



Atomistic Simulations of Materials

A Density Functional Approach To Computational Solid State Physics
Using Quantum ESPRESSO

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Why Density Functional Theory for Computation?

1. The goal of this research is to understand the physical properties of 2-dimensional materials like graphene and simple molecules like NH₃ and H₂O using computational tools like Quantum ESPRESSO which is based on density functional theory.
2. It is not always possible to synthesise a material in the lab to understand its properties. Feasibility, cost, time, and safety are some restrictions. We can simulate the material to get an excellent understanding and synthesise it if needed. Computational methods also allow the prediction of novel materials.
3. It is imperative to develop a powerful computational tool which is reliable and thus DFT was born.

History Behind 60 Years of Density Functional Theory

The ENIAC was the earliest use of computers in physics, used to calculate artillery trajectories and nuclear fusion reactions during the Manhattan Project. It has been a matter of great interest to solve complex problems computationally.

Before Walter Kohn, computational tools like Fermi's approach, Hartree's method or Hartree-Fock's method to simulate materials were plagued with enormous computational time with large errors. These methods were too simplistic and did not represent the physical reality accurately. His work with Pierre Hohenberg and Lu Sham put DFT on firm theoretical grounds and also won him the 1998 Nobel Prize in Chemistry.

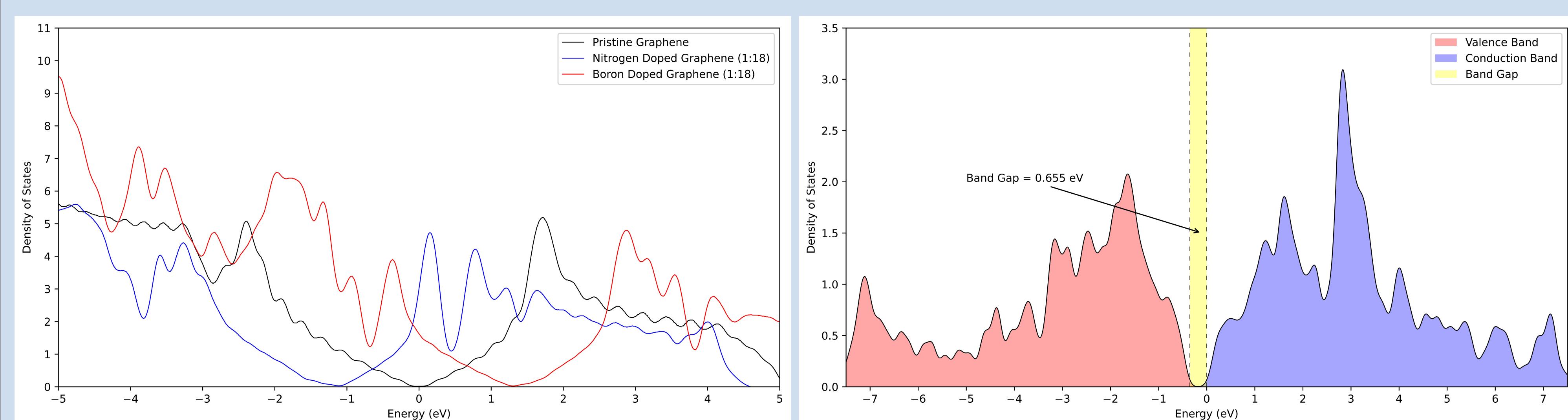
How Good Is Density Functional Theory?

With KS-DFT and standard PBE functional, the properties of some substances were calculated.

Substance	Property	Simulated Value	Experimental Value	Error
Crystalline Si	Band Gap	0.655 eV	1.12 eV	- 41.51%
	1 st Order Raman Peak	493 cm ⁻¹	520.2 cm ⁻¹	- 5.80%
H ₂ O	Bond Length	0.9756 Å	0.9584 Å	+1.79%
	Bond Angle	104.10°	104.45°	- 0.34%
H ₂	Bond Length	0.7495 Å	0.7414 Å	+1.09%
	Dissociation Energy	431.65 kJ/mol	430.53 kJ/mol	+0.26%
NH ₃	Bond Length	1.0227 Å	1.0124 Å	+1.02%
	Bond Angle	106.612°	106.670°	- 0.05%
	Inversion Barrier	0.2285 eV	0.2496 eV	+8.45%

Using hybrid functionals and fully relativistic pseudopotentials, more accurate estimates can be found but this drastically increases computational time. Errors can be brought to less than 1% this way but computation will take several weeks on a HPC cluster.

Visualisation of Computed Data



Acknowledgements

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Complete Project Report

A comprehensive project report is linked here.



References

- [1] P. G. et al. Quantum ESPRESSO: A Modular and Open-Source Software Project For Quantum Simulations Of Materials. *Journal of Physics: Condensed Matter*, 21(39):395502 (19pp), 2009.
- [2] P. G. et al. Advanced Capabilities For Materials Modelling With Quantum ESPRESSO. *Journal of Physics: Condensed Matter*, 29(46):465901, 2017.

Physics Behind DFT

In quantum mechanics, all physical information is contained in the wavefunction $\Psi(\mathbf{r}, t)$. Given a potential function, solve for $\Psi(\mathbf{r}, t)$ using Schrödinger's equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left(\frac{i^2 \hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t).$$

But potential function can not be written in a closed form for any arbitrary system like an electron in a crystal. Potentials are approximated. Schrödinger's approach can be summarised as:

$$v(\mathbf{r}) \xrightarrow{\text{SE}} \Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N) \xrightarrow{\langle \Psi | \dots | \Psi \rangle} \text{observables.}$$

In DFT, focus is shifted from $\Psi(\mathbf{r}, t)$ to ground state electron density $n(\mathbf{r})$.

$$n(\mathbf{r}) = N \iiint \dots \int \Psi^* \Psi d^3 \mathbf{r}_1 \dots d^3 \mathbf{r}_N$$

Ground state Ψ is a unique *functional* of $n(\mathbf{r})$.

Hohenberg-Kohm Theorems

1. The ground state expectation value of any observable \hat{O} is a functional of the ground state electron density, $n(\mathbf{r}_0)$.

$$O_0 = O[n_0] = \langle \Psi[n_0] | \hat{O} | \Psi[n_0] \rangle$$

2. The density which minimises the total energy is the exact ground state energy.

$$E_{\nu,0} = E_{\nu}[n_0] = \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle$$

In DFT, the total energy is a functional of electron density $\rho(\mathbf{r})$

$$E_{\text{total}}[\rho] = T_s[\rho] + E_{\text{ext}}[\rho] + E_H[\rho] + E_{xc}[\rho]$$

Computational Algorithm in DFT

