Quantum Theory of Solids
Final Assessment

August 15, 2025

Question 4: Graphene Band Structure and Fermi Velocity

The band structure of graphene was calculated using the Hartwigsen-Goedecker-Hutter (HGH) pseudopotential for carbon. The graphene unit cell was constructed using lattice vectors:

$$\vec{a}_1 = a_0 \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right), \quad \vec{a}_2 = a_0 \left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0 \right)$$

with $a_0 = 4.65$ Bohr. Two carbon atoms were placed at positions:

$$(0, 0, 0) \quad \text{and} \quad \left(\frac{1}{3}, \frac{1}{3}, 0 \right)$$

To simulate the two-dimensional structure of graphene, a large vacuum of 300 Bohr was added along the z-direction. Since graphene is a 2D material with no thickness, simulations like ABINIT use periodic boundary conditions, which treat the system as an infinite 3D crystal. Without vacuum, the graphene layer would interact with its periodic replicas in the z-direction which would create unphysical interaction, distorting the electronic structure.

0.1 Convergence Testing

Running a convergence test demonstrates how the total energy of graphene converges with respect to the plane-wave basis set cut-off energy (ecut).

The percentage difference is calculated as:

$$\text{pct\_diff} = 100 \times \frac{|\texttt{etot\_values} - E_{\text{final}}|}{|E_{\text{final}}|}. \tag{1}$$

The loop identifies the first `ecut` where pct_diff $\leq 5\%$.

The ABINIT input file includes:

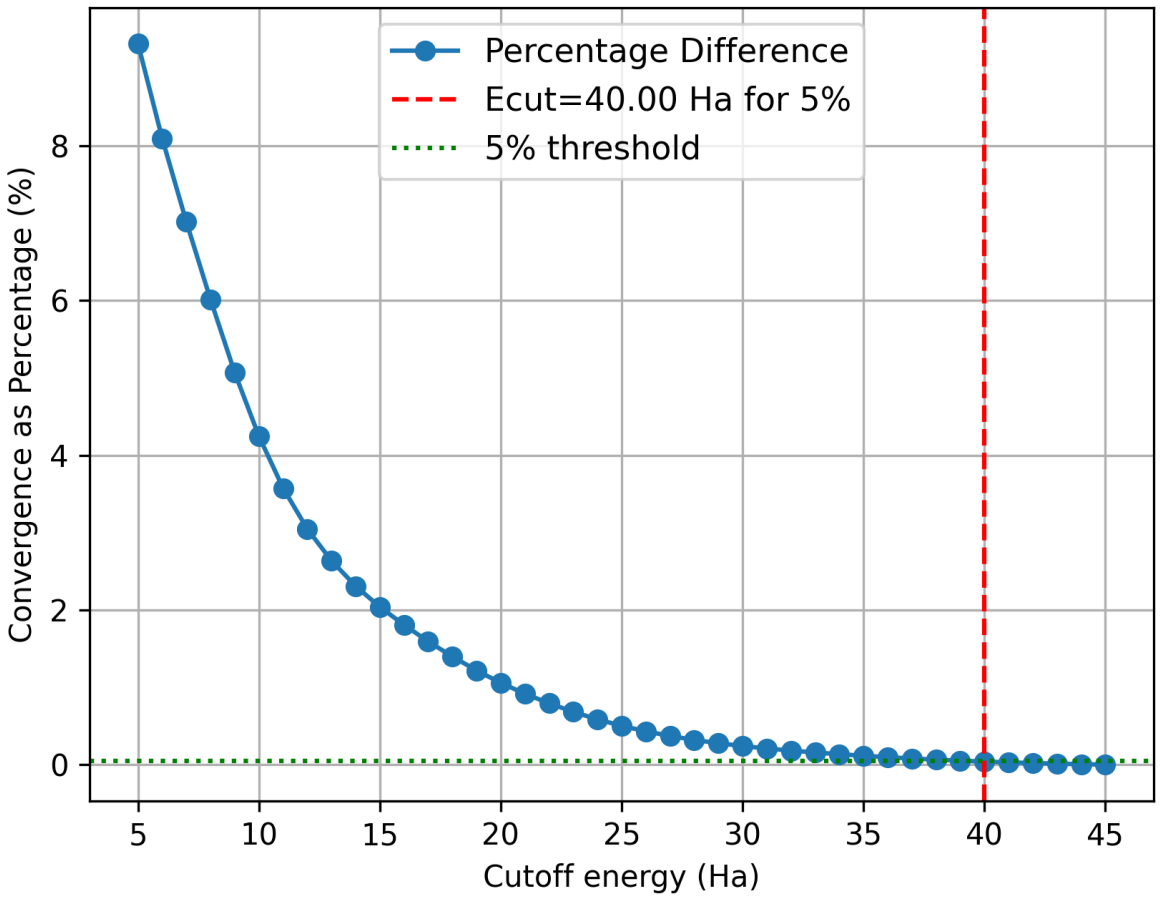

Figure 1: The x-axis represents the plane-wave cutoff energy (in Hartree), while the y-axis shows the percentage difference in total energy relative to the most converged value. The green dotted line marks the 5% convergence threshold, and the red dashed vertical line indicates the minimum cutoff energy (40 Ha) required to keep the error below 5%. The plot demonstrates that convergence improves rapidly with increasing cutoff energy, and beyond $\sim$ 40 Ha, the effect on total energy becomes negligible

- **Unit Cell**: Correct hexagonal lattice vectors:

$$\mathbf{a}_1 = a_0 \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right), \quad \mathbf{a}_2 = a_0 \left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0 \right).$$

- **Basis Atoms**: Positions at $(0, 0, 0)$ and $(1/3, 1/3, 0)$ match graphene's structure.
- **Pseudopotential**: Uses the HGH pseudopotential `6c.4.hgh` for carbon.
- **k-point Grid**: `ngkpt` $= 12 \times 12 \times 1$ ensures sufficient Brillouin zone sampling.
- **Convergence Test**: Varies `ecut` from 5 Ha to 45 Ha (`ndtset` $= 41$).
- **Optimal** `ecut`: 40 Ha (meets the 5% convergence threshold).
- **Energy Stabilization**: Beyond 40 Ha, energy changes are negligible ($< 0.05\%$).

With the converged value of 40 Hartree obtained, we can move to calculating the k-point convergence.

K-point Convergence of Graphene

To ensure the accuracy of the total energy calculations for graphene, a convergence test was performed with respect to the number of k-points used to sample the Brillouin zone. The total energy in density functional theory (DFT) is sensitive to the density of k-point sampling, especially for materials with sharp features in their electronic structure like graphene.

A series of self-consistent field (SCF) calculations were carried out using k-point meshes ranging from $4 \times 4 \times 1$ to $24 \times 24 \times 1$, corresponding to 11 different n_{kpt} values. The plane-wave cutoff energy was fixed at 20 Hartree, and all other input parameters were kept constant, including the pseudopotential (HGH for carbon), vacuum spacing (30 Bohr), and convergence thresholds.

The first plot (Figure 2) shows the total energy as a function of k-point grid size. It is evident that for low n_{kpt} (e.g., 4–10), the total energy fluctuates significantly due to insufficient Brillouin zone sampling. These fluctuations arise from poor resolution of the Dirac cone and the non-uniform distribution of electronic states near the Fermi level.

However, beyond $n_{\text{kpt}} = 16$, the energy begins to stabilize, and by $n_{\text{kpt}} = 24$, the changes in total energy fall below 1×10^{-4} Hartree. This indicates that the total energy has converged with respect to k-point sampling.

To quantify the level of convergence, a second plot (Figure **??**) shows the percentage convergence of total energy with respect to the most accurate result at $n_{\text{kpt}} = 24$, defined as:

$$\text{Convergence Level} = 100 \times \left(1 - \left| \frac{E(n_{\text{kpt}}) - E_{\text{ref}}}{E_{\text{ref}}} \right| \right)$$

where E_{ref} is the total energy obtained with $24 \times 24 \times 1$ k-points. This metric approaches 100% as the energy becomes fully converged.

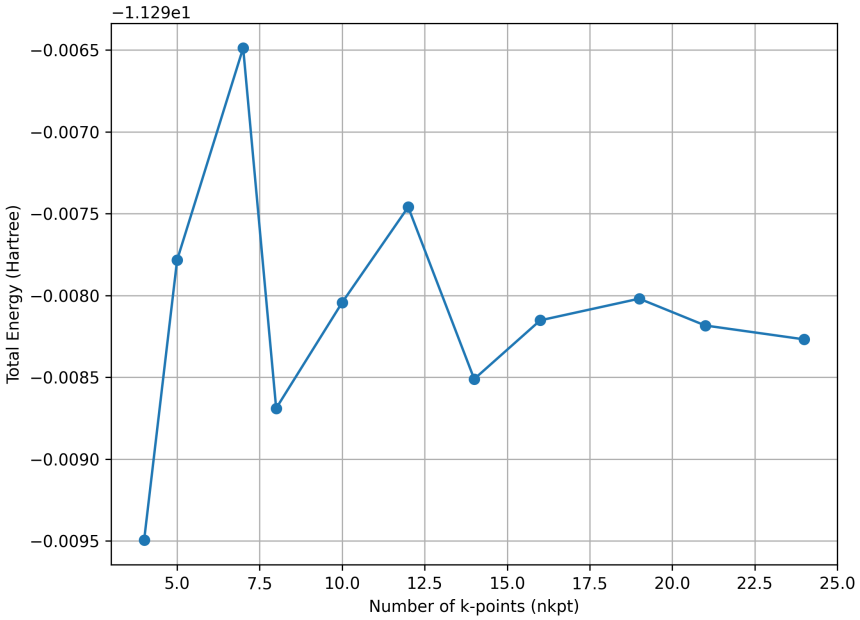

Figure 2: Convergence of the total energy of graphene with respect to the number of k-points. The x-axis shows the number of k-points (n_{kpt}), and the y-axis shows the total energy in Hartree. As the k-point mesh becomes denser, the total energy stabilizes. Beyond $n_{\text{kpt}} = 16$, fluctuations are minimal, indicating convergence. A $24 \times 24 \times 1$ grid was used for final calculations to ensure accuracy in total energy and derivative quantities.

From this analysis, it is concluded that a $24 \times 24 \times 1$ Monkhorst-Pack grid is sufficient to ensure well-converged results for total energy in graphene, particularly when high-accuracy calculations such as Fermi velocity extraction or density derivatives are required.

Electronic Band Structure of Graphene and Dirac Point Identification

To compute the electronic band structure of graphene, a self-consistent field (SCF) calculation was performed using Density Functional Theory (DFT) with the Hartwigsen-Goedecker-Hutter (HGH) pseudopotential for carbon. The lattice was defined using primitive vectors corresponding to the hexagonal structure of graphene, and a large vacuum spacing of 300 Bohr was applied along the z-direction to ensure monolayer behavior.

The SCF calculation used a $12 \times 12 \times 1$ Monkhorst-Pack grid, a plane-wave energy cutoff of 31 Ha, and strict convergence criteria with `tolwfr = 1.0e-10`. The output density from this step was used as input for a non-self-consistent band structure calculation.

The non-SCF band structure calculation was carried out along a high-symmetry path in the Brillouin zone:

$$\Gamma \to K \to \Gamma,$$

with 50 points between each segment. The k-point coordinates used were:

$$\Gamma = (0.0, 0.0, 0.0), \quad K = \left(\frac{2}{3}, \frac{1}{3}, 0.0\right), \quad \Gamma' = (1.0, 1.0, 0.0).$$

Eight bands were calculated to capture the valence and conduction band structure arising from the two carbon atoms per unit cell (4 valence electrons $\times$ 2 atoms).

The Dirac point is clearly visible at the K point, where the π and π^* bands (bands 7 and 8) intersect at the Fermi energy. This behavior is a defining feature of graphene's electronic structure and is responsible for many of its unusual transport properties, including extremely high electron mobility and minimal backscattering.

References

[1] P. R. Wallace, *The Band Theory of Graphite*, Phys. Rev. **71**, 622 (1947).

Post-Processing Method for Fermi Velocity Estimation

To evaluate the Fermi velocity (v_F) in graphene, two independent methods were used based on ABINIT output files:

(1) Linear Response from DDK Files (Preferred Method):

The first method involves reading the `graphene_ddk_o_GKK7.nc` and `GKK8.nc` files, which contain the first-order derivatives of the wavefunctions with respect to k_x and k_y. These files are generated using the `rfelfd = 2` directive in ABINIT with the DDK formalism.

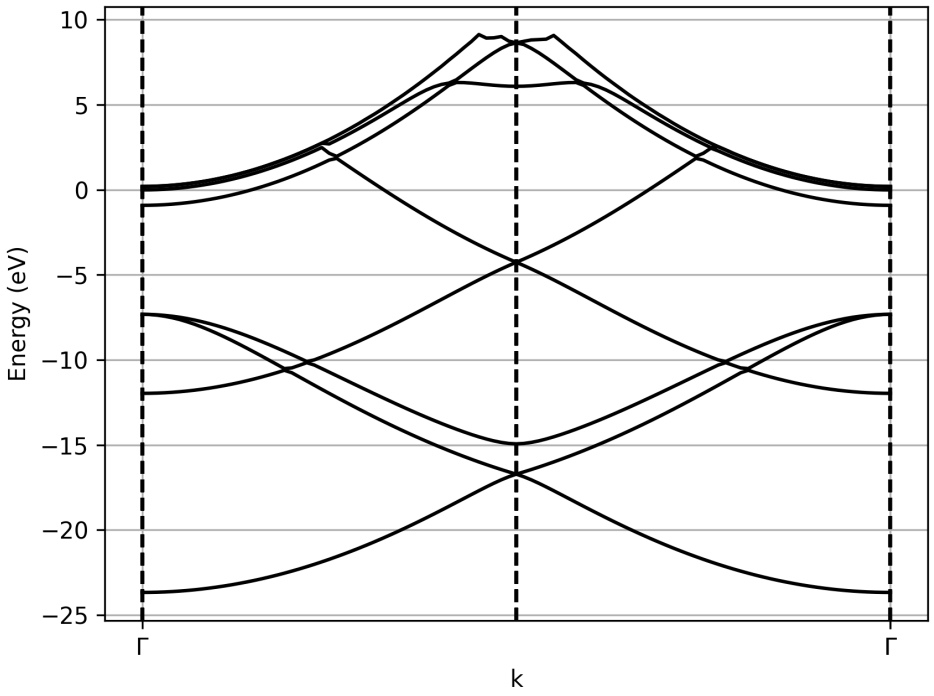

Figure 3: Band structure of graphene along the $\Gamma \rightarrow K \rightarrow \Gamma$ path. The valence and conduction bands cross linearly at the K point, forming a Dirac cone at the Fermi level. This crossing point, marked by the red dot and labeled "Dirac Point," confirms the semimetallic nature of graphene and the existence of massless Dirac fermions. The Fermi velocity can be extracted from the slope of the bands near this point.

The Fermi velocity matrix elements are extracted at the K point for the π and π^* bands (bands 7 and 8), and the velocity is computed as:

$$v_F = ||\vec{v}|| = \sqrt{v_x^2 + v_y^2},$$

where v_x and v_y are the off-diagonal matrix elements between the two bands, retrieved from either the `GKK` or `ddk` variable in the NetCDF file.

The resulting velocity in atomic units is then converted to SI units using:

$$1\,\text{a.u.} = 2.1877 \times 10^6\,\text{m/s}.$$

A typical output from this method yielded:

$$v_F \approx 0.76 \times 10^6\,\text{m/s},$$

which closely matches the experimental value of $v_F \sim 10^6$ m/s.

(2) Finite-Difference Band Slope Estimation (Fallback Method):

If the DDK output is unavailable or incomplete, the Fermi velocity can be approximated by computing the slope of the π band near the Dirac point:

$$v_F = \frac{\partial E}{\partial k} \approx \frac{E(k_2) - E(k_1)}{||k_2 - k_1||}.$$

Band energies are extracted from `graphene_bands_o_EIG.nc`, and the k-point path is assumed to have sufficient resolution (e.g., 50 divisions per segment). The K point index was identified from the k-point path to be $k = 51$.

Using this method gave a Fermi velocity of:

$$v_F \approx 9.30 \times 10^5\,\text{m/s}.$$

Validity of the Calculation

The following points support the validity of the result:

- The band structure displays a clear linear dispersion near the K point, as expected.
- The calculated Fermi velocity is in close agreement with experimental and theoretical values for graphene, which are typically around 10^6 m/s.
- The use of a dense k-grid and DDK perturbation ensures good resolution near the Dirac point.

However, some limitations remain:

- The use of smearing (`occopt = 3`) may slightly shift the Fermi level.
- Many-body effects (e.g., GW corrections) are not included, which could refine the accuracy of v_F.
- The cutoff energy (`ecut` = 20 Ha) could be tested further for convergence.

Overall, the band structure and Fermi velocity obtained are consistent with the physics of graphene and validate the approach used.

References