Computational Modeling Module: Electronic Band Structure Calculations
MSE 410, 10/03 & 10/5

Learning Outcomes and Topics

Learning outcomes:
- Get familiar with density functional theory (DFT) and simulation procedure.
- Prepare their own computational modeling input files.
- Apply the DFT simulation method to calculate band structure and explore band gap and alignment.
- Determine "physical validity" of calculation by comparing the simulated band diagram to what has been published in the literature.

What to simulate:
- Materials: Graphene with point defects and dopants
- Band Structure
- Electronic band engineering to control band gap size and alignment

Assessment:
- Reading HW
- Modeling HW

Reading / Self-Studying Resources

- Video # 1: Intro to Computational Modeling https://www.youtube.com/watch?v=4J6aStfuJAU

- Video # 2: Input Parameters for SIESTA Simulation https://www.youtube.com/watch?v=AVkQkNpzxio

- Must-remember notes for DFT

- LeSar Chapter 4 Electronic Structure Methods

- I will grade your reading HW and return to you in the next class.

nanoHUB

- Register at https://nanohub.org/register/
- Login to your account
- On "My Tools", select "MIT Atomic Scale Modeling Toolkit" as your "Favorites" tool.
- Launch "MIT Atomic Scale Modeling Toolkit" to run SIESTA

Semiconductor Band Gaps

Material	Energy gap (eV)	
	0K	300K
Si	1.17	1.11
Ge	0.74	0.66
InSb	0.23	0.17
InAs	0.43	0.36
InP	1.42	1.27
GaP	2.32	2.25
GaAs	1.52	1.43
GaSb	0.81	0.68
CdSe	1.84	1.74
CdTe	1.61	1.44
ZnO	3.44	3.2
ZnS	3.91	3.6

Use your laptop to search the answers of the following questions:

Q1. Why do we care about band gap?

Q2. In a band structure, what other features are as important as a band gap? What can they tell you?

Q3. What is graphene? Why is graphene of research interest in the electronic area?

Q4. Why are creating defects and doping of research interest?

Paper "Electronic and Structural Distortions in Graphene Induced by Carbon Vacancies and Boron Doping" by *Faccio et al.*

- Read abstract, introduction (I), methods (II), single-atom vacancies on graphene (III.i),boron-doped graphene (III.ii), and conclusions (IV).
- Re-answer the following questions:
  - Q1. Why do we care about band gap?
  - Q2. In a band structure, what other features are as important as a band gap? What can they tell you?
  - Q3. What is graphene? Why is graphene of research interest in the electronic area?
  - Q4. Why are creating defects and doping of research interest?

Hands-on Practice

- Repeat the band structure calculations in Figure 5(a) and compare your results to the paper.
- Increase B dopant concentration in graphene

    Analyze how the band structure changes

- Create one vacancy in graphene and then move it to different sites

    Analyze how the band structure changes

- Increase vacancy concentration in graphene

    Analyze how the band structure changes

Key DFT Parameters to Calculate Band Structure

1. XC Functional (Exchange-Correlation Functional)

$$\hat{H}(r)\psi(r) = E\psi(r)$$

- ➤ Simplify *n*-electron (interacting) system to a **1-electron (non-interacting) system plus an external energy** – includes all corrections
- ➤ All **energy terms** (kinetic energy, interaction energy, etc.) written as **functions of electron density**

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Method: Local density approximation (LDA) or Generalized gradient approximation (GGA)
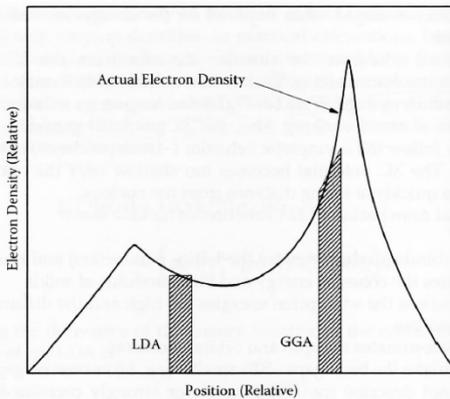
$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r)\varepsilon_{xc}^{hom}[\rho(r)]dr$$

$$E_{xc}^{GGA}[\rho(r), s] = \int \rho(r)\varepsilon_{xc}^{LDA}[\rho(r)]F(s)dr$$

$$s = C\frac{|\nabla\rho(r)|}{\rho^{\frac{4}{3}}(r)}$$

2. Basis Set – Just need to know

$$\phi_i = \sum_r c_{ri}\chi_r$$

- Basis set is used to determine wave function, Ψ.

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n$$

- SIESTA uses a linear combination of atomic orbitals basis set.
- A larger or more complicated basis set leads to a more accurate simulation, but it takes a longer computational time.
- In SIESTA, single zeta (SZ) is a minimum basis set for some quick simulation tests (but not accurate enough).
- Double zeta (DZ) is more accurate, because it considers the radial flexibility of an atomic orbital.
- DZP, P stands for Polarization (electron spin effect). It considers the angular flexibility of an atomic orbital.
- Choosing DZP as a basis set is accurate enough for any simulations.
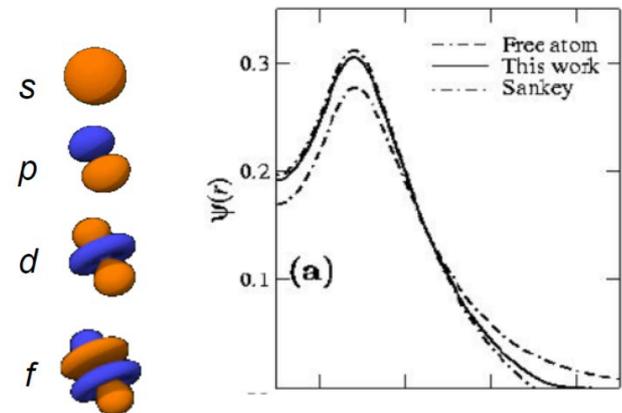
Basis set requirements in SIESTA:

- Basis functions have to be atomic-like (radial functions mutiplied by spherical harmonics)

https://en.wikipedia.org/wiki/Radial_basis_function

- They have to be of finite support, i.e., each orbital **becomes strictly zero** beyond some cutoff radius chosen by the user.

Strictly localised

(zero beyond cut-off radius)

Show Pseudo-Fe example

3. Mesh cutoff – Just need to know

- In SIESTA, mesh cutoff is an energy (default 100 Ry), which corresponds to a finite 3D grid for the calculation of electron density ρ(r) and potentials.

- Note that electron density is a function of position. We need to define the spacing of this 3D grid to map the electron density.

- Larger mesh cutoff ⇒ smaller spacing ⇒ more dense 3D mesh ⇒ more accurate simulation but longer computational time.

k-Point Density / Sampling in Brillouin Zone

Any point in the Irreducible Brillouin zone can represent a *k*-point, there are an infinite number of discrete *k*-vectors well qualified to be a wave function. The wave function and other properties vary smoothly over the IBZ, so we can just sample a finite number of *k*-points that represent each small region.

Choose k-points:
- Big system vs. small system
- Isolated molecule
- Symmetric system

Brillouin zone & k-point sampling

Go through
http://www.doitpoms.ac.uk/tlplib/brillouin_zones/intro.php

- Introduction
- Reciprocal lattice vectors
- Brillouin zone construction
- The general case in three dimensions
- Zone folding
- Examples of Brillouin Zones in three Dimensions

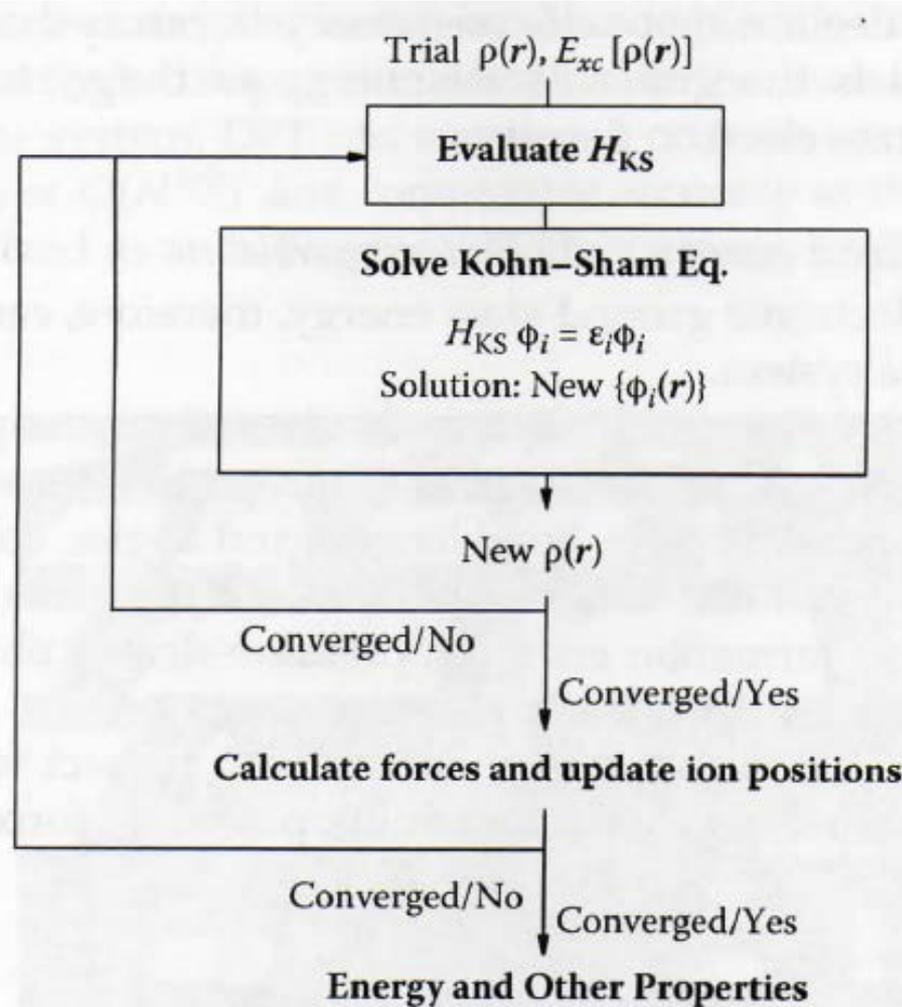| System	Symbol	Description
All	Γ	Center of the Brillouin zone
SC	H	Corner point joining four edges
(simple	N	Center of a face
cubic)	P	Corner point joining three edges
FCC	K	Middle of an edge joining two hexagonal faces
(face-	L	Center of a hexagonal face
centered	U	Middle of an edge joining a hexagonal and a square face
cubic)	W	Corner point
	X	Center of a square face
HCP	A	Center of a hexagonal face
(hexagonal	H	Corner point
close	K	Middle of an edge joining two rectangular faces
packed)	L	Middle of an edge joining a hexagonal and a rectangular face
	M	Center of a rectangular face

Each k-point contains rich information:

- k vector, wave length ($\lambda = 2\pi/k$), and kinetic energy ($E = k^2/2$).

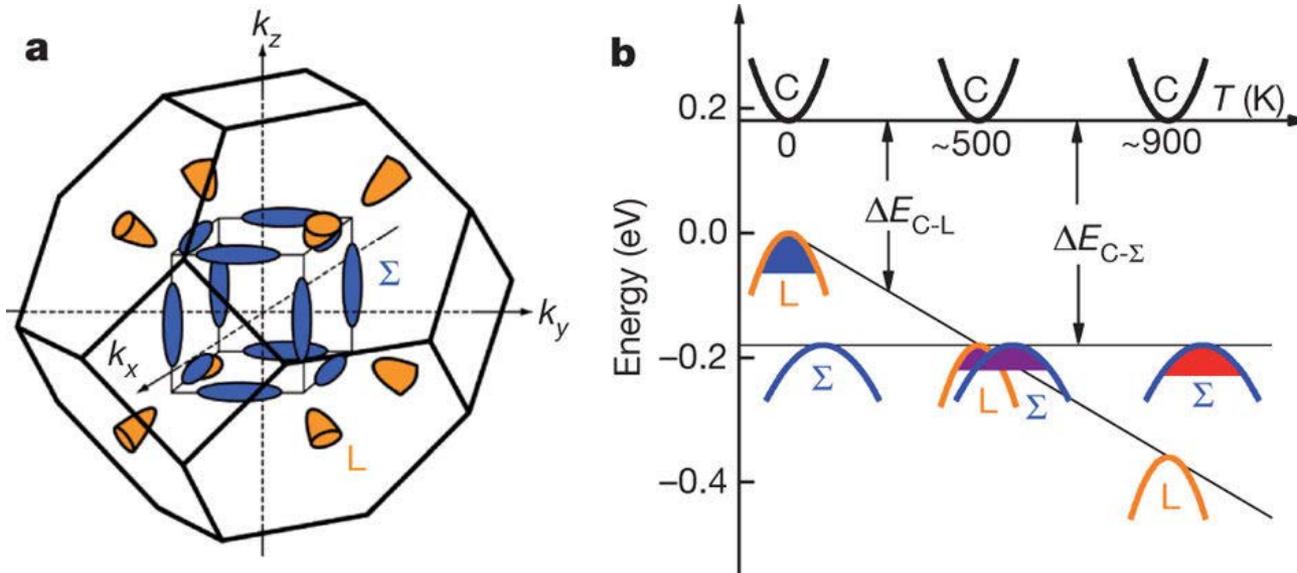- All the incoming energies on each k-point, it will form band structure.

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

What Does SIESTA Do?

$$\rho(r) = 2 \sum_{i}^{occ} |\phi_i(r)|^2$$

Trial $\rho(r)$, $E_{xc}[\rho(r)]$

Evaluate H_{KS}

Solve Kohn–Sham Eq.

$$H_{KS} \phi_i = \varepsilon_i \phi_i$$

Solution: New $\{\phi_i(r)\}$

New $\rho(r)$

Converged/No

Converged/Yes

Calculate forces and update ion positions

Converged/No   Converged/Yes

Energy and Other Properties

Convergence of Electronic Band

Band convergence $\Rightarrow$ Increase of Seebeck coefficient and electrical conductivity

- Seebeck coefficient: a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across the material

- Electrical conductivity: the degree to which a specified material conducts electricity, calculated as the ratio of the current density in the material to the electric field that causes the flow of current. It is the reciprocal of the resistivity.

Take-Home Exercise

- Literature review:
  - What other point defects and dopants in graphene are of research interest?
  - Why?
  - Any potential applications?

- Modeling HW (Email to me lanli@boisestate.edu by Fri, Oct 13)

Based on what you find in literature:
  - Choose one defect and one dopant
  - Calculate band structure as defect / dopant concentration changes
  - Analyze your results
  - Write a two-page report, including introduction, motivation (why are you interested in that type of defect / dopant), results and discussion (including band structure figures), conclusion, and references