

# ***Softwares for Density Functional Theory. II. Capabilities of DFT***

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## Last week on...

### **Energy Band Theory:**

Electron motion in solids should be described based on quantum mechanics.

*Wavefunction – solved by Schrodinger equation*

**Bloch Theorem:** electron motion in a periodic crystal is under the influence of a periodic potential.

The electronic structure of a periodic crystal is contained in the 1<sup>st</sup> Brillouin Zone (unit cell of reciprocal lattice).



## Last week on...

### **DFT:**

Solving N-particle (nucleus+electrons) Schrodinger equation is a complicated process.

To simplify, we can express the energy functional (Hamiltonian) in term of charge density, which reduce the degree of complexity from  $3N$  to 3.

The energy function is expressed in “known” and “unknown” terms. Approximating “unknown” terms is a critical issue in DFT implementation.

### **DFT softwares:**

DFT input, output, and general steps.



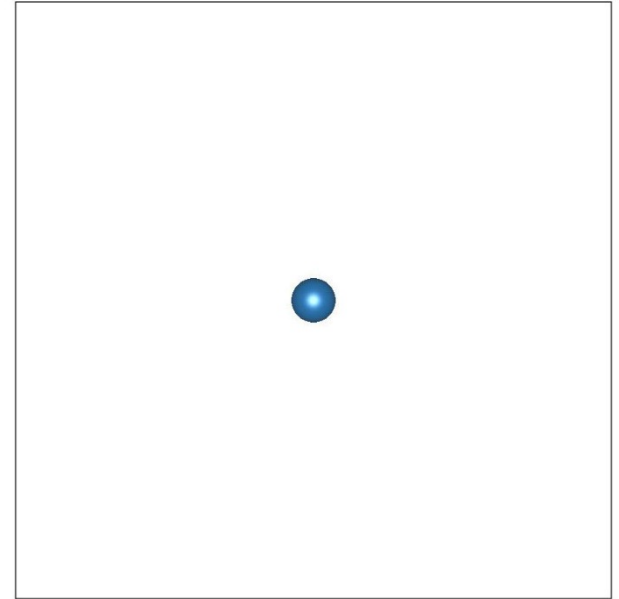
## In this Lecture: Demonstrating the capabilities of DFT calculations

- We will cover some basic DFT calculations, outlining the key steps and techniques:
- **Calculation of ONE atom**
- **Optimization of k-point grid size and energy cutoff**
- **Optimization of lattice parameters**
- **Band structure / Density of States**
- **Surface / adsorption calculation**



## Calculation involving only one atom

- Only one atom in the simulation box, surrounded by vacuum
- Check if the pseudopotential used to describe the atom is correct (or, if the software runs as we expect).
- Or used the energy of this isolated atom to obtain cohesive energy.
- Only 1 kpoint is needed.

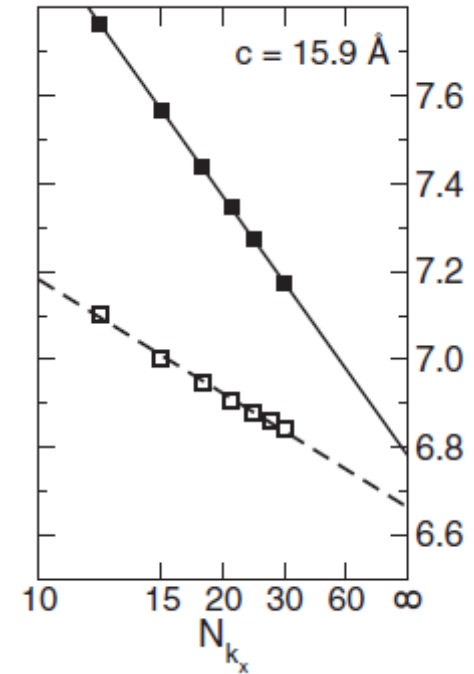


## Optimization of k-point grid and energy cut-off

- The number of sampled kpoints and the kinetic energy cut-off are two critical parameters affecting accuracy and efficiency of a DFT calculation.

Low number of kpoints / low energy cut-off: Fast calculation, but low accuracy

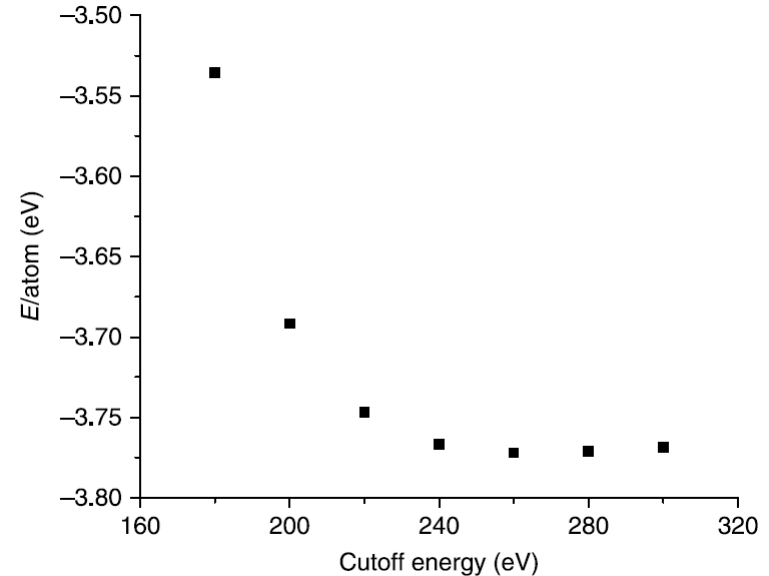
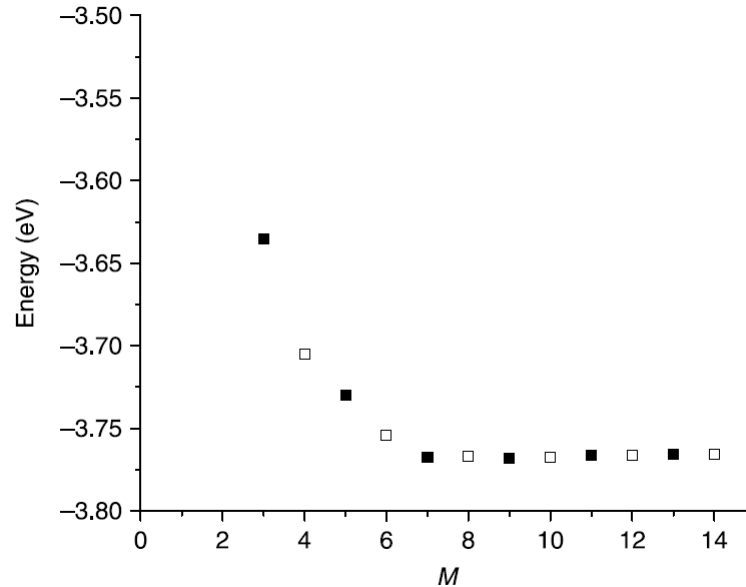
High number of kpoints / high energy cut-off: slow calculation, but high precision.



Band gap of graphene induced by adsorbed molecules vs. size of kpoint grid ( $N \times N \times 1$ )

## Optimization of k-point grid and energy cut-off

- Energy convergence test is often done to determine a reasonable value for k-point grid and energy cut-off. This is a standard practice in any DFT study.



## Optimization of lattice parameters

- DFT can be used to calculate lattice constant or predict crystal structure.

*Example: Predict the lattice structure and lattice constant of Copper (Cu).*

Candidates: simple cubic, face-centered cubic ( $a$ ), hexagonal close packed ( $a$  and  $c$ )

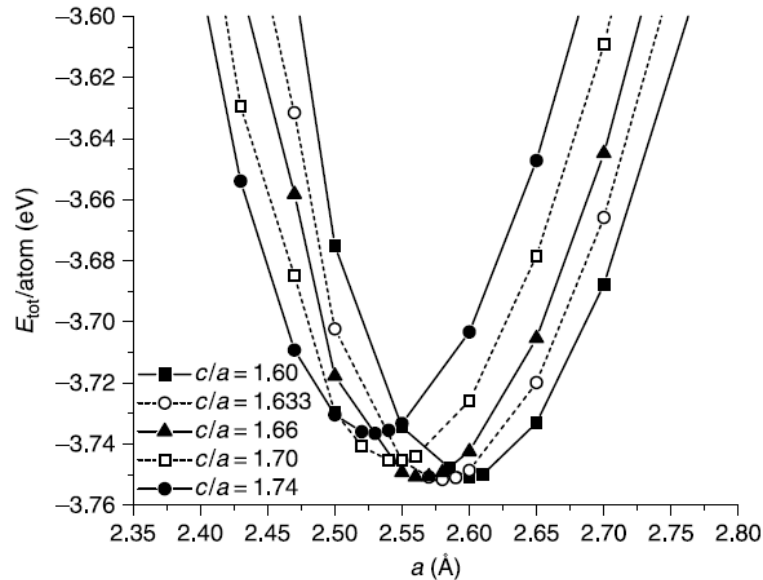
Solution: Fix  $c/a$  value and calculate a series of total energies as a function of  $a$ , and then change to next possible  $c/a$  value.





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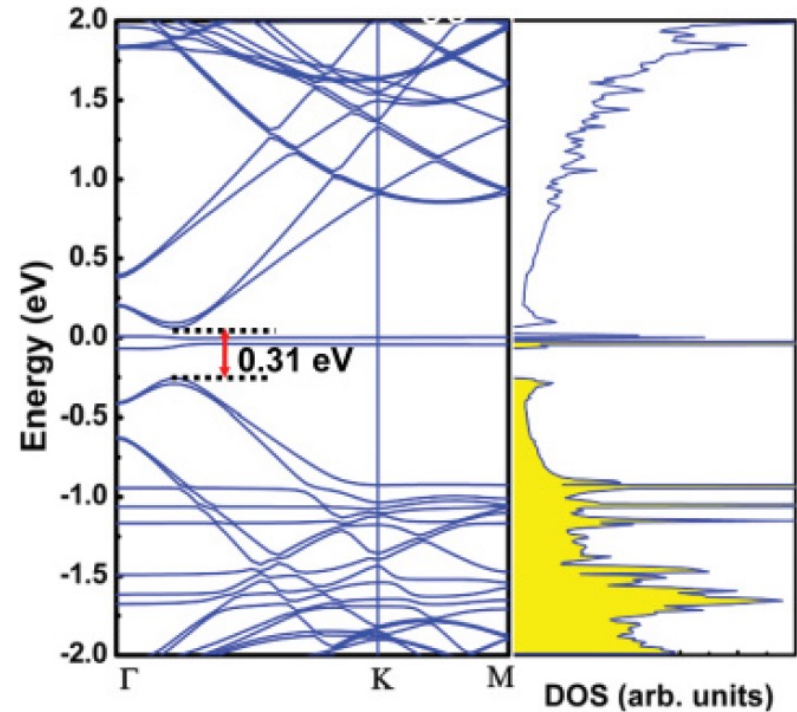
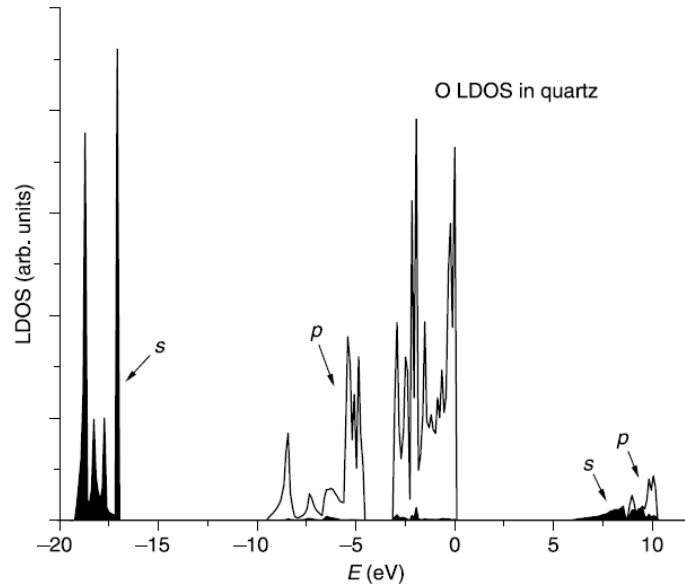
For hcp only **small  $c/a$**  value is favorable.

However, the minimum energy of HCP is larger than Cu with FCC structure.

FCC is therefore the preferred structure for Cu.

## Band structure / density of states

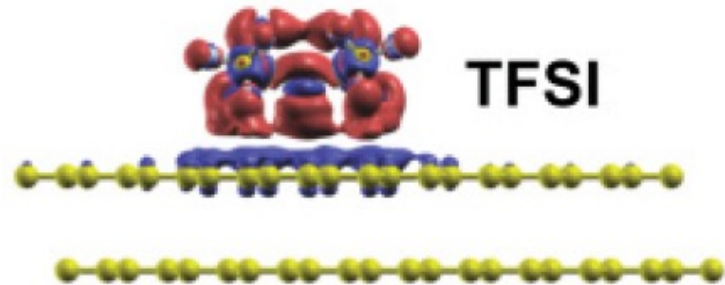
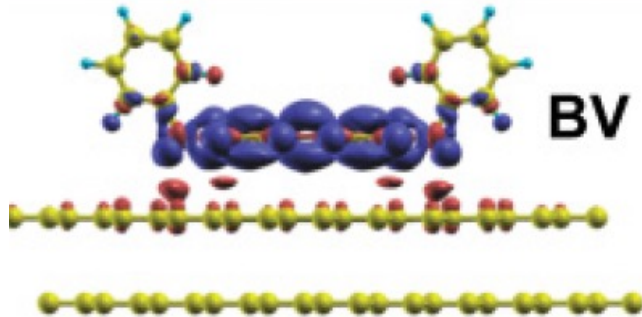
- Analysis on total density states, partial density states and band structure



## Charge transfer difference

- A useful analysis to visualize the charge transfer between the substrate and adsorbed molecules

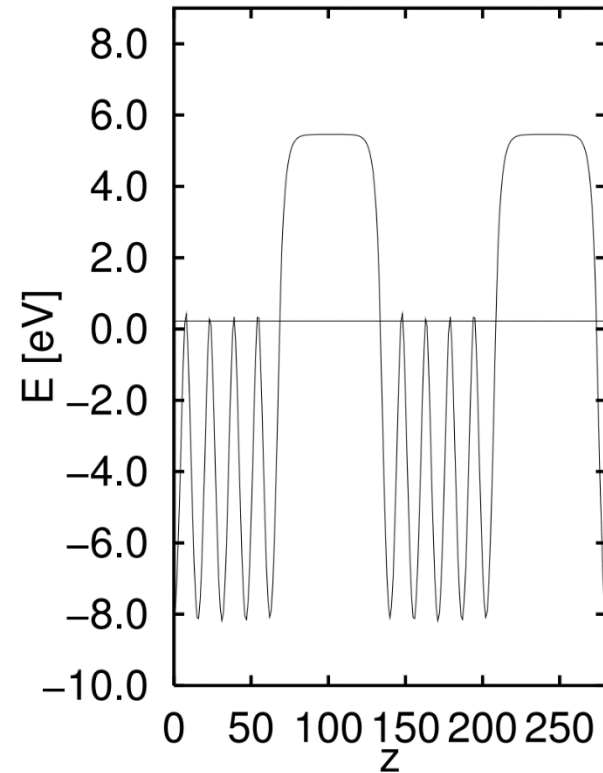
$$\Delta\rho = \rho_{surf+mol} - \rho_{surf} - \rho_{mol},$$



## Work function calculation

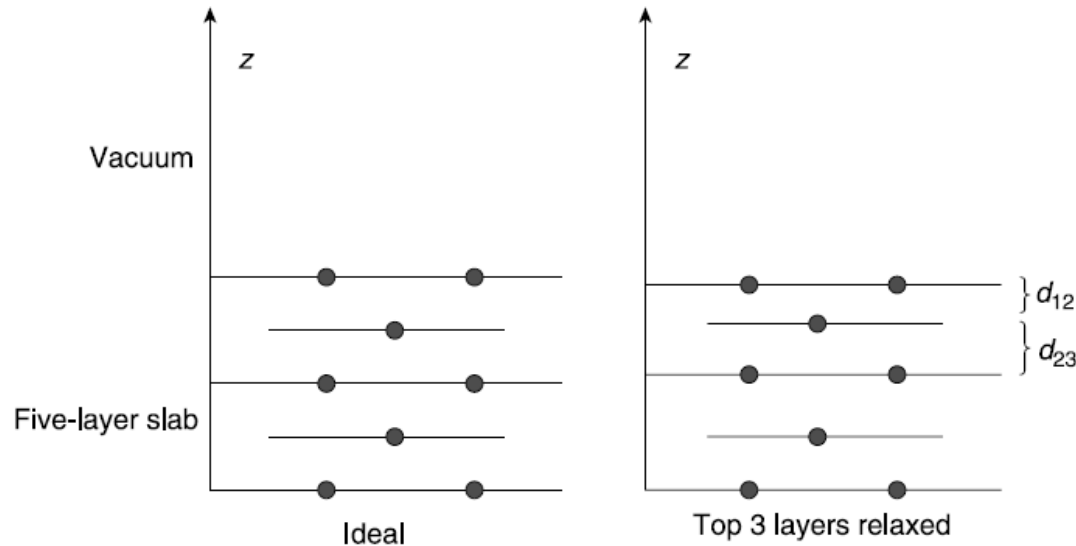
- The work function ( $W$ ) is the minimum energy required to move an electron from the solid to a point in the vacuum. It is obtained by calculating the local electrostatic potential.

$$W = E_{vac} - E_F$$



## Surface calculation

- Surface atoms can have significant different behavior compare to their bulk counterpart.
- We usually constrain the bottom layers in their bulk positions (“frozen” atoms).



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	Cu(001)		
	$\delta d_{12}$ (%)	$\delta d_{23}$ (%)	$\delta d_{34}$ (%)
5 layers	3.84	0.50	0.53
6 layers	1.93	+0.83	+0.37
7 layers	2.30	+0.55	0.25
8 layers	2.14	+0.85	+0.00
Expt.	$2.0 \pm 0.5^a$	$+1.0 \pm 0.7^a$	

Interlayer distance change as a function of number of layers

## Surface calculation

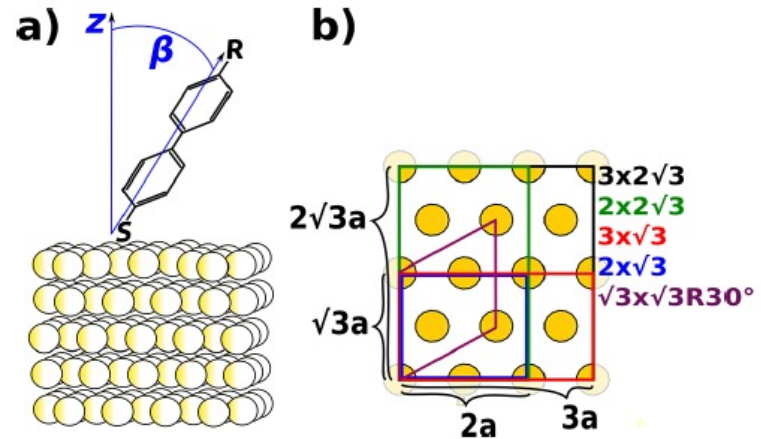
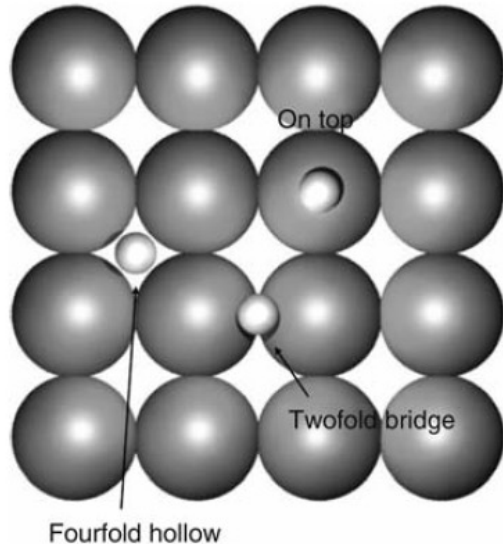
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## Adsorption calculation

- There are two critical factors when examining a adsorbate-substrate system: adsorption site and adsorption density.

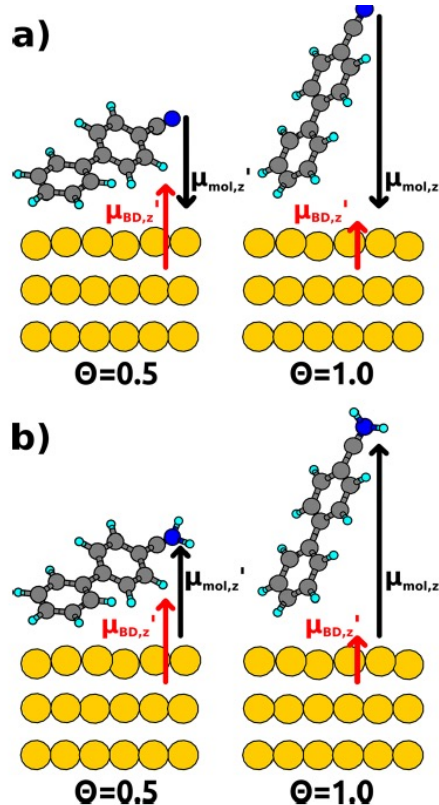




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Effect of adsorption  
configuration/density on the  
molecular dipole moment



## DFT: Capability and Disability

### DFT can predict

- Total energy
- Forces
- Lattice constants
- Bond lengths
- Vibrational frequencies
- Phonon frequencies
- Electron density
- Static dielectric response

### DFT cannot predict

- Excited state energies
- Band gap
- Band structures
- Wave functions
- Fermi surface
- Superconductivity
- Excitons
- Electronic transport



## Summary: Key Factors in DFT

- Born-Oppenheimer approximation;
- Density functional theory
  - LDA, GGA
  - LSDA
- Pseudopotential
- Kinetic energy cutoff
- $k$ -sampling
- convergence criterion
- . . .

