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Non Local Corrections to the Electronic Structure of Non Ideal Electron Gases: The Case of Graphene and Tyrosine

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ABSTRACT

We introduce a formal definition of a non local functional and show that the non local exchange-correlation potential functional, derived within Density-Functional Theory, is non local in the space of electronic densities. A previously developed non local exchange-correlation potential term, is introduced to approach the exact density-functional potential. With this approach, the electronic structure of the graphene surface and the tyrosine amino acid are calculated.

Keywords: Nonlocality; Interfaces; Exchange-Correlation Potential; Graphene

1. Introduction

Functional architectures at the nanoscale are natural candidates to overcome the limitations encountered by the conventional road map of micro technologies. The efficient realization of nanoscale devices demands the development of theoretical methods with enough precision to predict properties in a regime where physical interfaces play a key role. However, it is precisely the description of interfaces that is the main obstacle to rely in current theoretical methods. This is due to limitations in modeling and numerically assess the required quantum definition of electronic states. On the one hand, reduced models suffer from the inability to include actual many body potentials while retaining numerical efficiency. On the other hand, *ab-initio* approaches, while exactly introducing many body interactions, suffer from the lack of efficiency in terms of computational resources. Consensually [1], an efficient, elegant, and exact alternative involves *ab-initio* calculations by means of Density-Functional Theory (DFT).

While in principle, DFT can yield exact electron-electron interactions, its effectiveness relies in a combination of the Hohenberg-Kohn (HK) theorems [2] and the Kohn-Sham (KS) scheme [3]. The HK theorems reduce any property of the many-body interacting system to a functional of the ground state electronic density and then, the KS scheme replaces the original many-body problem by an auxiliary independent-particle problem, whereby all many-body interactions are mapped in an effective single-particle potential, namely, the exchange-correlation (*xc*) potential, v_{xc} [4]. This *xc* potential, which contains all the information regarding electron-electron interactions, is implicitly defined as a functional derivative of the *xc* energy, E_{xc}, in the space of electronic densities,

$$v_{xc}\left[n(r)\right]=\frac{\delta E_{xc}\left[n(r)\right]}{\delta n(r)} \tag{1}$$

However, in most general cases, an algebraic form for $E_{xc}\left[n(r)\right]$ is unknown. Thus, the definition of $n_{xc}\left[n(r)\right]$ is by far the most important task for an effective DFT.

Initially, the manageability of DFT arises from the introduction of the Local-Density Approximation (LDA) to v_{xc} [3]. LDA, and further extensions beyond it within local exchange models, such as generalized gradient approximations (GGA) [5] and Meta-GGA [6], work fairly well for homogeneous and well-behaved electronic densities [7]. While this is probably the case of bulk systems,

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it is no longer the expected behaviour for confined systems, such as nanostructures and interfaces, [8], therefore, failures within DFT can be attributed to the inability of local xc potentials, to retain all many body effects when the many body interacting wave function representation is mapped to a mean-field density-based representation [9]. Recent attempts to overcome such difficulties and to manage DFT are framed within the context of the controlled addition of the non local Fock exchange to current local *xc* potentials [10]. To some extent, such hybrid potentials correct the electronic structure, even when such improvements are not handled systematically [11,12].

Therefore, the purpose of this work is twofold. First, we provide a means to understand the role that non locality plays in DFT by introducing a formal definition of a non local functional which, as far as we know, is not presently available in the literature. The use of our definition provides a rigorous frame to assess the failure of DFT when describing non homogeneous electron systems. Secondly, we use a method developed previously by some of us to devise hybrid functionals in a systematic manner [13]. In this way, we analyze the role that non locality plays in the electronic characterization of two benchmark systems, graphene and tyrosine. The choice of these two systems responds to the emergence of these materials as platforms for effective molecular electronics [14], and thus pay particular attention to graphene interfaced with bio-systems [15,16].

2. Definition of Non Local Functional by Its Opposite

A fundamental issue to address when dealing with a mean field theory is the definition of effective potentials. DFT is a mean field theory within which the selection of the effective v_{xc} potential is controversial [9,17], with continuous efforts towards improvement in accuracy [11, 12,18-20]. It is our point of view that all such efforts suffer from the lack of a rigorous and explicit definition of one of the analytic properties that a v_{xc} functional must fulfill, namely the *non locality in the position space* [9]. Thus, in this section we introduce a definition for a non local functional. This definition should be sufficient to connect DFT with other effective theories and gain insights in the physical implications that the inclusion of non local effects has on mean field theories.

Two complementary definitions are given for a local functional as follows:

1) A local functional from F to $C^\infty\left(R^n\right)$:

A functional $\mu: F \to C^\infty\left(R^n\right)$ is local if for **any open set** $U \subset R^n$ and fields ϕ and $\phi' \subset F$, so that

$$\phi|_U = \phi'|_U \Rightarrow \mu[\phi]\|_U = \mu[\phi']\|_U \tag{2}$$

This means that $\mu[\phi]\|_U$ is determined by the values of ϕ in an arbitrarily set U.

2) A local functional from F to R:

A functional $\lambda: F \to R$ is local if it is given by the integral,

$$\lambda[\phi] = \int_{R^n} \mathrm{d}x \mu[\phi](x) \tag{3}$$

of a local functional

$$\mu: F \to C^\infty\left(R^n\right) \tag{4}$$

This means that the functionals which do not fulfill either of these two conditions in the fields where they are defined are called non local functionals. These two definitions should contribute to elucidate controversies concerning the inclusion of non local effects in current exchange-correlation potentials.

3. Non Locality in the Exchange-Correlation Potential

In the fundamentals of DFT by Hohenberg and Kohn [2], the analytical expression for the *xc* energy functional is determined for two particular cases, the electron gas with *almost constant density* and the electron gas with *slowly varying density*. By using the first of these two cases, we will show the non local character of the most general exchange-correlation functional.

The gas with almost constant density is defined in accordance with the conditions that follow,

$$n(r) = n_0 + \tilde{n}(r) \tag{5a}$$

with

$$\frac{\tilde{n}(r)}{n_0} \ll 1 \tag{5b}$$

and

$$\int \tilde{n}(r)\mathrm{d}r = 0 \tag{5c}$$

where $n(r)$ is the electronic density as a function of the position. HK proposed a formal expansion for E_{xc} provided such conditions above are met [2]. It is written as,

$$\begin{aligned} E_{xc}[n] = E_{xc}[n_0] &+ \int K(r-r')\tilde{n}(r)\tilde{n}(r')\mathrm{d}r\mathrm{d}r' \\ &+ \int L(r,r',r'')\tilde{n}(r)\tilde{n}(r')\tilde{n}(r'')\mathrm{d}r\mathrm{d}r'\mathrm{d}r'' + \cdots \end{aligned} \tag{6}$$

In order to capture the essential physics of the problem in question, and to avoid tedious mathematical treatments, we reduce all the expressions above to their one dimensional (1D) form. Then, by doing the *functional derivative* we obtain an enlightening expression for the *xc* potential. It is then written as,

$$\begin{aligned} v_{xc}[n(x)] = &\int K(x-x')\tilde{n}(x')\mathrm{d}x' \\ &+ \int L(x,x',x'')\tilde{n}(x)\tilde{n}(x')\mathrm{d}x'\mathrm{d}x'' + \cdots \end{aligned} \tag{7}$$

Noticeably, the spatial integrals of the electronic density products are, by themselves, non local mathematical operations in the space in which they are defined, see definition of non locality above. Thus, for the most general case, this analytical expression for v_{xc} is non local in the *x*-space provided that $\tilde{n}(x)$ is different from zero.

4. Non Local *xc* Potentials for Interfaces

The choice of the *xc* functional describing the most general physical system must fulfill the following conditions: 1) it has to be non local in the space of electronic densities [9]; 2) it should correct self-interaction errors in exchange functionals [10]; 3) it should contain a fraction of the Fock potential to approach exact exchange [13]; and 4) it must agree with the adiabatic connection theorem [21]. With these conditions in mind, and as an improvement to the first hybrid approaches introduced by Becke [22], we propose the following analytical equation to evaluate numerically v_{xc},

$$v_{xc}(\alpha) = \alpha v_x^{\text{Fock}} + (1-\alpha) v_x^{\text{local}} + v_c^{\text{local}} \quad (8)$$

Here v_x^{Fock} is the Fock-like potential contribution, which accounts for non local effects, the $v_{x,c}^{\text{local}}$ contributions are given by any of the available exchange (*x*) or correlation (*c*) local functionals. Finally, α is a single fitting parameter to be determined by exact rules.

To estimate α, we follow an exact methodology within mean-field Green's function schemes [23,24]. The value is chosen so that $\Delta_{\text{HOMO-LUMO}}$ matches the charge gap, *GAP*. This quantities are defined as

$$\Delta_{\text{HOMO-LUMO}} = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}} \quad (9)$$

and

$$GAP = 2E_0(N) - E_0(N+1) - E_0(N-1) \quad (10)$$

respectively, where *N* represents the number of electrons, E_0 is the total energy for the selected ground states in the Kohn-Sham system of independent electrons with single particle energies denoted as $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$, for the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) respectively [4]. The choice of the finite region in which to search for α is constrained by two conditions: 1) it must contain the zone which confines the electron and 2) the HOMO and LUMO orbitals must be well localized in to the cluster model.

Finally, we should remark that from the reasoning presented here we could not derive an explicit mathematical relation between the non local corrections to v_{xc} required by seminal DFT [2], and our adjustable hybrid approach defined by Equation (8). However, we note that both *xc* potentials are non local functionals of the electronic density. It is this common property that justifies an algebraic connection between both equations. Moreover, the fundamental physical relation between both corrections is now clear: in both cases non local corrections are included beside the causal effects, when non ideal electron gases are described in terms of the electronic density.

5. Numerical Results and Discussion

In this section the influence of the gradual inclusions of non local effects in v_{xc} upon the electronic structure of two confined systems, tyrosine and graphene, is discussed. To do this, we analyze the evolution of the $\Delta_{\text{HOMO-LUMO}}$, when the non local Fock contribution to $v_{xc}(\alpha)$ varies [see Equation (8)].

The code GAUSSIAN09 is used for numerical DFT calculations [25]. The local DFT functional introduced to define v_{xc} in the Equation (8) is PW91 [26], which is used either to account for local exchange and local correlation effects.

In regard to the other two inputs required to manage DFT approaches, *i.e.*, 1) finite cluster models definition and 2) the selection of basis sets, the following reasoning was followed. First, the atomic structure of the amino acid reported in the pdb data base is selected [27], and a finite cluster model for the ideal semi-infinite graphene is chosen. To this end, we calculate the position of the ionization potential $IP = E_0(N-1) - E_0(N)$ when the size of graphene cluster models is increased [see **Figure 1**].

Graphene is known to have an *IP* close to 5 eV [28]. Thus, this reference value was used to estimate the level of certainty of our finite model approach to the semi-infinite graphene system [29]. Using these results, see **Figure 1**, we select a 10 × 10 unit cells cluster to model graphene[1]. Second, the basis sets are selected such that they are 3 - 21 g for all the atoms in the amino acid and graphene systems. Higher order basis sets were in- troduced to prove the robustness of our results for all the calculations in this work[2]. The convergence criterium was set to the 10 percent for the single particle energy levels as well as for ground state energies calculated with fully local v_{xc} potentials.

Figures 2 and **3** show $\Delta_{\text{HOMO-LUMO}}$ and *GAP* energies calculated for graphene and tyrosine respectively, using a

[1]Bigger cluster sizes will certainly increase the accuracy of the calculations but will also increase the computational time by orders of magnitude. e.g. Using 3 - 21 g basis sets [25], and going from a cluster with 1 carbon atom [0 unit cells] to clusters with 240 carbon atoms [10 × 10 unit cells], the time consumption is increased by 3 orders of magnitude. In addition, improvements to the accuracy of self-consistent energies do not affect the main message of this work.

[2]The electronic structure has been optimized using localized-atomic-orbitals-basis sets for all the atoms in the structure. The basis selected where sto-3 g, 3 - 21 g, 6 - 31 g and cc-pvtz. http://www.emsl.pnl.gov/forms/basisform.html

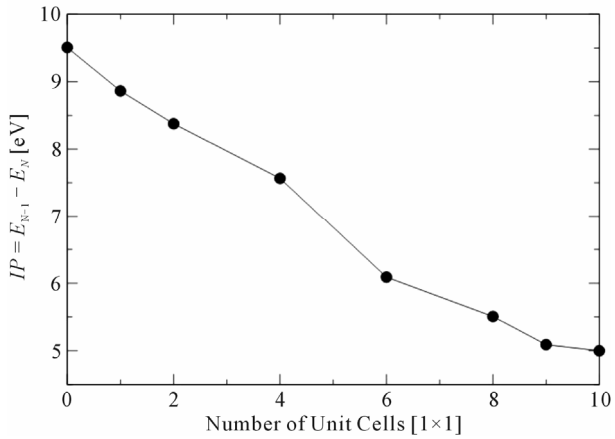

Figure 1. Ground state energy calculations of the ionization potentials, *IP*, as a function of the number of unit cells used in graphene. Numerical results are represented by filled dots and the solid line is a guide to the eye.

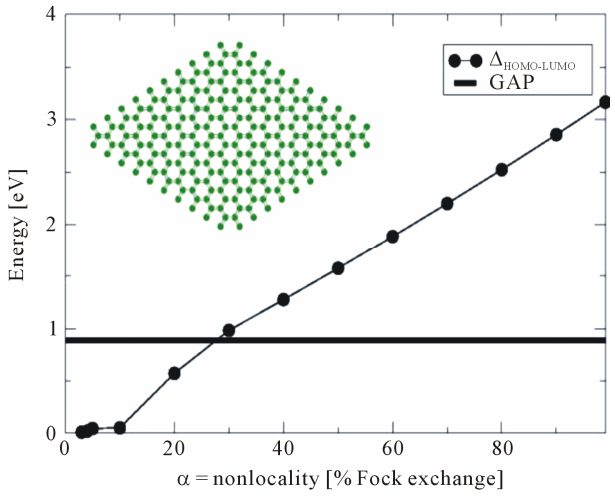

Figure 2. Evolution of $\Delta_{HOMO-LUMO}$ gap for a 10 × 10 unit cell model of graphene [see inset], when non local Fock exchange is included in the *ab-initio* approach to v_{xc}. The dots represent numerical calculations for the $\Delta_{HOMO-LUMO}$ gap when the non local Fock exchange contribution varies in the *ab-initio* approach to v_{xc}. These points are interpolated with a thin solid line as a guide of the eye. The horizontal solid line represents the *GAP* value calculated using ground state energies and a local approach to v_{xc}. As explained in the main text, the intersection between both continuous lines, when $\Delta_{HOMO-LUMO}$ = *GAP*, determines the proportion of non local exchange required to improve models to v_{xc}.

wide range of v_{xc} functionals, while a clear indication on the amount of non local effects included is made. Here, it is initially shown that the inclusion of non local Fock exchange has a strong influence on the charge gap for both systems, which rapidly increases with the percentage of Fock-like exchange in the hybrid functional.

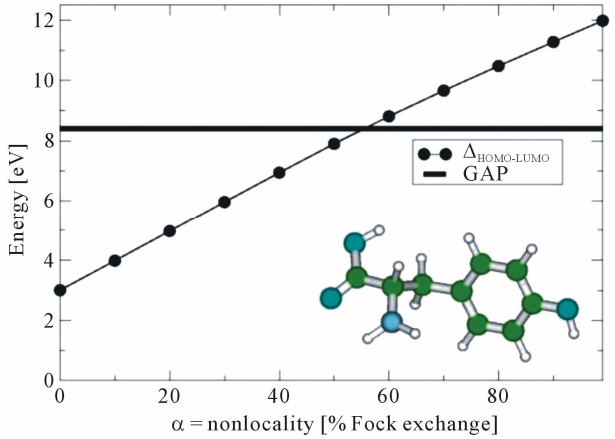

Figure 3. Evolution of $\Delta_{HOMO-LUMO}$ gap for a tyrosine aminoacid [see inset] when non local Fock exchange is included in the *ab-initio* approach to v_{xc}. The dots represent numerical calculations for the $\Delta_{HOMO-LUMO}$ gap when the non local Fock exchange contribution varies in the *ab-initio* approach to v_{xc}. These points are interpolated with a thin solid line as a guide for the eye. The horizontal solid line represents the *GAP* value calculated using ground state energies and a local approach to v_{xc}. As explained in the main text, the intersection between both continuous lines, when $\Delta_{HOMO-LUMO}$ = *GAP*, determines the proportion of non local exchange required to improve models to v_{xc}.

By adjusting this percentage, with the aid of the method previously developed [13], we conclude that the best approach to the electronic structure of the graphene ribbon is ~28% Fock-like, and that the best approach to the electronic structure of the amino acid should contain ~58% of Fock exchange contribution. As expected, the value of α decreases as we move to the infinite systems, *i.e.* as we move from a graphene ribbon to the semi infinite graphene model, where local (~0% Fock-like) approaches are expected to perform better. By contrast, the non local exchange is more important to describe electronic density regions were the confinement is more stronger, e.g. a 3D confinement as occurring in an isolated molecule exemplified by the tyrosine amino acid.

6. Conclusion

In this paper, a formal definition for a non local functional has been introduced. This definition should open new doors to DFT approaches, while distinguishing whether v_{xc} proposals actually fulfill the requirement of non locality in the space of electronic densities, as dictated by the original DFT theory [1,9]. In conjunction with previously developed non local hybrid approach to v_{xc} [13], we show how including non local effects in v_{xc} affects the electronic structure calculations on two benchmark systems: graphene and tyrosine. It is shown that the proportion of non-local Fock exchange required to repro-

duce correctly the gap energy increases with increasing the degree of confinement in the system. The discrepancies between our non local corrected calculations and the local calculation results, suggest that care should be taken when forthcoming local density-functional approaches in favour of those results obtained by means of hybrid density-functional approaches. However, in light of the results discussed here, it is still difficult to assess to what extent current hybrids v_{xc} potentials can describe the electronic states in a more general frame of non ideal electron gases, e.g. nanostructures and interfaces, where the amount of non local corrections is expected to vary. Therefore, further developments of hybrid functionals should also include the spatial dependence of non local contributions while exactly approaching the *xc* potentials.

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