Band-structure of graphene above the vacuum level

Vladimir U. Nazarov

Research Center for Applied Sciences, Academia Sinica
Taiwan

In collaboration with:
Eugene Kogan, Bar-Ilan University, Ramat-Gan, Israel;
Vyacheslav Silkin, Eugene Krasovskii, Donostia International Physics Center, San Sebastian, Spain.
Ab initio band-structure of graphene.
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Motivation

Repeated geometry calculation:
Are spurious bound-states introduced?
In the case of a potential well in $z$ direction and a uniform potential in $xy$ plane, two perpendicular motions decouple.

Therefore, states **bound in** $z$ direction, may have arbitrarily large energy due to the lateral motion of an electron.

Does this change and how if a laterally periodic potential is applied?
Obviously, the in-plane and the perpendicular motions do couple in the presence of a periodic lateral potential.

We consider a model system with the potential

\[ V(r) = V(r_\parallel) \times \delta(z), \]  

(1)

where \( V(r_\parallel) \) is a 2D periodic function. By Fourier transform

\[ V(r_\parallel) = \sum_G V_G e^{iG \cdot r_\parallel}. \]  

(2)

\( V_0 \) is chosen negative to ensure the existence of a bound-state in \( z \) direction.
We are solving the single-particle Schrödinger equation

\[
\left[-\frac{1}{2} \Delta + V(\mathbf{r}_\parallel) \delta(z) \right] \psi(z, \mathbf{r}_\parallel) = E \psi(z, \mathbf{r}_\parallel).
\]  

(3)

Solutions localized near and continuous across the \( z = 0 \) plane are

\[
\psi(z, \mathbf{r}_\parallel) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{-\sqrt{(G+k)^2 - 2E} |z|} e^{i(G+k) \cdot \mathbf{r}_\parallel}
\]

(4)

where \( a_{\mathbf{G}} \) satisfy the system of linear equations

\[
\sum_{\mathbf{G}'} V(\mathbf{G} - \mathbf{G}') a_{\mathbf{G}'} = -\sqrt{(G+k)^2 - 2E} a_{\mathbf{G}}.
\]  

(5)

Eqs. (5) constitute a non-linear eigenvalue problem with respect to the eigenvalue \( E \).
Stand-alone vs. repeated geometry

Stand-alone 2D-periodic layer.

Repeated geometry representation.

Bound-states above the vacuum level are resolved inside the continuous spectrum. Price: Non-linear eigenvalue problem.

Continuous spectrum and bound-states are intermixed above the vacuum level. Conventional (linear) eigenvalue problem.
An important exact property of the model

\[ \sum_{G'} V(G - G') a_{G'} = -\sqrt{(G + k)^2 - 2E} a_G. \]  

(6)

First, if \( E > (G + k)^2/2 \) with an arbitrary \( G \) then the eigenvalue problem involves complex matrix elements. We, however, prove the following Lemma:

**Lemma**

*The problem (6) admits no resonance solutions, i.e., all the eigenvalues \( E \) are real.*

**Proof.**

\[ \sum_{G'} a_{G'}^* V(G - G') a_{G'} = -\sum_{G} \sqrt{(G + k)^2 - 2E} |a_G|^2. \]  

(7)
We are numerically solving the non-linear eigenvalue problem

\[ \sum_{G'} B_{G,G'}(E) a_{G'} = a_G, \]  

where

\[ B_{G,G'}(E) = -\frac{V(G - G')}{\sqrt{(G + k)^2 - 2E}}. \]  

The eigenvalue of matrix $B$ as a function of $E$. 
Model band-structure of a single periodic layer (red points) and layers in repeated-geometry (blue lines).
Projection on the *ab initio* graphene problem

$\psi(z)$

$\Gamma K M \Gamma$

Energy (eV)

0 200 400

$|\psi(z)|^2$

$z$ (bohr)

0 200 400

$z$-dependence of the wave-functions of the states above the vacuum level obtained in the repeated geometry calculation.
• Our analysis shows that the graphene band-structure is affected drastically by the possibility for an electron above the vacuum level to escape from the layer;
• Whether or not at a particular $k$ point a state above the vacuum level is bounded to the graphene layer is determined by the symmetry of that point.