Lamb shift of the Dirac cone of graphene

PEDRO MIGUEL M. C. DE MELO\(^1,2\) and ANDREA MARINI\(^1,3\)

\(^1\) Istituto di Struttura della Materia of the National Research Council - Via Salaria Km 29.3, I-00016 Monterotondo Stazione, Italy
\(^2\) Centre for Physics of the University of Coimbra - CFisUC, Department of Physics, University of Coimbra Rua Larga, 3004-516 Coimbra, Portugal
\(^3\) European Theoretical Spectroscopy Facility - ETSF

received 28 September 2016; accepted in final form 19 December 2016

PACS 31.15.A – Electronic structure of atoms and molecules: theory: Ab initio calculations
PACS 71.10.-w – Theories and models of many-electron systems

Abstract – The fluctuations of the electromagnetic vacuum are one of the most powerful manifestations of the quantum structure of nature. Their effect on the Dirac electrons of graphene is known to induce some spectacular and purely quantistic phenomena, like the Casimir and the Aharonov-Bohm effects. In this work we demonstrate, by using a first-principles approach, that the Dirac cone of graphene is also affected by a sizeable Lamb shift. We show that the microscopic electronic currents flowing on the graphene plane are strongly coupled with the vacuum fluctuations causing a renormalisation of the electronic levels (as large as 4 meV). This shift is one order of magnitude larger than the value predicted for an isolated carbon atom, which imposes a reinterpretation of the Lamb shift as a collective effect.

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Introduction. – Graphene, a two-dimensional hexagonal lattice composed of carbon atoms, has become one of the most intensively studied materials in recent years due to its potential applications in technology [1] and in many different fields of theoretical and computational Physics and Chemistry [2].

An intriguing aspect of graphene is represented by the interaction of its Dirac cone electrons with the quantised electromagnetic field. This is a peculiar effect as most of the equilibrium [3] as well as out-of-equilibrium [4,5] physics studied in semiconductors and nano-structures rely on a classical description of the external electric and magnetic fields. This assumption is motivated by the use of low-intensity fields, well described within a classical framework.

Nevertheless, the interaction of electrons with quantised magnetic fields is the driving mechanism, among others, of the Aharonov-Bohm (AB) [6] and the Casimir force [7,8] effects.

The AB effects are purely quantum-mechanical phenomena which do not have a counterpart in classical mechanics. Quantum mechanics, indeed, predicts that a magnetic field \(B\) confined in a closed region inside a carbon nano-tube alters the kinematics of the electrons travelling around the tube [9,10]. This effect disappears when the external magnetic field is removed. Nevertheless, even in the case where no external magnetic and electric field are present, the electromagnetic-field vacuum is still characterised by a finite, non-vanishing energy: the zero-point energy (ZPE). This energy is equivalent to the ZPE of a quantistic harmonic oscillator. In the case of the electromagnetic field the oscillators are the photons.

A known manifestation of the ZPE of the electromagnetic field is the Casimir effect. If we take two neutrally charged bodies and place them at close distance, the electromagnetic ZPE will lead to the appearance of an additional force between them, the Casimir force. The strength of the Casimir effect on graphene has been studied using quantum field theory together with a Dirac model used to describe the \(\pi/\pi^*\) bands [7,8]. Surprisingly, a graphene mono-layer placed parallel to a perfect flat conductor exhibits stronger Casimir forces at large separation distances and temperature than what was expected for a material as thick as an atom [8]\(^1\).

In contrast to the AB and Casimir effects, the Lamb shift affects even a single electron immersed in the vacuum of a quantised electromagnetic field and it does not require

\(^1\)The intensity of the Casimir force between two graphene sheets rapidly decreases when we reach the micrometer scale and approaches an intensity of a thousandth of the predicted value for two infinite parallel perfect conducting planes placed at the same distance [11,12]
the presence of substrate or of an external perturbation. The original observation of the Lamb shift in the hydrogen atom has represented a cornerstone in the development of quantum electrodynamics. Nevertheless it is still an active field of research [13,14] especially in the case of N-atoms systems where the Lamb shift is expected to be amplified by cooperative effects. It has been observed [15], indeed, that the presence of additional proximate atoms changes the strength of the interaction with the virtual photons. This cooperative Lamb shift gives rise to super-radiance phenomena and corrections to the energy levels of the compound system [16,17]. Super-radiance effects have been observed, for example, in atomic vapours [2] and mesoscopic atomic arrays [18].

A crystalline solid is a simple but clear example of a N-atoms system. As such we expect the cooperative emission of virtual photons to be amplified. If we add this simple argument to the special interaction of the Dirac electrons with the quantised electromagnetic field we are led to the conclusion that the Lamb shift in graphene can be sizeable.

In this work, indeed, we use an ab initio and atomistic approach to calculate the effect of the interaction of electrons with the quantised electromagnetic vacuum. The problem is rewritten in a Kohn-Sham (KS) basis and the electron-photon interaction Hamiltonian is expanded in plane-waves. We show that this interaction leads to a Lamb shift of the energy levels of graphene as big as $−4$ meV and a consequent reduction of its electronic speed. We show that only by using an ab initio approach it is possible to describe the multitude of states involved in the virtual transitions caused by the Lamb shift. In addition we will discuss that, physically, the microscopic mechanism that drives the Lamb shift is the interaction of the electromagnetic field with the microscopic currents caused by the material spatial discontinuity. These currents represent an intrinsic property of any material and, in general, they can be excited only by using an external perturbation. The Lamb shift is a striking quantistic manifestation of their intrinsic existence.

Methods. – In order to describe the effect induced by the electromagnetic-vacuum fluctuations we first introduce the Hamiltonian describing the interaction of the paramagnetic current $\hat{j}(r)$ with an electromagnetic field, $\hat{A}(r)$:

$$\hat{H}_{\gamma} = -\frac{1}{c} \int d^3r \, \hat{A}(r) \cdot \hat{j}(r).$$

We are interested in calculating the effect of $H_{\gamma}$ in extended systems. Therefore, we use a super-cell approach where the atomic lattice is described by a volume $\Omega$ repeated periodically. As a consequence, in order to introduce the second quantization for the vector potential, we Fourier-expand it:

$$\hat{A}(r) = \sum_{\alpha} \int \frac{dQ}{(2\pi)^3} \sqrt{\frac{2\pi c^2 \Omega}{\omega_Q}} \left[ d_{Q\alpha} \hat{e}_Q \cdot r + H.c. \right] e^{iQ \cdot r} \hat{e}_{Q\alpha},$$

with $Q \equiv q + G$ a generic point in the reciprocal space composed by a sum of the vector inside the Brillouin zone ($q$) and a vector of the reciprocal lattice ($G$).

In eq. (2) $e_{Q\alpha}$ (see footnote 2) is the photon polarization vector relative to the photon branch $\alpha$ and orthogonal to $Q$ (we are working in Coulomb’s gauge, so $\nabla \cdot A(r) = 0$). $\omega_Q = c|Q|$ is the energy of the free photon whose creation and annihilation operators are $d_{Q\alpha}$ and $d_{Q\alpha}^\dagger$.

In this work we treat the electrons within an ab initio approach based on Density Functional Theory (DFT) [19]. By doing this, we can perform accurate calculations without the need of an adjustable parameter and have access to any necessary number of empty states, which are fundamental in the evaluation of the energy corrections, due to the large number of virtual transitions needed (see eq. (4)) as can be seen in fig. 1. This would not be possible if we were to use a low-energy tight-binding or Dirac-model based approach.

Thusly, the paramagnetic electronic current density operator, which is defined as $\hat{j}(r) \equiv -\frac{1}{c} \nabla \psi(r) \nabla \psi(r) - H.c.$, can be easily rewritten in the KS basis by expanding the field operators, $\hat{\psi}(r) = \sum_{n\Gamma k} c_{n\Gamma k}^\dagger \phi_{nk}(r)$. Here $\phi_{nk}(r)$ is a KS orbital with energy $\epsilon_{nk}^\Gamma$ and creation and annihilation operators $c_{nk}$ and $\hat{c}_{nk}^\dagger$. It follows that

$$\hat{j}(r) = \frac{1}{2} \sum_{\alpha \mu \nu \Gamma \lambda} \left[ \hat{c}_{nk}^\dagger \hat{c}_{mp}^\dagger \phi_{nk}^\Gamma (r) + H.c. \right],$$

with $p_{nk}^{\Gamma \mu \nu}(r) \equiv (e^{-i} \phi_{nk}^\Gamma (r) \partial_{r_\lambda} \phi_{mp}^\Gamma (r))$. Thanks to eq. (3) it follows that all ingredients of our approach are calculated ab initio, in a parameter-free way.

Now that the interaction Hamiltonian is defined we can apply standard perturbation theory. At difference with the electron-electron or electron–phonon cases, the electron-photon interaction can be treated perturbatively as it strength is dictated by the small fine-structure constant $\alpha = -\frac{e^2}{\hbar c}$ and $\frac{1}{2}$ (see footnote 4). It is indeed well known that the first non-vanishing order in the perturbation expansion of the energy correction in powers of $H_{\gamma}$ accounts for the biggest part of the correction to the energy levels [20].

It is then straightforward to show that the second-order contribution to the renormalisation of the level $n\mathbf{k}$ is $\varepsilon_{nk} = \varepsilon_{nk}^\Gamma + \Delta_{nk}(\{N_{Q\alpha}\}) + i\Gamma_{nk}$, with $\{N_{Q\alpha}\}$ the occupation factors of the photon population, while $\Delta_{nk}$ is the single particle energy shift and $\Gamma_{nk}$ represents its lifetime. The Lamb shift appears when we assume that there are no

2Together with the photon momentum $Q$ the vectors $e_{Q\alpha}$ form an orthogonal basis. The form of $e_{Q\alpha}$ is dependent on the polarization of light: for linear polarization $e_{Q\alpha} = e_{\{\alpha\} / / \gamma}$; for circular polarization $e_{Q\alpha} = \cos \theta_{\alpha} e_\gamma + \sin \theta_{\alpha} e_\sigma$. In the derivation of eq. (4) we assume the photon momentum to be aligned with the $z$ Cartesian direction.

3We neglect renormalisation effects of the photons, that are assumed to be the quanta of a free field. This approximation is well motivated for an isolated graphene sheet as the photons are not spatially confined and the electronic screening can be safely assumed to be negligible.

4In atomic units.
photons and \( N_{Q_0} = 0 \). In this limit \( \Delta \epsilon_{n \mathbf{k}} \) is not zero and provides the zero-point correction to the energy levels:

\[
\Delta \epsilon_{n \mathbf{k}} = \sum_{m} \int \frac{dQ}{(2\pi)^3} \epsilon_{n \mathbf{k}}^{KS} \left[ \sum_{ij} \frac{1}{2\epsilon_{n \mathbf{k}}^{KS} - \epsilon_{n \mathbf{k} - \mathbf{q}}^{KS} - \omega_k + i0^+} - \sum_{ij} \frac{1}{2\epsilon_{n \mathbf{k}}^{KS} - \epsilon_{n \mathbf{k} - \mathbf{q}}^{KS} + \omega_k - i0^+} \right].
\]

In eq. (4), \( \sum_m \) excludes the contribution \( m = n \) when \( Q \rightarrow 0 \). We have also defined

\[
P_{n \mathbf{k} \mathbf{q}, \mathbf{i}}^{Q} = \int d\mathbf{r} e^{i\mathbf{r} \cdot \mathbf{Q}} \left[ P_{n \mathbf{k} - \mathbf{q}, \mathbf{i}}^{\mathbf{r}}(\mathbf{r}) + H.c. \right],
\]

and the transverse matrix \( \tau_{ij}^{Q} = \sum_{n} \epsilon_{Q_{n\sigma}} \epsilon_{Q_{n\sigma}} \) (see footnote 5).

From eq. (4) we notice that, as \( \omega_k \) is linear in \( |Q| \), \( \Delta \epsilon_{n \mathbf{k}} \) is divergent for \( Q \rightarrow \infty \). As explained in the Supplemental Material Supplementarymaterial.pdf (SM)\(^6\), the regularization of \( \Delta \epsilon_{n \mathbf{k}} \) is obtained by splitting the real part of eq. (4) into the \( G = 0 \) and \( G \neq 0 \) parts, so that we can define

\[
\Delta \epsilon_{n \mathbf{k}}|_{\text{regular}} = \Delta \epsilon_{n \mathbf{k}}|_{G=0} + 2\Delta \epsilon_{n \mathbf{k}}|_{G \neq 0}.
\]

with \( \Delta \epsilon_{n \mathbf{k}}|_{G \neq 0} \) corresponding to the real part of eq. (4), with the index \( m = n \) running only on filled levels. The graphene ground state has been calculated using the QE [22] code and the Perdew-Wang functional parametrization (PW92) for the Local Density Approximation (LDA) [23]. Equation (4) has been implemented in the Yambo code [24], that is interfaced with QE and can use the calculated KS graphene. Graphene is simulated by using a 24\( n \)-by-24\( n \) \( k \)-point grid, where \( n \) is an integer, with a unit cell with a lattice parameter of 4.60 (a.u.), a layer separation of 14.0 (a.u.), and a kinetic cut-off of 80 Ry. The resulting corrections to the eigenvalues and electronic structure are then interpolated with a quadratic polynomial function, using (24\( n \))^\(-3\) as the independent variable.

Results. – In fig. 1 we show the dependence of the corrections to the energy levels at the point \( K \) of the Brillouin zone for \( \Delta \epsilon_{n \mathbf{k}}|_{G=0} \) term of eq. (6), which is the only one dependent on the number of empty states (see SM for more information). If we were to use tight-binding or

\(^5\) It is straightforward to show that \( \tau_{ij}^{Q} = \sum_{n} \epsilon_{Q_{n\sigma}} \epsilon_{Q_{n\sigma}} = \delta_{ij} - \frac{Q_{ij}}{Q^2} \), where \( \delta_{ij} \) is the Kronecker delta function. This matrix eliminates all components which are parallel to the photon momentum \( Q \), and removes any dependence on the photon polarisation, which should not exist in this case as we are dealing with the vacuum fluctuations of the electromagnetic field, which are not polarised.

\(^6\) There we follow the same renormalisation treatment as in [21], where the self-interaction terms are isolated and removed from the contribution to the energy correction.

Dirac models we would no be able to access this wealth of knowledge of the empty states and use them in the summation of the virtual transitions in eq. (4).

In fig. 2 we show the Lamb correction to the energy level. Two aspects are clearly visible: the first is that the Dirac cone is down-shifted of 0.6 meV. This shift is large if compared both to previous calculations and to the case of heavy atoms. Indeed it has been previously predicted [25] that graphene acquires a band-gap as large as 50\( \mu \)eV induced by the interaction with the electromagnetic-field fluctuations. However, in ref. [25] graphene is described with a single-band model and, as was made clear in fig. 1, this represents an approximation that dramatically fails in describing the wealth of virtual states involved in the proper evaluation of the Lamb shift. The result we find is two orders of magnitude larger than in this over simplified model.

In addition our correction is large even if compared to the case of heavy atoms. Indeed, for isolated atoms the Lamb shift is known to scale as an \( Z^2 \). This means that it is, indeed, larger for heavy atoms.\(^7\) These corrections approximatively follow a simple rule: \( \Delta E \sim \Delta E_0 Z^2 \) with \( \Delta E_0 \approx 16.86 \mu \)eV that would imply, for a carbon atom, a \( \Delta E_0 \approx 0.6 \) meV, one order of magnitude smaller than the value we found.

As graphene is composed only by light carbon atoms the reason for such a large Lamb correction must be searched elsewhere and not in arguments based solely on the atomic number. Equation (4) describes \( \Delta \epsilon_{n \mathbf{k}} \) as a process where

\(^7\) In the case of the muonic deuterium [26] the Lamb shift, \( \Delta E \), is as large as -240 meV. Similarly large it is for heavy relativistic atoms [27] like roentgenium \((Z = 272, \Delta E \sim -96 \)meV), caesium \((Z = 55, \Delta E \sim -98 \)meV), E119 \((\Delta E \sim -232 \)meV) and E120 \((\Delta E \sim -250 \)meV).
the initial state $|n\mathbf{k}\rangle$ undergoes virtual transitions to all possible states $|m\mathbf{k} - \mathbf{q}\rangle$ emitting a photon $|\mathbf{Q},\alpha\rangle$. The creation of a virtual population of photons that is annihilated at the end of the process, is an alternative physical picture of the Lamb shift that makes clear its link with the potential space of final states that can be reached.

The dimension of this space represents the multitude of potential final states. This multitude is reminiscent of the multitude of charges that characterise the collective Lamb shift [15] and suggests that indeed, the shift can be large in extended systems. The crucial importance of the space spanned by the virtual transition in eq. (4) is highlighted in fig. 1, where we show the changes in the Lamb shift of the Dirac point coming from adding more possible virtual transitions between different bands.

Another important aspect that emerges clearly from our calculations is that the $\sigma$ bands are also affected by a correction that is smaller (even if of the same order of magnitude) of the one relative to the Dirac cone. The difference between the $\sigma$ bands down-shift and the shift of the point $K$ results in a reduction of the occupied band with of 2.13 meV.

In order to pin down the physical motivation of this large Lamb shift we propose an alternative approach. Indeed, the Lamb shift is historically connected with the virtual emission and absorption of photons. This picture is a direct consequence of the perturbative treatment of the interaction Hamiltonian, eq. (1). Nevertheless, an alternative microscopic interpretation, is based on the classical picture of the interaction of electrical currents with the electromagnetic field. This interaction is at the basis of the Lorentz force, for example, and it is linked with the form of the interaction Hamiltonian.

Even if there are no external fields any material is crossed by microscopic currents caused by the intrinsic spatial discontinuity of the material. Indeed, even if for continuous materials $\langle \mathbf{j}(\mathbf{r})\rangle = 0$, for systems like graphene a finite current flows between regions with different density. On the average these currents do not produce a macroscopic current but, nevertheless, do interact with the electromagnetic field. This microscopic interaction is the source of the Lamb shift. It is important to note, here, that it is possible to enhance these microscopic currents by spatially confining the electrons. It is indeed known [3] that when the electrons are confined, the local electric fields induced by the charge discontinuity are enhanced. This confinement is obtained, for example, by reducing the system dimensionality. In practice, when moving from bulks to systems with lower dimensionality (e.g., surfaces) the magnitude of the Lamb shift experienced by the electronic levels is expected to increase [28].

The projection of the electronic current $\mathbf{j}(\mathbf{r})$ along the graphene plane is shown in fig. 3.

Here we can clearly see that the microscopic current is mostly zero, with the non-zero regions concentrated along the sides of the graphene hexagon. Therefore, these current fluctuations mainly interact with states which wave function amplitudes oscillates along the hexagonal edges of the unit cell alternating positive to negative regions. As exemplified in fig. 4, the $\pi$ and $\pi^*$ states, as well as some
σ bands, show this alternating behaviour and, therefore, more strongly interact with the vacuum fluctuations. The more s-like orbitals, instead, have a uniform spatial distribution (see the σ3 state shown fig. 4) and their Lamb shift is smaller.

**Conclusion.** – In conclusion, using an ab initio approach, we have predicted that the Dirac cone of graphene is characterised by a sizeable Lamb shift induced by the interaction of the electrons with the vacuum fluctuations. We predict this shift to be larger than what is expected from semi-empirical model calculations and also if compared to the case of heavy isolated atoms. This is explained in terms of cooperative effects caused by the presence of a multitude of atoms. Moreover, we trace back the different corrections for σ and π bands to their peculiar contribution to the microscopic currents flowing in the material. The present results do contribute to improve the state-of-the-art understanding of the Lamb shift in realistic and extended materials. They clearly bind a quantitative description of the shift to a careful and parameter-free description of the full spectrum of the graphene electronic states.

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