13], however, nonperturbative methods yield a semimetal excitonic insulator transition at sufficiently high coupling strengths [14–18].

As a convenient measure of the relative strength of the Coulomb interaction, one can use the effective fine-structure constant $α_G = e^2 / 4πε_0ε_r v_F$, where $ε_r = ε_0$ or $(1 + ε_0)/2$ is the effective background dielectric constant for a single layer of graphene embedded in, or grown on top of a substrate, respectively. As we discuss in this Letter, the Coulomb interaction introduces a sensitivity to the dielectric environment via background screening, contradicting the widely believed paradigm that the physical properties of graphene are largely independent of the environment. For freestanding graphene in vacuum $α_G \approx 2.41$, indicating prominent Coulomb interaction effects.

It is well known from semiconductor physics that the Coulomb attraction between electrons and holes may lead to the formation of bound electron-hole pairs, i.e. excitons. While excitonic effects in metals are generally believed to be of minor importance because of strong screening, in graphene the screening of the long-ranging part of the Coulomb interaction is suppressed by the vanishing density of states at the Dirac points. Hence, it is not surprising that excitonic resonances have been observed in one-dimensional metallic carbon nanotubes [26]. Excitonic binding energies in these systems ranging from 50 to 100 meV have been calculated by solving the Bethe-Salpeter equation and within a density matrix approach [23,27]. For planar 2D graphene, first-principles calculations have become available only recently [20]. They predict a self-energy correction of the Fermi velocity that is in good agreement with experimental findings [5] and an excitonic shift of the dominant optical absorption peak as large as 600 meV. Hartree-Fock based configuration-interaction calculations for graphene quantum dots yield an excitonic redshift of approximately 300 meV [19].

In this Letter, we show that the relative importance of the Coulomb interaction effects in graphene is dominated by its dielectric environment. In particular, we predict that freestanding graphene in vacuum has Coulombic properties that are very different from those of epitaxially grown graphene on substrates like SiO$_2$ or SiC with relative $ε$ in the THz range of 4.45 and 9, respectively.

A useful and convenient criterion for the importance of Coulomb interaction effects is the existence of bound electron-hole pairs, i.e. excitons. The prediction of a finite exciton binding energy in a gapless system like graphene, is an indication for the fact that the system energy an be reduced below the tight binding (TB) ground-state level by exciton formation. In order to investigate this feature, we consider the infinitesimal transformation $U(β) = \exp(βB^λ_κ)$ generated by the exciton operator $B^λ_κ = \sum_κ ϕ^∗_λ(κ)e^κ_h^−_κ$ where $ϕ_λ(κ)$ is a normalized wave function, and $e^κ_h$ and $h^−_κ$ are electron and hole creation operators defined within the bands. Starting from the TB ground state, an infinitesimal transformation yields an energy shift

$$\delta E = β^2 \left( \sum_κ [κ_ε^λ_κ |ϕ^∗_λ(κ)|^2 - \sum_{κp} ϕ^∗_λ(κ) V^+_κp ϕ_λ(p)] - \frac{1}{2} \sum_{κp} [V^κp ϕ^∗_κ(κ)ϕ^λ_κ(p) + V^κp ϕ_λ(κ)ϕ_κ(p)] \right) \quad (1)$$

Here, $ε_κ = ε^e_κ + ε^h_κ$ are the electron and hole dispersion re-
Coulomb interaction is described by the potential electron-hole dispersion as\[ cially solving the Wannier equation (2).\]

To characterize the influence of the dielectric environment, we\[ nontrivial dependence on the background dielectric constant.\]

ics are closely related to the exciton problem and indicate a\[ 35\]. Although restricted to positiv energies, the addressedtop-\[ effective fine structure constant exceeds a critical value \[32–\]

solutions of Eq. 2 clearly limit the validity range of a weakly\[ (c.o.m.) motion problems \[31, 32\], the smallest pair energyis\[ (decreased \( \alpha_G \approx 2.41 \) for graphene in vacuum \( \epsilon = 1 \) and\]

ments within the TB approximation \[1–3\] and \( V_{k,p}^\pm \) are the\[ Coulomb matrix elements calculated with the electron and\]

hole wave functions\[28, 29\]. As shown in Fig. 1, the Coulomb potential can be approxi-\[ 10^3 \](lower scale) and\[ \alpha_G \approx 1/\epsilon.\]

We find the very large binding energy \( E_{1s} = -3.8 \text{ eV} \) for the lowest exciton state of graphene in vacuum \( \epsilon = 1 \), \( \alpha_G = 2.41 \). This energy rapidly decreases with increasing \( \epsilon \) (decreased \( \alpha_G \)), e.g. \( \epsilon = 2 \ (\alpha_G = 1.21), 3 \ (\alpha_G = 0.80), \) and \( 4 \ (\alpha_G = 0.60) \) produce \( E_{1s} = -0.47 \text{ eV}, -44 \text{ meV}, \) and\( -0.94 \text{ meV}, \) respectively. As discussed below, these numbers scale strictly as \( 1/d \) if the effective thickness of graphene is changed. Fig. 2 shows the full \( \epsilon \) (lower scale) and \( \alpha_G \) (upper scale) dependency of \( E_{1s}. \) Within the numerical accuracy, we find a critical value \( \epsilon_{ion} \approx 4.8 \ (\alpha_{ion} \approx 0.5). \) For \( \epsilon < \epsilon_{ion} \) \( (\alpha_G > \alpha_{ion}), \) we always find a negative value for \( E_{1s}, \) indicating the existence of a bound exciton state. Above (below) the threshold value our computations produce strictly positive-valued \( E_{1s}, \) indicating that only ionized electron–hole states exist. Hence, our results show that the presence of bound electron–hole pairs, i.e. strong Coulomb interaction effects, depends extremely sensitively on the dielectric environment of the graphene.

The transition from the strongly to a weakly Coulomb interacting regime can be detected even more clearly by studying the ratio between the Coulomb and the kinetic energy computed using the numerically determined wave functions \( \phi_{1s}(k). \) In Fig. 2b, we plot \( g = E_{\text{coul}}/E_{\text{kin}} \) as function of \( \alpha_G \) (lower scale) and \( \epsilon \) (upper scale). For the bound states, the Coulomb energy dominates the kinetic energy so that \( g \) is larger than one, while the kinetic energy exceeds the Coulomb energy for ionized electron–hole pairs. The shaded area in Fig. 2b indicates the region of ionized states. We see that \( g \) crosses from the region of bound states to the region of ionized states roughly at \( \epsilon_{ion} = 4.8 \ (\alpha_{ion} = 0.5), \) in full agreement with the ionization threshold observed in Fig. 2b. If we regard \( g \) as an order parameter, the exciton binding experiences a second-order phase transition at \( \alpha_{ion} \) because \( \partial g/\partial \alpha_G \) becomes dis-

\[ \frac{1}{\epsilon} V_q^2 \text{F}(qd), \]
continuous at $\alpha_G = \alpha_{ion}$.

In order to analyze the graphene Wannier equation further, we introduce the dimensionless quantities $k = \bar{k}d$, $\bar{E}_\lambda = E_\lambda d/2\hbar v_F$, $\phi(k) = \phi(k)/d$, and take the continuum limit $\sum_k \rightarrow A/(2\pi)^2 \int d^2k$. This yields the dimensionless equivalent to Eq. (3)

$$\bar{k} \phi_\lambda(k) = \frac{\alpha_G}{4\pi} \int d^2k' F(\bar{k} - \bar{k}') \phi_\lambda(k') = \bar{E}_\lambda \phi_\lambda(k)$$

(4)

which has to be solved subject to the normalization condition $\int d^2k |\phi_\lambda(k)|^2 = 1$. Equation (4) shows that the effective graphene fine-structure constant $\alpha_G = e^2/4\pi\epsilon_0\hbar v_F$ is the single parameter combination characterizing the solution. In particular, any solution is independent of the sheet thickness $d$ and hence, valid for all graphene-like systems. The effective thickness is needed only to fix the length and energy scale. Moreover, one recognizes that any solution of Eq. (4) with a finite eigenvalue $\bar{E}_\lambda$ produces a divergent physical energy eigenvalue in the strict 2D limit $d \rightarrow 0$.

Assuming $d \neq 0$, and using the dimensionless scaling parameter $u = d/d$, we treat the energy eigenvalue $\bar{E}_\lambda$ as functional of the scaling parameter:

$$\bar{E}_\lambda = \frac{1}{u} \left[ T[^1] - \alpha_G V_\lambda(u) \right],$$

(5)

with $V_\lambda(u) = \frac{1}{u} \int d^2y y^2 \int d^2y' \psi_\lambda(y'; u) \frac{E(y - y')/u}{|y - y'|} \psi_\lambda(y'; u)$ and $T[^1] = \int d^2y y^2 |\psi_\lambda(y'; u)|^2$. Stationary points of Eq. (5) correspond to either bound states or resonances of the system, depending on the sign of $\bar{E}_\lambda$.

If it exists, the lowest bound state defines the characteristic length and energy scales of the exciton, i.e. the exciton Bohr radius and binding energy, in terms of the sheet thickness $d$ and the energy unit $2\hbar v_F/d$. Since the wave function scales with the sheet thickness which is independent of $\alpha_G$, and the stationary points of Eq. (5) depend on $\alpha_G$ via the wave equation, the scaled wave function $\psi(y; u)$ has an implicit nontrivial $u$ dependence. As a consequence, $T[^1]$ and the Coulomb integral also depend on $u$. In contrast, the implicit $u$ dependence of the total energy vanishes for any solution of the wave equation. Hence, stationary points of Eq. (5) are found for $d\bar{E}_\lambda/du = -\bar{E}_\lambda/u - \alpha_G u^{-1} \partial V(u)/\partial u = 0$. Since $V(u)$ is a monotonically increasing function of $u$, this predicts stable bound states for any value of $u$ with $\bar{E}_\lambda < 0$. From these arguments, we obtain the condition $\alpha_G > \alpha_{ion} = T[^1]/V_\lambda(u)$. For every regular, normalized wave function, $T[^1] > 0$ and $V(u)$ does not diverge, and hence, graphene has a finite ionization threshold $\alpha_{ion}$. This value separates the strong Coulomb-interaction regime where bound states exist from the weakly interacting configurations without bound states.

An analytical estimate for $\alpha_{ion}$ can be obtained using a variational analysis with a trial wave function $\psi(y; u) \rightarrow f(y)$ with fixed width to calculate the ratio $g = E_{Coal}/E_{kin}$ of the Coulombic and kinetic energy contributions. Figure shows the results for $f(y) = (1 + y^2)^{-3/2}$ with the ionization threshold $\alpha_{ion} = \pi/4$ (dashed line) and $f(y) = \sqrt{\pi} e^{-y^2}$ with $\alpha_{ion} = 1$ (dotted line) as function of $\alpha_G$. We notice that the resulting ionization values of the fine-structure constant depend on the explicit form of the trial wave function. Clearly, these estimates only provide an upper bound since the true wave function may vary its shape via the $u$ dependence to minimize the energy.

The same analysis can be repeated for a model system with a parabolic electron–hole dispersion $\epsilon_k = \hbar^2 k^2/2m$ parametrized by the mass $m$. This situation corresponds to a two-band model for an effectively 2D quantum well system. Here, we obtain $E_{ion}^\infty = \hbar^2/2m_0 [T[^2] - a^2_0 V(d/a)]$ where $a_0 = 2\pi \hbar^2 \epsilon_0/m e^2$ assigns a new length scale. Whereas this cannot be done for graphene, for the parabolic model we may now set $d = 0$ to proceed to the ideal 2D case. In this situation, the kinetic energy scales like $1/a^2$ while the Coulomb energy is proportional to $1/a$. The variational condition $\partial E_{ion}^\infty/\partial a = -E_\lambda - E_{kin}/a = -2E_\lambda/a + E_{Coal}/a = 0$ yields the well known virial theorem, the Bohr radius $a = a_0$, and the binding energy $E_{ion}^\infty = -\hbar^2/2m_0 T[^2]$ for any bound state solution regardless of $\epsilon$. Hence, there is no ionization threshold in parabolic-band semiconductors.

Returning to graphene, we now derive an expression which explicitly shows the extreme sensitivity of $E_{ion}$ on $\epsilon$ (or $\alpha_G$). For this purpose, we combine the properties resulting from Eq. (5) with the numerical results. A direct differentiation of Eq. (5) produces $\partial E_{ion}/\partial \alpha_G = \partial E_\lambda/\partial \alpha_G - V(u)/u = ...$
\( -E_{\text{core}}/\alpha_{G} \) since \( \partial E_{1s}/\partial u \) vanishes for the ground state. As suggested by Fig. 2 we can use \( E_{\text{core}}/E_{1s} - 1 = c(\alpha_{G} - \alpha_{\text{ion}}) \). A straightforward integration gives

\[
E_{1s} = \frac{E_{\text{vac}}}{\epsilon} \left( \frac{\epsilon_{\text{ion}} - \epsilon}{\epsilon_{\text{ion}} - 1} \right)^{P}, \quad \epsilon \leq \epsilon_{\text{ion}},
\]

where \( E_{\text{vac}} \) is the binding energy of graphene in vacuum and \( P = 1/\epsilon_{\text{ion}} \).

Based on Fig. 2 we use \( P = 4.5 \), \( \epsilon_{\text{ion}} = 4.8262 \), and \( E_{\text{vac}}^{1s} = -0.0542 \). In particular, we see that \( E_{1s} \) scales like \( (\epsilon_{\text{ion}} - \epsilon)^{4.5}/\epsilon \rightarrow (\epsilon_{\text{ion}} - \epsilon)^{4.5} \) close to the ionization threshold which explains the rapid decrease of the binding energy before the ionization is reached. The shaded area in Fig. 2 shows the analytic estimate of \( E_{1s} \) together with the numerically obtained binding energy (solid line), nicely demonstrating that Eq. (6) captures the essential features.

In conclusion, our calculations predict an extreme sensitivity of the Coulomb effects in graphene on the dielectric properties of the environment. We find strongly bound excitons for freestanding graphene in vacuum, whereas all bound states disappear for the effective background dielectric constant \( \epsilon_{\text{ion}} = 4.8 \) which corresponds to the graphene fine-structure constant \( \alpha_{G} = 1/2 \). Our results are in general agreement with an analytical real space analysis of the 2D Dirac two-body problem \[2\], studies of the Coulomb scattering at an impurity charge Ze in graphene \[3,5\], as well as Monte Carlo calculations \[17,18\], predicting instabilities for critical values in the range of 0.5 to 1.66. Physically, this situation is realized, e.g., when graphene is deposited onto substrates or sandwiched between dielectric media such that the effective background dielectric constants exceeds 4.8. While in the regime of weak Coulomb interaction quasi-free electrons and holes are responsible for the low-energy electronic and optical properties, those are dominated by bound excitons for small background dielectric constants. On this basis, we expect a pronounced influence of the dielectric environment on the graphene ground state and on properties like the low-density conductivity, the quantum Hall effect, or the terahertz response.

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