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Strong Charge-Transfer Excitonic Effects and the Bose-Einstein Exciton Condensate in Graphane

Pierluigi Cudazzo,¹ Claudio Attaccalite,² Ilya V. Tokatly,^{1,3} and Angel Rubio^{1,4}

¹Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain

²Institute Neel, CNRS-UJF, Grenoble, France

³IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Theory Department, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

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Using first principles many-body theory methods (GW +Bethe-Salpeter equation) we demonstrate that the optical properties of graphane are dominated by localized charge-transfer excitations governed by enhanced electron correlations in a two-dimensional dielectric medium. Strong electron-hole interaction leads to the appearance of small radius bound excitons with spatially separated electron and hole, which are localized out of plane and in plane, respectively. The presence of such bound excitons opens the path towards an excitonic Bose-Einstein condensate in graphane that can be observed experimentally.

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Despite the short life of graphene [1] and its derivatives the understanding and control of their properties rapidly approach maturity [2,3]. Chemical modifications by oxidation [4], functionalization and doping [5] have enhanced foreseen applications in nanotechnology. Recent synthesis of fully hydrogenated graphene (named “graphane”) [6], which has been predicted to be a wide band-gap insulator with gap of 5.4 eV [7,8], adds to the portfolio of carbon-based structures for nanodevice applications [3,7]. The stability of the new 2D material has been analyzed and two geometries (chair and boat) have been proposed [7]. However, there are still a few open questions that need to be addressed: (i) How much H is really incorporated in the samples? (ii) Does graphane inherit the negative electron affinity of hydrogenated diamond samples used for electron emitters? (iii) What is the role of electron correlations in the band structure and screening; are electron-hole effects as important as for carbon nanotubes [9–11] or small as in diamond [12]? The present Letter addresses these issues, in particular, the last three, by means of first-principles calculations based on many-body Green function theory. Our results indicate the possibility of having an excitonic Bose-Einstein condensate by continuous pumping of excitons by light. Similar to the recent induced photoluminescence in graphene oxygenation [13], the strong spatial localization of the excitons in graphane points to a highly efficient defect-induced luminescence in chemically (or doped) modified graphene. In our ground state calculations of the most stable chair conformation of graphane [Fig. 1(b)] we used a pseudopotential plane-wave approach [14,15] within the local density approximation (LDA) to density functional theory (DFT) [16]. While excited states have been treated using the state-of-the-art many-body approach [15,17–19].

Before addressing the excitonic effects in the optical properties of graphane including the formation of a Bose-Einstein condensate, we emphasize that although the dynamical stability of the ideal graphene in the chair conformation [Fig. 1(b)] has been recently shown [20], the calculated phonon spectra agrees only partially with the measured Raman data [6]. In particular, the measured D peak agrees well with the calculated Raman active E_g phonon at 1340 cm^{-1} while the D' at 1620 cm^{-1} most likely originates from impurities as H vacancies. This means that there is a large defect density in graphane making it a hole-doped semiconductor with H vacancies acting as the center for induced luminescence (see below). However at low doping H vacancies do not affect significantly the electronic structure, so that ideal graphane allows us to obtain a realistic description of the electronic and optical properties of this system. On the other hand, the

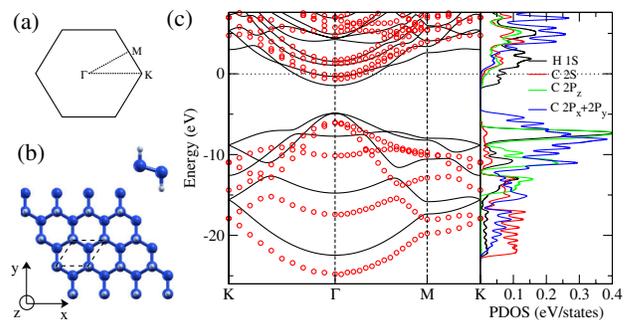


FIG. 1 (color online). First Brillouin zone (a) and unit cell and bases of graphane in the chair conformation (b). Blue and white balls represent carbon and hydrogen atoms, respectively. (c) Band structure in LDA (full line) and GW approximation (circles) and projected density of states of graphane. The zero indicates the vacuum level position.

stability of graphane as hole-doped semiconductor, suggests the possibility to achieve a metallic phase under strong hole doping by dehydrogenation. Under this condition, we have observed a strong electron-phonon renormalization of the phonon frequencies around the Brillouin zone (BZ) center (Kohn-anomaly) [15]. Similar to the case of doped diamond [21], this is a manifestation of a strong electron-phonon coupling pointing to the possibility of a high T_c superconducting phase.

Electronic properties.—The band structure of graphane [Fig. 1(c)] is mainly dictated by the sp^3 hybridization of carbon orbitals [see Fig. 1(b)]. This causes a band-gap opening (3.4 eV at the DFT-Kohn-Sham level) with respect to graphene. The classification of states is especially simple at the Γ point. The top (bottom) valence E_g (A_{1g}) corresponds to the C-C bonding σ states, while two intermediate occupied bands corresponds to C-H bonding σ states (A_{1g}). The bottom of the conduction band is the antibonding A_{2u} C-H σ state and the antibonding E_u C-C σ state appears at higher energy (4.38 eV). The other bands correspond to free-electronlike, out-of-plane states. Electron self-energy effects computed at the GW level [15,17,19] modify strongly the band structure [red dots on Fig. 1(c)]: the fundamental energy gap at Γ increases from 3.4 eV to 5.4 eV, while the gaps at the high symmetry points M and K become 14.2 eV and 15.9 eV, instead of LDA values of 10.6 eV and 11.8 eV, in agreement with recent calculations [8]. Moreover, we found that the vacuum level is at about 4.9 eV from the top of the LDA valence band [see Fig. 1(c)] so that graphane has a positive electron affinity both in LDA (1.44 eV) and GW (0.66 eV).

Optical properties of graphane.— In Fig. 2 we plot the imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$ for a light propagating along the graphane plane in the x direction. To reveal the physical origin of different

features in the optical spectrum we compare $\text{Im}\epsilon_M(\omega)$ calculated (i) without taking into account both the inter-electron and the electron-hole correlations, LDA-RPA, that is the random phase approximation (RPA) on top of the bare LDA band-structure, (ii) RPA using the GW quasiparticle spectra (GW -RPA) which neglects electron-hole correlations, and, finally, (iii) from the full solution of the Bethe-Salpeter equation (BSE) which accounts the excitonic effects [15,18,19].

The LDA-RPA absorption spectrum (green line in Fig. 2) does not show any significant feature near the LDA band gap (3.4 eV) due to the small overlap between the top-valence (localized on the C-C bond,) and bottom-conduction (localized on the C-H bond) states. Pronounced features in $\epsilon_M(\omega)$ are present at higher energies. The step feature about 8.5 eV is related to the vertical transitions from two valence bands with Kohn-Sham energies in the range of $-7.30 \text{ eV} \leq \epsilon_{nk}^{\text{KS}} \leq -6.90 \text{ eV}$ to the lowest conduction band states. The transitions from the highest valence states to the lowest conduction states at the M point are responsible for the structure around 10 eV. The highest peak at 11.7 eV arises from a Van Hove singularity near the M point, and corresponds to transitions from the valence bands to out-of-plane states with Kohn-Sham energies between 3.37 eV and 4.14 eV.

The main effect of the quasiparticle corrections is a strong global shift of the absorption spectrum to higher energies (GW -RPA curve in Fig. 2). Since the optical transition energy increases, the amplitude of $\epsilon_M(\omega)$ is reduced to satisfy the f -sum rule. However, we show that electron-hole correlations dramatically modify the shape of $\epsilon_M(\omega)$ (see BSE curve in Fig. 2). The “bulk” of the absorption spectrum nearly comes back to the original LDA-RPA position, but with a significant redistribution of the oscillator strengths from the higher to the lower energies, and an appearance of a number of pronounced excitonic resonances that are related to electron-hole pairs with electrons in the delocalized out-of-plane states [15].

In this work we concentrate on the most prominent physical effect of the electron-hole interactions in graphane, the appearance of bound excitons below the GW gap (see inset in Fig. 2). These excitations, which are completely missing in RPA, are responsible for the UV absorption of graphane. The absorption spectrum for light propagating along x shows two bound excitons (B and C) with large binding energies of 1.6 eV and 0.3 eV, respectively. The solution of the Bethe-Salpeter equation also reveals the existence of a dark exciton (A), 2 meV below the first optically active B exciton. The exciton C is related to transitions from the highest valence band with quasiparticle (QP) energy close to -6.50 eV to the first out-of-plane band with QP energy close to 0.20 eV and its wave function is delocalized out of plane [15]. In contrast, the spatial extension of the strongly bound excitons A and B is very small, $r_{\text{ex}} \approx 5.0 \text{ \AA}$, as it can be seen in Figs. 3(b) and 3(d). These excitons are formed from the states of the

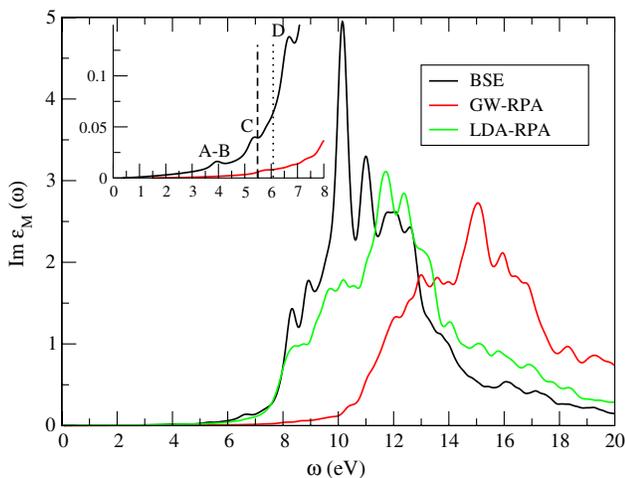


FIG. 2 (color online). Imaginary part of the macroscopic dielectric function for light polarized along the graphane plane. The dashed and dotted lines in the inset indicate the position of the GW gap and vacuum level, respectively. For light propagating along the z axes the spectrum (not shown) is flat up to 6 eV.

double degenerate (at Γ point) E_g valence band and the A_{2u} conduction band (the hole states in these excitons belong to the lowest, $E_g^{(2)}$, and the highest, $E_g^{(1)}$, bands respectively). Their wave functions reflect the C-H antibonding character of the states with the electron mainly localized on top of the H atoms. Since the hole is localized on the C-C bonds, the creation of such excitons corresponds to a charge transfer from the middle of the carbon plane to the side planes on top of the hydrogen atoms [see Figs. 3(a) and 3(c)].

It is instructive to compare absorption spectra of graphane [22] and graphane. Electron-hole interaction is important in both systems. However, in the former it leads only to a redistribution of the oscillator strength resulting in the appearance of a resonant exciton at 4.5 eV, while in the latter it gives rise to a strongly bound exciton at 3.8 eV where the spectrum of graphane is completely flat. This can be used as an additional experimental fingerprint of the presence of hydrogenated platelets embedded in graphane.

Considering the light propagating in the y direction we find that the role of the strongly bound excitons is inverted: A exciton becomes optical active, while B exciton is dark. Since the two excitons are nearly degenerate and have identical oscillator strengths for the corresponding polarization of light the absorption spectra remain almost unchanged. The reason for this is the symmetry of Bloch states involved in the formation of the excitons: the electronic states have A_{2u} symmetry, while the hole states belong to the 2D irreducible representation E_g with the eigenfunctions $\psi_{E_g}^{(1)}$ and $\psi_{E_g}^{(2)}$. A group theoretical analysis [15] shows that the only nontrivial dipole matrix elements are: $\langle \psi_{A_{2u}} | x | \psi_{E_g}^{(1)} \rangle$ and $\langle \psi_{A_{2u}} | y | \psi_{E_g}^{(2)} \rangle$, which explains why

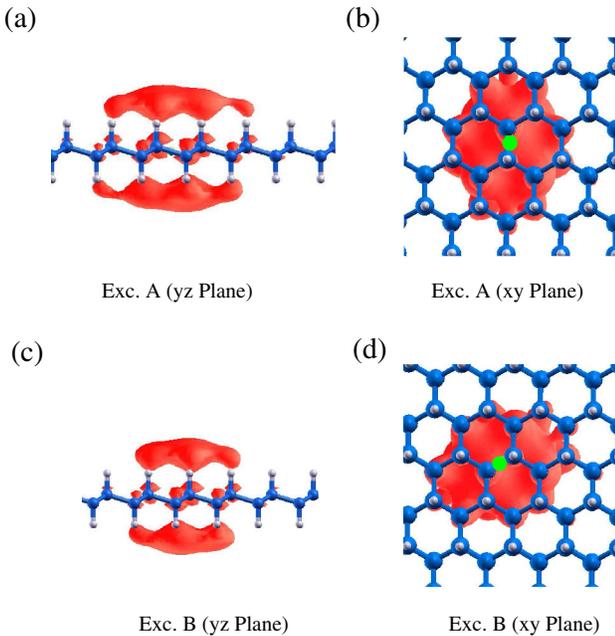


FIG. 3 (color online). 3D shape of the low energy excitons wave function for fixed position of the hole (green circle on C-C bond).

the A and B excitons are only visible for the y and x polarization, respectively. For the light propagating perpendicular to the graphene plane, both excitons are dipole forbidden.

The presence of H vacancies together with the strong spatial localization of the lowest A exciton should result in luminescence with a high yield upon UV excitations, similarly to layered h -BN where a high luminescence yield is observed from a strong localized exciton [23].

A striking feature of the excitons A and B is their large binding energy, which at least by an order of magnitude exceeds that in typical wide gap semiconductors. This becomes especially surprising if we note that both the A_{2u} conduction band and the E_g valence bands are nearly perfect parabolas over a large fraction of the BZ, and, therefore, the excitons, despite their small radius, should be reasonably well described within the effective mass approximation. Using the standard method of invariants [24] we derived the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian at Γ for the valence bands

$$\hat{H}(\mathbf{k}) = \alpha \hat{I}(k_x^2 + k_y^2) + \beta [\hat{\sigma}_z(k_x^2 - k_y^2) + 2\hat{\sigma}_x k_x k_y], \quad (1)$$

and for the conduction band $\hat{H}(\mathbf{k}) = \frac{k_x^2 + k_y^2}{2m_e}$ [15], from which we find the value of the reduced electron-hole mass $\mu_{\text{ex}} = 0.29m_0$, which is very typical for most known semiconductors (here m_0 is the bare electron mass, and for simplicity we model the two valence bands by a single parabola with an average mass). A resolution of the apparent paradox is an unusual form of the effective electron-hole interaction in graphane. In 3D dielectric media the effective interaction is obtained by the replacement $e^2/r \rightarrow e^2/\epsilon r$, where ϵ is the static dielectric constant. This simple recipe does not work in graphane that is a 2D dielectric, where the very notion of the dielectric constant makes no sense. In fact, an external electric field E induces a polarization P which is bound to the plane: $P(\mathbf{r}) = \alpha_{2D} E(\mathbf{r}) \delta(z)$, where α_{2D} is the internal polarizability of the 2D dielectric. Using the above relation in the Poisson equation for a point charge we get the following effective interaction potential (its 2D Fourier component)

$$V_{\text{eff}}(\mathbf{q}) = \frac{2\pi e^2}{|\mathbf{q}|(1 + 2\pi\alpha_{2D}|\mathbf{q}|)} \quad (2)$$

which is very different from the trivial renormalization of charge in 3D systems. The only parameter entering Eq. (2) is the polarizability α_{2D} of a single graphane layer, which we extract from our *ab initio* results. Since our calculations are performed for a periodic stack of layers with sufficiently large interlayer distance L , the 2D polarizability is related to the actually calculated 3D polarizability as follows $\alpha_{2D} = L \frac{\epsilon - 1}{4\pi}$, where ϵ is the dielectric constant of our 3D multilayer system. We can also estimate the exciton binding energy E_{ex} by the variational solution of the Schrödinger equation with the effective potential in Eq. (2) using the simplest trial wave function, $\psi \sim e^{-r/a}$,

where a is the variational parameter [25]. The result $E_b = 2.0$ eV is very close to the *ab initio* value of 1.6 eV, while the optimized value of the variational parameter $a = 7.7$ a.u. almost perfectly matches the actual excitonic radius. Hence, we clearly see that unusual strong binding of excitons in graphane is a result of a weak and specifically nonlocal 2D dielectric screening.

Because of the small radius and the large binding energy of excitons, it is tempting to consider graphane as a potential candidate for a realization of the Bose-Einstein condensation (BEC) of optically pumped excitons. Indeed, using the standard expression for the degeneracy temperature T_0 of a 2D Bose gas [26]:

$$k_B T_0 = \frac{2\pi\hbar^2 n}{M_{\text{ex}}} \quad (3)$$

(here $M_{\text{ex}} = m_c + m_v \approx 1.3m_0$ is the excitonic mass) we find that at room temperature $T_0 = 300$ K the quantum degeneracy of excitonic gas in graphane is reached for the density $n \approx 5 \times 10^{12} \text{ cm}^{-2}$, which is 2 orders of magnitude smaller than $\frac{1}{\pi a_{\text{ex}}^2} = 5.1 \times 10^{14} \text{ cm}^{-2}$ (the latter value sets an order of magnitude of the Mott critical density for the transition from the gas of excitons to a gas or liquid of unbound electrons and holes). Another argument in favor of excitonic BEC in graphane is a spatial separation of the charges in the excitonic state—the hole is localized in the middle C layer, while the electron is on top of the H layers. Therefore graphane looks quite similar to the coupled quantum wells structures, which are very popular for experiments on excitonic BEC [27,28]. In coupled quantum wells [27,28] such a separation leads to a very long excitonic life time that reaches microseconds. To estimate the radiative lifetime τ of the excitons in graphane we adopted a 2D version of the approach of Ref. [29], which leads to the following relation

$$\frac{1}{\tau} = \frac{4\pi e^2 \Omega}{\hbar c} \frac{d^2}{A}, \quad (4)$$

where Ω , d and A are the exciton frequency, dipole matrix element, and the unit cell area, respectively. The result we find, $\tau = 15$ ps, is not very encouraging—the value is too small to unconditionally speak about BEC. On the other hand, it is still larger than the lifetime of cavity polaritons where BEC has probably been observed [30]. Clearly a detailed analysis of the thermalization kinetics is needed to make more definite predictions. Defects will also play a role in pinning the exciton condensate. Nonetheless, we believe that BEC of strongly bound, small radius excitons in graphane is an interesting possibility which deserves to be carefully studied both experimentally and theoretically.

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