The (absence of) many-body interactions in graphene: Time-dependent density-functional theory study

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• Brief reminder of DFT and time-dependent DFT (TDDFT);

• Single-particle linear response of Dirac electrons: 2D (graphene) and 3D (cubic inverse perovskites) cases;

• *Ab initio* band-structure calculations results;

• Inclusion of many-body dynamic interactions through meta-GGA-based TDDFT;

• Conclusions.
Short reminder of static DFT

(Kohn & Sham, 1965)

\[ E = \int v_{ext}(r)n_0(r)dr + \frac{1}{2} \int \frac{n_0(r')}{|r' - r|} dr dr' + E_{xc}[n_0(r)], \quad (1) \]

Kohn-Sham equations:

\[ \left[ -\frac{1}{2} \Delta + v_{eff}(r) \right] \psi_\alpha(r) = \epsilon_\alpha \psi_\alpha(r). \quad (2) \]

**Universal functional**

\[ v_{eff}(r) = v_{ext}(r) + \int \frac{n_0(r')}{|r' - r|} dr' + v_{xc}(r). \]

**External potential**

**Hartree potential**

\[ v_{xc}(r) = \frac{\delta E_{xc}}{\delta n_0(r)} : \text{Exchange-correlation potential} \]
Electron density

\[ n_0(\mathbf{r}) = \sum_{\alpha \in \text{occ}} |\psi_\alpha(\mathbf{r})|^2. \]

- **LDA** : \( E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r})]d\mathbf{r} \) : local;
- **GGA** : \( E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r}), \nabla n_0(\mathbf{r})]d\mathbf{r} \) : semi-local;
- **MGGA** : \( E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r}), \nabla n_0(\mathbf{r}), \tau(\mathbf{r})]d\mathbf{r} \) : non-local.

where

\[
\tau(\mathbf{r}) = \frac{1}{2} \sum_{\alpha \in \text{occ}} |\nabla \psi_\alpha(\mathbf{r})|^2
\]

is the density of *kinetic energy*. 
TD Kohn-Sham equations:

\[
i \frac{\partial}{\partial t} \psi_\alpha(\mathbf{r}, t) = \left[ -\frac{1}{2} \Delta + v_{\text{eff}}(\mathbf{r}, t) \right] \psi_\alpha(\mathbf{r}, t),
\]

(3)

\[
v_{\text{eff}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int \frac{n_0(\mathbf{r}', t)}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}, t).
\]

(4)

Zero in the random phase approximation (RPA).

**Q.** Why TDDFT in excitation processes?  
**A.** In static DFT, the distances between the single-particle energy-levels are not the true excitation energies of a many-body system; In TDDFT, the positions of peaks in linear-response spectra are.

Linear response by TDDFT  
\[\text{True excitation energies!}\]

Frequency
TD linear response

\[ n(\mathbf{r}, t) = n_0(\mathbf{r}) + n_1(\mathbf{r}, t) + \ldots, \]  
\[ n_1(\mathbf{r}, t) = \int \chi(\mathbf{r}, \mathbf{r}', t - t') v_{ext}(\mathbf{r}', t') d\mathbf{r}' dt'. \]  

Interacting-particles response function (unknown).

\[ n_1(\mathbf{r}, t) = \int \chi_s(\mathbf{r}, \mathbf{r}', t - t') v_{eff}(\mathbf{r}', t') d\mathbf{r}' dt', \]  

Lindhard's independent-particles response function.
Our starting point is the $\omega \rightarrow 0$ limit of the conductivity of pure graphene, which is known to be (Ludwig, Fisher, Shankar, & Grinstein, 1994)

$$\sigma = \frac{e^2}{4\hbar}.$$ (8)

It is well reproducible in *ab initio* RPA calculations:

Conductivity of graphene vs. frequency (full band-structure calculation)
According to the Lindhard’s formula (Lindhard, 1954):

\[
\chi_s(q, \omega) = \frac{2}{(2\pi)^2} \sum_{\alpha\beta} \int_{FBZ} \frac{f_{\alpha k} - f_{\beta k+q}}{\omega - \epsilon_{\beta k+q} + \epsilon_{\alpha k} + i\eta} \left| \langle u_{\alpha k} | u_{\beta k+q} \rangle \right|^2 dk. \tag{9}
\]

\[
\psi_{\alpha k}(r) = u_{\alpha k}(r) e^{i k \cdot r}. \tag{10}
\]

Denominator in Eq. (9) is given by Eqs. (11).

**But where the wave-functions overlap** \( \langle u_{\alpha k} | u_{\beta k+q} \rangle \) **is to be taken from ?**
Degenerate perturbation theory in $K$ point

\[ \hat{H}_k u_{\alpha k}(r) = \epsilon_{\alpha k} u_{\alpha k}(r); \quad \hat{H}_k = -\frac{1}{2} \nabla^2 - i k \cdot \nabla + \frac{k^2}{2} + v_s(r), \quad (12) \]

\[ \epsilon_{v k} = -v_f |k - k_K|, \quad (13) \]

\[ \epsilon_{c k} = +v_f |k - k_K|. \]

For small $q$

\[ \hat{H}_{kK+q} \approx \hat{H}_{kK} + (-i \nabla + k_K) \cdot q. \quad (14) \]

The degenerate perturbation theory requires that (Landau & Lifshitz, 1981)

\[ \langle u_{\beta k_0} | (-i \nabla + k_K) \cdot q | u_{\alpha k_0} \rangle = 0, \quad \alpha \neq \beta. \quad (15) \]

Then Eqs. (13) and (15) are sufficient to prove that

\[ |\langle u_{\alpha kK+k} | u_{\beta kK+q} \rangle|^2 = \frac{1}{2} \left( 1 - \frac{k}{|k|} \cdot \frac{k + q}{|k + q|} \right). \quad (16) \]

If, moreover, $q \ll k$, then expansion of Eq. (16) in $q/k$ gives

\[ |\langle u_{\alpha kK+k} | u_{\beta kK+q} \rangle|^2 \approx \frac{k^2 q^2 - (k \cdot q)^2}{4 k^4}. \quad (17) \]
Degenerate perturbation theory in $K$ point

We then easily find

$$\text{Im} \chi_s(q, \omega) = -\frac{q^2}{8\pi \omega} \times \int_{S_1+S_2+S_3+S_4+S_5+S_6} (1 - \cos^2 \phi) d\phi = -\frac{q^2}{4\omega}. \quad (18)$$

And recalling that

$$\sigma = \frac{i\omega \chi_s}{q^2}, \quad (19)$$

we have for the conductivity

$$\sigma = \frac{1}{4} \left( \frac{e^2}{\hbar} \right). \quad (20)$$
In the range of the C-C distances when the Dirac’s cone exists, the static limit of graphene’s conductivity remains constant.
2D vs. 3D cases

2D

\[ \text{Im} \chi_s(q, \omega) \propto \frac{q^2}{\omega}, \]

\[ \sigma(\omega) = \text{const.} \] \hspace{1cm} (21)

3D

The cubic inverse perovskite Ca$_3$PbO supports 3D Dirac’s massless (or almost massless) electrons (Kariyado & Ogata, 2011).

In exactly the same manner as above, in the 3D case we arrive at

\[ \text{Im} \chi_s(q, \omega) \propto q^2, \]

\[ \sigma(\omega) \propto \omega. \] \hspace{1cm} (22)
3D Dirac massless electrons: Ca$_3$PbO
Stability of the graphene's conductivity: xc potential

Graphene

- LDA
- GGA (PBE)
- MGGA (RPP09)
3D Dirac massless electrons: Ca$_3$PbO

![Graph showing σ vs ω and DOS vs energy](image)

- **σ (a.u.)**
- **ω (eV)**
- **DOS**

- **Energy (eV)**

Two curves are plotted:
- **LDA** (black line)
- **MGGA (RPP09)** (red line)
The concept of the exchange-correlation kernel $f_{xc}$

\[
\chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} - f_{xc}(\mathbf{r}, \mathbf{r}', \omega),
\]

\[
f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta v_{xc}(\mathbf{r}, \omega)}{\delta n_1(\mathbf{r}', \omega)}.
\]

(23)

- $f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = 0$: RPA;
- $f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}, \mathbf{r}', \omega = 0)$: Adiabatic TDDFT:
  - Adiabatic LDA: $f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}^{LDA}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} = \frac{d^2 E_{xc}^h(n)}{dn^2} \bigg|_{n=n_0(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}');$
  - Adiabatic MGGA: $f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}^{MGGA}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$. 
\[ E_{xc} = \int \varepsilon_{xc}[n_0(r), \nabla n_0(r), \tau(r)] dr, \quad (24) \]

\[ v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} = \frac{\partial \varepsilon_{xc}}{\partial n}(r) - \nabla \frac{\partial \varepsilon_{xc}}{\partial \nabla n}(r) + \int \frac{\partial \varepsilon_{xc}}{\partial \tau}(r') \frac{\delta \tau(r')}{\delta n(r)} dr'. \quad (25) \]

And sorry for the upcoming Eq. (26) ...
\[ f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \]
\[ = \frac{\partial^2 \varepsilon_{xc}}{\partial n^2}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') - \left[ \nabla \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \nabla n}(\mathbf{r}) \right] \delta(\mathbf{r} - \mathbf{r}') - \nabla_i \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla_i n \partial \nabla_j n}(\mathbf{r}) \nabla_j \delta(\mathbf{r} - \mathbf{r}') \\
+ \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \tau}(\mathbf{r}) \frac{\delta \tau(\mathbf{r})}{\delta n(\mathbf{r}')} + \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \tau}(\mathbf{r}') \frac{\delta \tau(\mathbf{r}')}{\delta n(\mathbf{r})} \\
- \nabla \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla n \partial \tau}(\mathbf{r}) \frac{\delta \tau(\mathbf{r})}{\delta n(\mathbf{r}')} \nabla' \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla' n \partial \tau}(\mathbf{r}') \frac{\delta \tau(\mathbf{r}')}{\delta n(\mathbf{r})} + \int \frac{\partial^2 \varepsilon_{xc}}{\partial \tau^2}(\mathbf{r}'') \frac{\delta \tau(\mathbf{r}'')}{\delta n(\mathbf{r})} \frac{\delta \tau(\mathbf{r}'')}{\delta n(\mathbf{r}')} d\mathbf{r}'' \\
+ \int \frac{\partial \varepsilon_{xc}}{\partial \tau}(\mathbf{r}'') \frac{\delta^2 \tau(\mathbf{r}'')}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \ dn(\mathbf{r}') \]
\[ (26) \]

which is the ‘exact’ adiabatic MGGA \( f_{xc} \) (Nazarov & Vignale, 2011).
Since
\[ \sigma(q, \omega) = \frac{i\omega}{q^2} \frac{\chi_s(q, \omega)}{1 - \chi_s(q, \omega) f_{xc}(q, \omega)}, \quad \text{and} \quad \chi_s(q, \omega) \xrightarrow{q \to 0} \text{const} \times q^2, \]
(27)
we need
\[ f_{xc}(q, \omega) \xrightarrow{q \to 0} \frac{\alpha}{q^2}, \quad \text{with} \quad \alpha \neq 0. \]
(28)

True for MGGA!
Wrong for LDA & GGA

Main approximation to Eq. (26)
\[ f_{xc}(q) \approx -\frac{\partial \epsilon_{xc}}{\partial \tau} \chi_s^{-1}(q), \]
(29)
\[ \alpha = -\frac{\partial \epsilon_{xc}}{\partial \tau} \lim_{q \to 0} q^2 \chi_s^{-1}(q). \]
(30)
Dielectric function of diamond structure and zincblende semiconductors (Nazarov & Vignale, 2011).
MGGA-TDDFT for Dirac’s massless electrons

With VS98 MGGA xc functional (Voorhis & Scuseria, 1998)

The key quantity

\[
\frac{\partial \varepsilon_{xc}}{\partial \tau} = \begin{cases} 
  +0.024 \text{ (negligible)} & \text{Graphene,} \\
  -0.18 & \text{Ca}_3\text{PbO.}
\end{cases}
\]
The Elk FP-LAPW Code

An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code with many advanced features. Written originally at Karl-Franzens-Universität Graz as a milestone of the EXCITING EU Research and Training Network, the code is designed to be as simple as possible so that new developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

Latest version: 1.3.31

Features

- High precision all-electron DFT code
- FP-LAPW basis with local-orbitals
- APW radial derivative matching to arbitrary orders at muffin-tin surface (super-LAPW, etc.)
- Arbitrary number of local-orbitals allowed (all core states can be made valence for example)
- Every element in the periodic table available
- Total energies resolved into components
- LSDA and GGA functionals available
- Core states treated with the radial Dirac equation
- Simple to use: just one input file required with all input parameters optional
- Multiple tasks can be run consecutively

Structure and symmetry

- Determination of lattice and crystal symmetry groups from input lattice and atomic coordinates
- Determination of atomic coordinates from space group data (with the Spacegroup utility)
- XCrysDen and V_Sim file output
- Automatic reduction from conventional to primitive unit cell
- Automatic determination of muffin-tin radii
- Full symmetrisation of density and magnetisation and their conjugate fields
- Automatic determination and reduction of the k-point set

Magnetism

The Elk FP-LAPW code (http://elk.sourceforge.net) was used with our implementation of meta-GGA.
Conclusions

• For systems supporting Dirac’s massless electrons, TDDFT represents an attractive alternative to both the tight-binding model and many-body perturbation theory;

• We have applied our recently developed meta-GGA-based TDDFT to 2D (graphene) add 3D (Ca$_3$PbO) systems;

• We have found the static and dynamic many-body interaction effects negligible for the former and appreciable for the latter.


