Density Functional Theory. I. Intro
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Quantum Mechanics and Ab Initio Calculations

The big deal in QM and Ab Initio calculations is that we need to know $\psi(r)$.

We find $\psi(r)$ by solving the many-body Schrödinger Equation:

$$\hat{H}\psi = E\psi$$

This has an infinite number of solutions all with different energies

For a multi atom system containing interacting electrons and nuclei:

$$\widetilde{H} = -\frac{1}{2}\sum_{J}\frac{1}{M_J}\nabla^2 - \frac{1}{2}\sum_{j}\nabla^2 + \frac{1}{2}\sum_{j\neq k}\frac{1}{|r_j - r_k|} - \sum_{j,J}\frac{Z_J}{|r_j - R_J|} + \frac{1}{2}\sum_{J\neq K}\frac{Z_J Z_K}{|R_J - R_K|}$$

Quantum Mechanics and Ab Initio Calculations

However, even a single atom contains a nuclei and many electrons. The Wavefunction, $\psi(r)$, gives the

probability of locating all the particles.

This multi-particle $\psi(r)$ can become very complex, especially for heavy atoms.

The general principle for Ab Initio Calculations is simple: apply the Hamiltonian, to $\psi(r)$ to calculate the energy, E, of your atom. Iteratively do this for different arrangements of sub-atomic particles (electrons) until E reaches a minimum.

Density Funtional Theory Theorems

- **First theorem of Density Functional Theory:**
- The ground-state energy from Schrodinger's equation is a unique functional of the electron density.

What is functional?

Function: A function takes a value of a variable or variables and defines a single number from those variables.
Functional: takes a function and defines a single number from the function.

$$F[f] = \int_{-1}^{1} f(x)\, dx,$$

<u>Density Funtional Theory Theorems</u>

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- *So now the ground state energy E at a state is expressed alternatively as E[n(r)], where n(r) is the electron density. And that's the origin of the name: DENSITY FUNCTIONAL THEORY.*

- Electron density is closely linked with the wave function. We can derive that at an unique electron density, the other properties like the energy and the wave function of the ground state are determined. Therefore we can reduce the number of dimensions involved in finding the solution of the Schrodinger equation (i.e. seeking the ground-state energy), from 3N to 3.

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Density Funtional Theory Theorems

- **Second theorem of Density Functional Theory:**
- The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation.

- *The second theorem tells what the functional actually is.*

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Density Funtional Theory Theorems

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- *The second theorem tells what the functional actually is.*
- Write the energy functional in term of the single-electron wave function

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

Density Funtional Theory Theorems

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- *The second theorem tells what the functional actually is.*
- The known term:

$$E_{\text{known}}[\{\psi_i\}] = -\frac{\hbar^2}{m}\sum_i \int \psi_i^* \nabla^2 \psi_i d^3 r + \int V(\mathbf{r})n(\mathbf{r})\, d^3 r$$

$$+ \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3 r\, d^3 r' + E_{\text{ion}}.$$

The terms on the right are, in order, the electron kinetic energies, the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between pairs of electrons, and the Coulomb interactions between pairs of nuclei.

Kohn-Sham Equation

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

- Foundation of DFT

- *A rough algorithm of solving this equation:*
- 1. Give a trial electron density n(r);
- 2. Solve the Kohn-Sham equation defined by the trial electron density to gain the single-particle wave function;
- 3. Calculate the electron density defined by the Kohn-Sham single-particle wave function.
- 4. compare this with trial, if the same, then the density is the ground-state electron density, and the total energy can be computed with the density. If different, the trial density must be updated to back to Step 2.

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More Practical: How do we implement DFT in MSE?

- There are many DFT programs available now for MSE simulations.

- *VASP*
- *CASTEP*
- *WIEN2k*
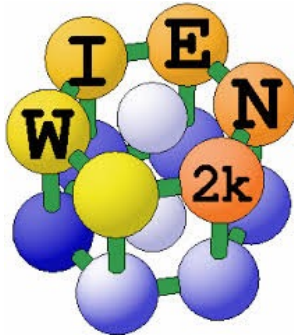
Input files in VASP

- **Position file** (POSCAR)

- **K-point grid file** (KPOINTS)

- **Potential file** (POTCAR)

- **Determines "what to do and how to do it"** (INCAR)

Input files in VASP

- **POSCAR**
- *The file contains the initial configurations (including definition of periodic lattice and ionic positions.)*

Graphene
1.0000000000
2.466900000000 0.000000000000 0.000000000000
1.233450000000 2.136398070000 0.000000000000
0.000000000000 0.000000000000 14.000000000000
C
2
Direct
0.000000000000 0.000000000000 0.500000000000
0.333333333333 0.333333333333 0.500000000000
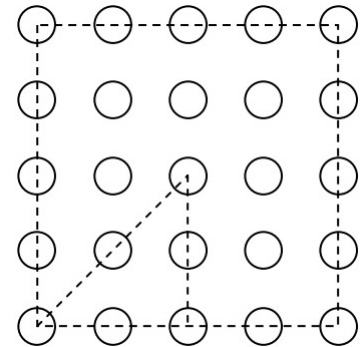

(a)
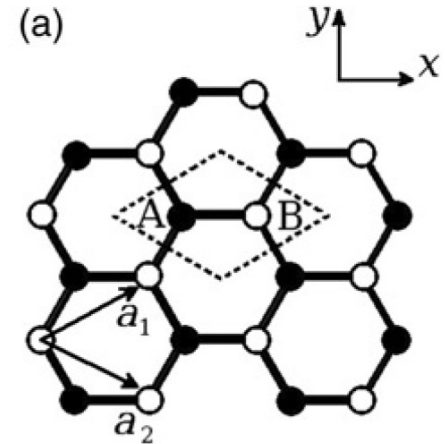
Input files in VASP

- **KPOINTS**
- *Many calculations in crystals involve integration of Bloch wave vector over the entire Brillouin zone or specified portions. To optimize the amount of calculation, it is helpful to compute the integration at a carefully selected set of points in Brillouin zone.*

- *This set of points is k-points.The file KPOINTS contains the k-point coordinates and weights or the mesh size for creating the k-point grid.*

Example of a k-point sampling:
5*5 k-point grid
25 total k-points, but can be reduced to 6 unique points
(the dashed triangle) applying symmetry degeneration.
"Weight": contribution of each unique kpoint to the whole
k-space, in this example, 1 point with weight 1, 4 point
with weight 4, 1 point with weight 8

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Input files in VASP

- **POTCAR**
- *This file contains the parameters for the potential that govern exchange correlation of the interaction charges and the pseudopotentials that control the interactions of core + ions with valence electrons.*
- *There are various types of POTCAR files in the library, classified according to:*
- ***Pseudoization scheme**: ultrasoft pseudopotential and Projector Augmented Wave (PAW) formalism.*
- * **Exchange correlation potential:** local density approximation (LDA) and generalized gradient approximation (GGA).*
- ***Valence states:** extensions pv and sv indicate that p and s semi-core states are treated as valence states.*
- *Value of **ENCUT**: extension s indicates that lower ENCUT value is applied.*

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- ***Valence states:*** *extensions pv and sv indicate that p and s semi-core states are treated as valence states.*
- ***Value of ENCUT***: *extension s indicates that lower ENCUT value is applied.*

Input files in VASP

- **INCAR**
- *INCAR file is the core script of VASP. It contains commands that tells the program 'what to do and how to do it'.*

- *Includes:*
- ***Initializing parameters***
- ***Precision setting***
- ***Criteria for relexation***
- ***Degree of freedom in the cell boundary***
- ***Specific parameters for calculating specific properties (e.g. work function).***

Output files in VASP

- **General outputs and iteration results** (OUTCAR)

- **Output position** (CONTCAR)

- **Charge density** (CHGCAR)

- **Density of states (**DOSCAR)

- **Energy profile (**OSZICAR)

Output files in VASP

- **OUTCAR**
- *OUTCAR presents comprehensive results obtained form a VASP calculation.*

- *Includes:*
- *Volume of the cell*
- *Fermi level*
- *Reciprocal lattice vector*
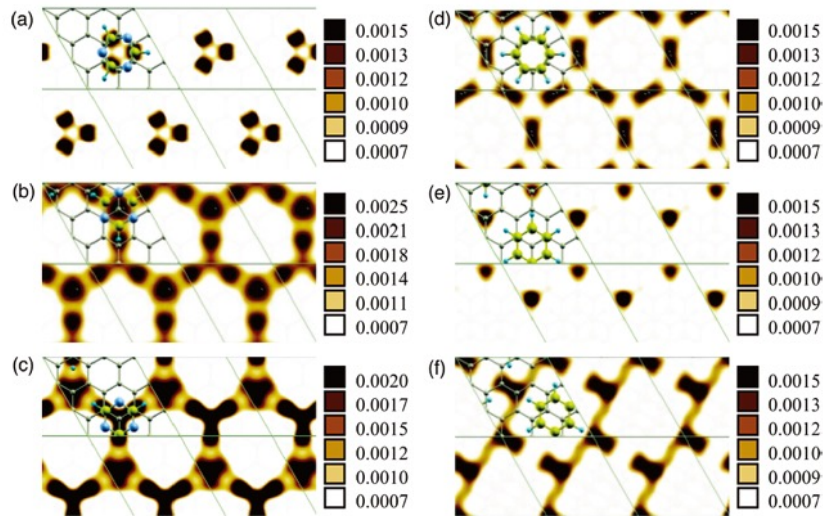- *Force act on atoms*

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Output files in VASP

- **CONTCAR**
- *After each ionic step and at the end of each job a file CONTCAR is written. This file has a valid POSCAR format and can be used for 'continuation' jobs.*

Output files in VASP

- **CHGCAR**
- *CHG and CHGCAR record charge density of the system*

Can be used to conduct analysis on charge transfer in the interface.

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Output files in VASP

- **DOSCAR**
- *DOSCAR file contains information on density of states (DOS) and integrated DOS. The DOS at certain point is defined as the average value of the difference of the integrated DOS between the point and previous one.*

$$n(a_i) = (N(a_i) - N(a_{i-1}))/\Delta e$$

- *The integrated DOS*

$$N(a_i) = \int_{-\infty}^{a_i} n(e)de$$

Output files in VASP

- **OSZICAR**
- *Gives the total energy after obtaining convergence.*

- *Also presents the energy profile during structural relaxation.*

Beyond VASP

- The outputs from VASP can be analyzed using other tools.

- *Includes:*
- *Bader charge transfer analysis*
- *Visualization*
- *Plotting band structure*
- *Calculating electrostatic potential*
- *Calculating magnetic moment*
- *….*