Compéné between exchange-driven dimerization and magnetism in diamond(111)

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(Dated: March 25, 2019)

Strong electron-electron interaction in ultraflat edge states can be responsible for correlated phases of matter, such as magnetism, charge density wave or superconductivity. Here we consider the diamond(111) surface that, after Pandey reconstruction, presents zig-zag carbon chains, generating a flat surface band. By performing full structural optimization with hybrid functionals and neglecting spin polarization, we find that a substantial dimerization (0.090 Å / 0.076 Å bond disproportionation in the PBE0/HSE06) occurs on the chains; a structural effect absent in calculations based on the LDA/GGA functionals. This dimerization is the primary mechanism for the opening of an insulating gap in the absence of spin polarization. The single-particle direct gap is 1.7 eV (1.0 eV) in the PBE0 (HSE06), comparable with the experimental optical gap of 1.47 eV, and on the larger(smaller) side of the estimated experimental single particle gap window of 1.57-1.87 eV, after inclusion of excitonic effects. However, by including spin polarization in the calculation, we find that the exchange interaction stabilizes a different ground state, undimerized, with no net magnetization and ferrimagnetic along the Pandey π-chains with magnetic moments as large as 0.2 – 0.3 μB in the PBE0. The direct single-particle band gap in the equal spin-channel is approximately 2.2 eV (1.5 eV) with the PBE0 (HSE06) functional. Our work is relevant for systems with flat bands in general and wherever the interplay between structural, electronic and magnetic degrees of freedom is crucial, as in twisted bilayer graphene, IVB atoms on IVB(111) surfaces such as Pb/Si(111) or molecular crystals.

I. INTRODUCTION

The occurrence of strongly correlated states requires the dominance of the electron-electron interaction over the electronic kinetic energy. In the case of 3d transition metal oxides or high Tc superconductors, Mott insulating, magnetic, and superconducting states are stabilized via the strong localization of electrons in 3d orbitals. Recently, it has been shown that a new class of strongly correlated systems can be achieved in ultraflat edge-states or surface bands having small Fermi velocities but not necessarily 3d states, as it happens in twisted bilayer graphene or multilayer graphene with rhombohedral stacking. All these works expand the range of materials hosting strong correlation effects and exotic states of matter and point to the need of understanding exchange and correlation effects in flat edge-states.

One of the simplest and most studied systems hosting a flat edge-state prone to strong exchange-correlation effects is the diamond(111) surface – the structure of which is still under debate more than 100 years after Bragg got the Nobel prize and applied their diffraction technique to determine the structure of bulk diamond. The formation of the surface state can be understood by considering that in bulk diamond each carbon atom undergoes sp3 hybridization and has four neighbors at distance of ≈1.54 Å and bond angle at 109.5°. The atoms on the (111) surface have, however, one missing bond and only three nearest neighbors. This dangling bond generates the so-called Pandey reconstruction resulting in a 2 × 1 superstructure forming 1D zig-zag chains (see Fig. 1) and a surface electronic band. The weak, but not negligible, hopping integral in the direction parallel to the surface but perpendicular to the chains is responsible for the ≈0.5 eV energy dispersion of the band. Even if this surface state is not as flat as the one detected in twisted bilayer graphene or in multilayer graphene with rhombohedral stacking, it is substantially more extended in reciprocal space and it holds a larger number of electrons. For this reason diamond(111) should be prone to strong exchange and correlation effects.

Despite its apparent simplicity, the theoretical and experimental description of the structural and ground state properties of the diamond(111) surface has proven to be an exceptionally difficult and yet unsolved problem. Although it is well accepted (both in theory and experiments) that the surface is a Pandey π-chain, the microscopic details, such as dimerization, buckling, deeper layer distortions are still under debate. While X-ray diffraction and ion scattering data suggest buckling of the surface atoms, low-energy electron diffraction measurements show that the buckling is negligible, but the dimerization is inconclusive within the experimental error. For the electronic structure, angle-resolved photoemission spectroscopy (ARPES) measurements find an insulating state with the occurrence of the flat surface state 0.5 eV below the Fermi level. Electron energy loss spectroscopy measurements suggest a band gap of ~1 eV, and reflectance anisotropy spectroscopy measurements give larger values of the optical band gap of ~1.47 eV.

From the theoretical point of view, the first density functional theory (DFT) calculations within the standard local density (LDA) and generalized gradient (GGA) approximations gave conflicting results for the surface chain. This disagreement is most likely explained by the fact that calculations were very heavy
The main problem of all previous theoretical works is the occurrence of magnetic solutions. We further increase the energy tolerance to 10⁻¹⁰ Ha for the total energy convergence. Fermi-Dirac smearing for the occupation of the electronic states of 0.001 Ha is used for all of the calculations. In the magnetic case, we use hybrid functionals with the LDA and GGA functionals [20, 25] and Gaussian basis sets [30] and CRYSTAL codes [33, 34]. Pioneering works by Marsili et al. [24, 25, 27] show that quasiparticle GW calculations on top of the GGA crystal structure lead to a gap opening only within the self-consistent G¹W¹ scheme and starting from an artificial band occupation. However, GW calculations were performed with very coarse grids (5 or 9 k-points in the Brillouin zone) that tend to substantially overestimate the band gap (see Appendix A), and in the absence of spin polarization. In these works, the band gap opening is attributed only to an electronic mechanism at fixed ionic coordinates. Finally, the magnitude of excitonic effects has been evaluated to be of the order of 0.1 – 0.4 eV [22], leading to an experimental single particle gap of the order of 1.57 – 1.87 eV, when added to the experimental gap of 1.47 eV.

The main problem of all previous theoretical works is that they rely on the GGA minimized structure, mostly because structural optimization within GW is not possible for solids and non-local exchange calculations in a plane-wave framework are too expensive for such a large system (24 atoms per cell and very dense electronic momentum k-point mesh). Moreover, all calculations neglected magnetism. In this work, we circumvent the difficulties of geometrical optimization with a dense mesh of electronic momentum k-points even in the existence of Hartree-Fock exchange by using a combination of plane waves [28, 29] and Gaussian basis sets [30] that allow for fast structural optimization. We use hybrid functionals with exact exchange and range separation to understand the effects of the exchange interaction on the geometry and electronic structure of diamond(111). Finally, we also explore the occurrence of magnetic solutions.

The structure of the paper is the following: after explaining technical details in sec. II, we present results for non-magnetic (sec. III A) and magnetic (sec. III B) calculations.
bond lengths of the atoms that make up the zigzag chain on the topmost layer. The dimerization is then defined as: $\Delta = |d_1 - d_2|/(d_1 + d_2)$. The buckling of the atoms, $\Delta z$, on this layer is simply the difference in their position along the z-direction (see Fig. 1).

TABLE I. Bond lengths ($d_1$ and $d_2$) of the atoms in the Pandey π-chains in the topmost layer, dimerization $\Delta$, and buckling $\Delta z$ for different exchange and correlation functionals (XC).

| XC       | $d_1$ (Å) | $d_2$ (Å) | $\Delta$ | $\Delta z$ (Å) |
|----------|-----------|-----------|----------|----------------|
| PBE      | 1.440     | 1.440     | 0.000    | 0.0048         |
| HSE06    | 1.476     | 1.490     | 0.026    | 0.0052         |
| PBE0     | 1.483     | 1.393     | 0.031    | 0.0054         |
| B3LYP    | 1.482     | 1.396     | 0.030    | 0.0048         |

Table I shows the calculated values for the topmost layer for the optimized atomic structures. With all three functionals, the buckling of the top layer is estimated to be very small, with $\Delta z \sim 0.005$ Å, which agrees well with the low-energy electron diffraction measurements of about 0.01 Å[2]. With the PBE functional, the two bond lengths are equal, $d_1 = d_2$, hence there is no dimerization. The inclusion of unscreened exchange with the PBE0 functional, or of screened exchange via the HSE06 functional, gives a significant imbalance between the two bond lengths, predicting a dimerization of the surface structure with $\Delta \sim 0.026$ in the HSE06 case. The dimerization is slightly larger with the PBE0 functional than with the HSE06 functional. In general, we find that the larger the amount of Hartree-Fock exchange included in the calculation and the more unscreened the exchange, the larger the dimerization. The energy gain induced by the dimerization is substantial, as shown in Table II.

TABLE II. The energy difference between the dimerized and undimerized structures and between magnetic and non-magnetic structures using different hybrid functionals. We use for the undimerized structure the PBE one, as the HSE06 and PBE0 functionals do not have a stable undimerized solution. We then obtain its energy in the HSE06 and PBE0 at fixed atomic positions. The magnetic structure is fully optimized and has no dimerization. The non-magnetic is also completely optimized and has dimerization.

| $\Delta$ E (eV/cell) | HSE06 | PBE0 | B3LYP |
|----------------------|-------|------|-------|
| dimerized – undimerized | -0.042 | -0.062 | -0.022 |
| magnetic – non-magnetic | -0.007 | -0.008 | -0.002 |

In a previous calculation using similar settings and the B3LYP functional, the author of Ref. [26] found no dimerization in the carbon chains. We repeated this calculation starting (i) from the undimerized PBE structure and (ii) from the dimerized HSE06 structure. In the first case, the simulation remains in the undimerized structure as in Ref. [26]. However, in the second case, the structural optimization with the B3LYP functional converges to a dimerized structure that is lower in energy than the undimerized one, on the same line of what has been obtained with the other hybrid functionals.

As hybrid functionals give only a slight underestimation of the experimental band gap in bulk diamond[35,36], the $32\%$ (0.47 eV) underestimation in HSE06 of the optical gap with respect to the experiments[35,36] is fairly surprising. The situation is much better in the PBE0 lead-
value is in better agreement with experiments; if we add the excitonic effects of $0.1 - 0.4$ eV to the experimental gap of 1.47 eV, this leads to an experimental single particle gap of 1.57 - 1.87 eV. The PBE0 value is thus on the lower side of the window (1.7 eV). However, all calculations presented up to now have been carried out neglecting spin-polarization. The occurrence of a flat band could also lead to magnetic solutions as it happens in multilayer graphene with rhombohedral stacking. For this reason, we investigate below the occurrence of magnetism using the HSE06 and PBE0 functionals.

**B. Magnetic calculations**

We first perform magnetic calculations at atomic coordinates fixed at the dimerized solution, referred to as “unrelaxed” in the remainder of the figures and tables. We choose as initial condition of the simulation a fully ferromagnetic (FM) and antiferromagnetic (AFM) configuration on the two surface atoms of the topmost layer along the zig-zag chain. As expected, the PBE functional does not stabilize a magnetic state, therefore we focus on the PBE0 and HSE06 functionals. In both cases, we find that the spin-polarized structural optimization restores the non-dimerized solution with a negligible dimerization remaining on the surface atoms, as shown in Table V. Similarly, the dimerization of the atoms on the second layer, i.e. atoms 4 and 5, also becomes negligible, while the bond lengths remain unchanged in the deeper layers. We have also checked the effect of the cell relaxation with the PBE0 functional. The in-plane lattice parameter decreases to $a = 4.289$ Å from the experimental value of $a = 4.369$ Å. However, the conclusions after the ionic relaxation remain, that the dimerization of the surface atoms is still negligible.

Our calculations show that even in the absence of dimerization, within hybrid functionals the ground state is a zero magnetization state, weakly ferrimagnetic on the two surface atoms, as shown in Table V. After the ionic relaxation, the magnetic moment of the atoms changes by $\sim 0.1\ \mu_B$, and the small imbalance on the magnetic moments of the surface atoms remains to be $\sim 0.002 - 0.003\ \mu_B$. We have further checked the effect of the cell relaxation on the magnetic moments using the PBE0 functional. While the magnetic moment of the surface atoms decreased by $\sim 0.01\ \mu_B$ with respect to the ion-relaxed calculation, the conclusion that the ferrimagnetism of the top surface atoms is stabilized remains.

The weak ferrimagnetism of the two surface atoms is visible also in the electronic structure as it splits the degeneracy of the spin bands in $\alpha$ (majority) and $\beta$ (minority) spin bands. Table V shows the band gap values at the high-symmetry points of the Brillouin zone with the magnetic calculations. The optical direct band gap between equal spin states is now $\sim 2.174(2.060)$ eV for majority(minority) spins at the J-point with the PBE0 functional. Finally, if we add the excitonic effects of $0.1 - 0.4$ eV
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that is a prototype of dimerization in one dimension. This system is very pathological for what concerns structural and magnetic instabilities and is known to be non-magnetic, but dimerized. Our calculations show that the HSE06 functional favors the polyyne (dimerized carbyne) structure rather than cumulene (non-dimerized carbyne) structure – unlike the standard LDA/PBE functionals. This is in agreement with the literature. Furthermore, we have started with an initial AFM configuration on the two atoms and found that the final state is non-magnetic. Therefore, we show that in a similar carbon-based system, magnetism is not stabilized even when we use a hybrid functional. Hence the magnetism in diamond(111) surface can be a physical effect and our calculations predict that the magnetic solution is the most stable with a slight energy difference of a few meV/cell from the non-magnetic solution as shown in Table II. Further experiments are needed to verify this hypothesis.

Our work demonstrates that, within hybrid functionals, the ground state of the diamond(111) surface is then insulating with zero net magnetization and ferrimagnetic order along the top surface atoms of the Pandey π-chains; a very surprising result given that diamond is non-magnetic and the atomic orbitals forming the surface state are of \( p \) character and thus, at the atomic level, not as localized as 3\( d \) orbitals.

IV. CONCLUSION

We have studied the diamond(111) surface by using hybrid-functionals with different degrees of screened exchange. Contrary to all previous theoretical works, we include the exchange interaction at all levels in the calculation, both in the structural optimization and in the calculation of electronic and properties. Moreover, we allowed for magnetism in calculations.

In the absence of spin polarization, the primary effect responsible for the gap opening is the dimerization of the Pandey π-chains, that is enough to lead to an insulating state. This is at odds with all previous spinless calculations that were either finding no gap, or claimed that gap opening was purely an electronic mechanism. The PBE0 band gap of 1.672 eV is on the higher side, while the HSE06 band gap of 1.006 eV is on the lower side of the experimental window for single particle gap of 1.57-1.87 eV obtained by summing excitonic effects to the experimental gap. Thus, in the absence of spin polarization the system could be classified as a Peierls-Slater insulator.

By including spin polarization, we find that the flatness of the diamond(111) edge-state stabilizes an insulating state with zero net magnetic moment and with ferrimagnetic ordering along the top surface atoms of the chain with sizable magnetic moments of the order of 0.2 − 0.3 \( \mu_B \). As the magnetic moment depends weakly on the underlying crystal structure, the electronic structure depends weakly on the amount of dimerization. Interestingly, structural optimization in the presence of magnetism converges to a ground state with a negligible dimerization on the surface atoms. We find that the PBE0 gap of ≈ 2.174(2.060) eV is on the higher side, while the HSE06 gap of 1.493(1.433) eV for majority (minority) spin electrons is on the lower side of the experimental window. Thus, within a hybrid functional approach the ground state is essentially antiferromagnetic with negligible dimerization, i.e. a Slater insulator.

As diamond(111) can be seen as formed from buckled graphene layers with rhombohedral (ABC) stacking (see Fig. 1), it is instructive to compare our magnetic state with the one recently detected in multilayer graphene with ABC stacking. In ABC graphene multilayers the state is globally antiferromagnetic, but weakly ferrimagnetic on the outer layers, exactly as in the present case. However, the magnetic moment per carbon atom is much smaller than in diamond(111). It is, however, important to recall that the flat edge states in ABC graphene extends in an extremely small part of the Brillouin zone and hosts less electrons than the flat band of diamond(111). The similarity of these two states suggests the occurrence of a magnetic state even in diamond(111).

The fundamental point underlined by our work is that there are two competing mechanisms for opening of a gap in diamond(111), namely magnetization or dimerization. Experimentally, it would be possible to detect the occurrence of magnetism via spin-resolved scanning tunneling spectroscopy by using magnetic tips.

Finally, our work demonstrates that in order to describe the correlated states in flat edge bands, it is necessary to include the electron-electron interaction at all levels in the calculations, both in the structural and electronic properties. This is relevant far beyond the case of diamond(111), and it is most likely also crucial to describe the phase diagram of twisted bilayer graphene or other low dimensional system presenting edge states such as IVB atoms on top of IVB(111) surfaces such as Pb/Si(111) or one dimensional polyenes.

ACKNOWLEDGMENTS

This work is supported by the Graphene Flagship, by RhomboG grant (ANR-17-CE24-0030) from Agence Nationale de la Recherche and by PRACE. Calculations were performed at IDRIS, CINES, CEA, BSC TGCC, and CAC(Tardis). B. P. acknowledges National Science Foundation (Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-1539918.
Appendix A: Band gap convergence with respect to k-points

We test the convergence of the band gap with respect to the electronic momentum k-point mesh shown in Fig. 4. For this purpose, we perform electronic structure calculations with the PBE0 functional on top of the undimerized structure obtained with the PBE functional (PBE0@PBE). The band gap can be similarly compared with the second panel of Fig. 2 (HSE06@PBE) of the manuscript. Our tests show that the band gap strongly depends on the k-point grid. A coarse k-point mesh of $4 \times 6 \times 1$ clearly overestimates the band gap with respect to the denser k-point meshes. This mesh is comparable with that used in previous GW calculations.\cite{24, 25}

Appendix B: Comparison with ARPES data

We calculate the electronic band structure using the HSE06 and PBE0 functionals. The electronic structure along the high-symmetry points of the Brillouin zone is given in Fig. 5 and Fig. 6 respectively. The valence band maximum is at the K-point and the conduction band minimum is at the J-point. The experimental data are taken from the ARPES measurements.\cite{13} We calculate the full path both for the non-magnetic and magnetic calculations with ionic relaxations.

The slope of the calculated path from the K-point towards the Γ-point depends on the amount of exchange and on the range of the interaction. For the PBE0 functional the best agreement is found with inclusion of magnetism.

FIG. 4. The electronic momentum (k-point) mesh convergence for the PBE0@PBE structure without magnetism.

FIG. 5. The electronic band structure of the surface states of diamond C(111)$2 \times 1$ surface, calculated with the HSE06 functional. Blue dots are the experimental ARPES data from Ref. 13. The ARPES data are shifted such that the valence band maximum of calculation and experiment match at the K-point.

FIG. 6. The electronic band structure of the surface states of diamond C(111)$2 \times 1$ surface, calculated with the PBE0 functional. Blue dots are the experimental ARPES data from Ref. 13. The ARPES data are shifted such that the valence band maximum of calculation and experiment match at the K-point.

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