计算化学介绍

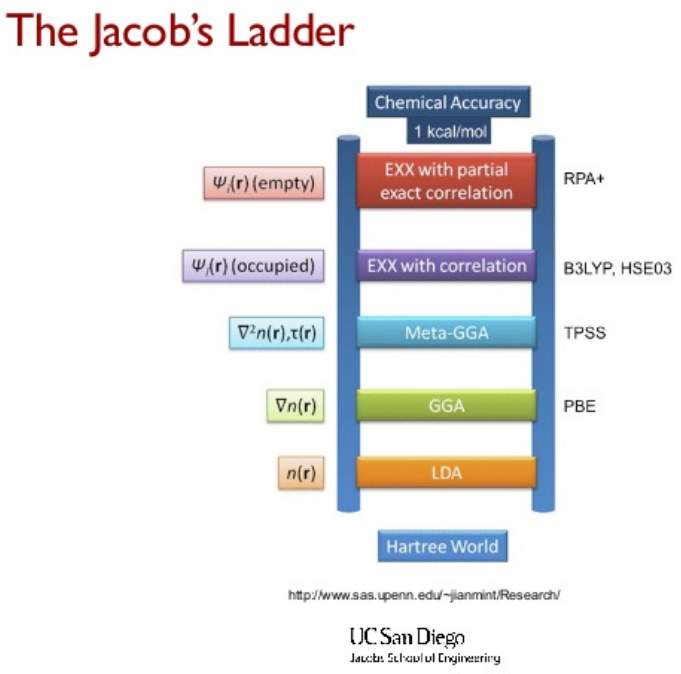
计算化学尺度

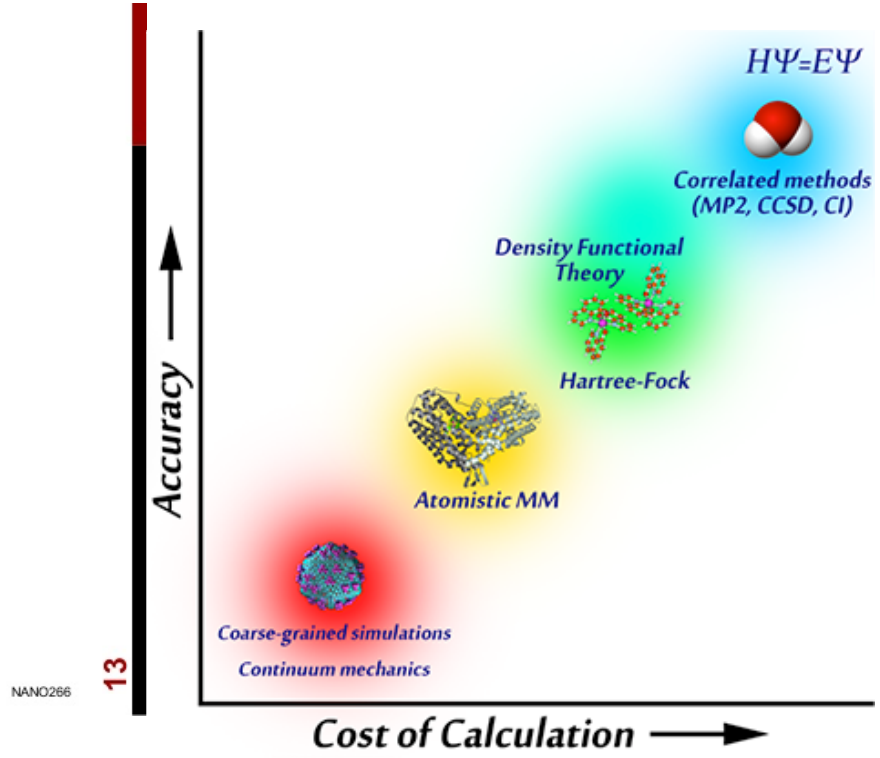
- 研究的尺度不同，
  - 量子力学（Ab-initio or DFT）
  - 力场(Force field)
- 从研究方向上分
  - 化学反应
    - 有机反应
    - 固体表面反应
  - 物理化学性质
    - 能带，态密度，电荷分析

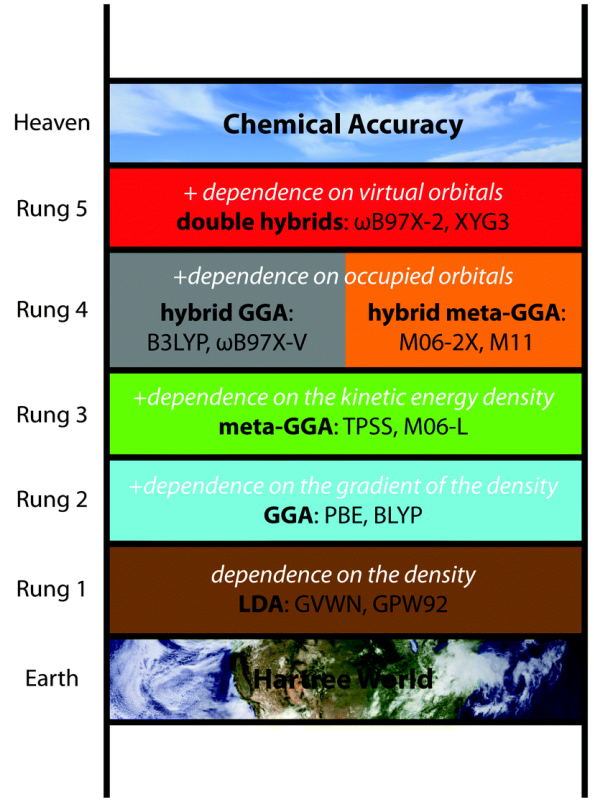
常用计算软件

- 计算非周期性体系：Gaussian, Orca, CP2K
- 计算周期性体系，尤其是固体：VASP, quantum espresso, CP2K
- 从头计算法分子动力学：CP2K
- 经典力学分子动力学：LAMMPS, GROMACS

计算精度

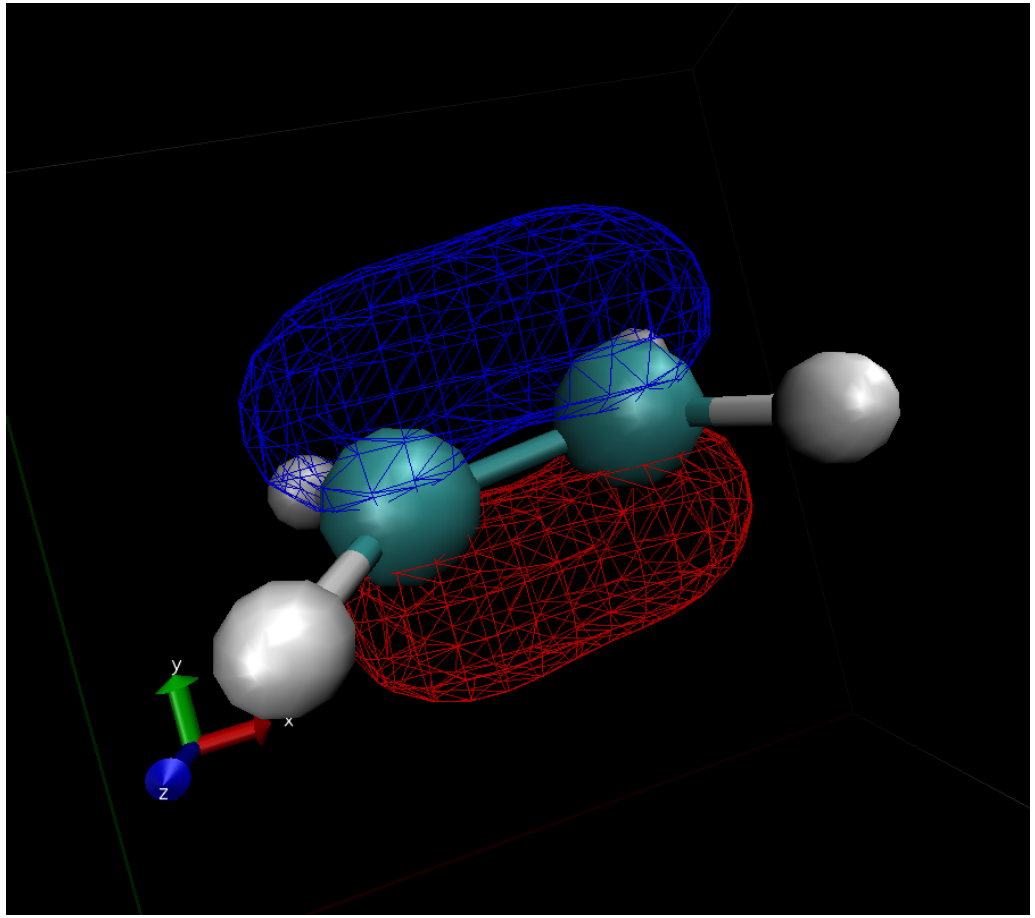

The Jacob's Ladder
Chemical Accuracy
1 kcal/mol
$\Psi_i(\mathbf{r})$ (empty)
EXX with partial exact correlation
RPA+
$\Psi_i(\mathbf{r})$ (occupied)
EXX with correlation
B3LYP, HSE03
$\nabla^2 n(\mathbf{r}),\tau(\mathbf{r})$
Meta-GGA
TPSS
$\nabla n(\mathbf{r})$
GGA
PBE
$n(\mathbf{r})$
LDA
Hartree World
http://www.sas.upenn.edu/~jianmint/Research/
UC San Diego
Jacobs School of Engineering


$H\Psi=E\Psi$
Correlated methods (MP2, CCSD, CI)
Density Functional Theory
Hartree-Fock
Atomistic MM
Coarse-grained simulations
Continuum mechanics
Accuracy
Cost of Calculation
NANO266
13

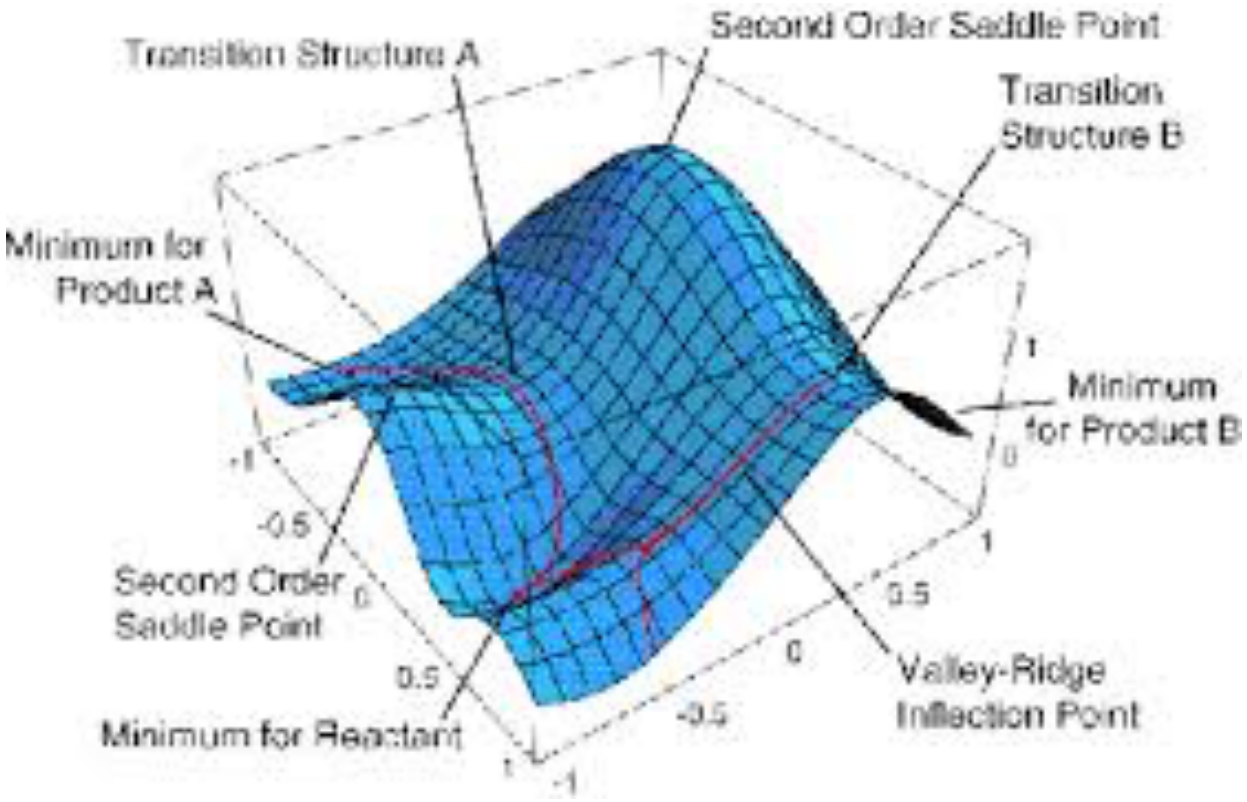

Heaven
Chemical Accuracy
Rung 5
+ dependence on virtual orbitals
double hybrids: ωB97X-2, XYG3
Rung 4
+dependence on occupied orbitals
hybrid GGA: B3LYP, ωB97X-V
hybrid meta-GGA: M06-2X, M11
Rung 3
+dependence on the kinetic energy density
meta-GGA: TPSS, M06-L
Rung 2
+dependence on the gradient of the density
GGA: PBE, BLYP
Rung 1
dependence on the density
LDA: GVWN, GPW92
Earth
Hartree World

常见计算类型

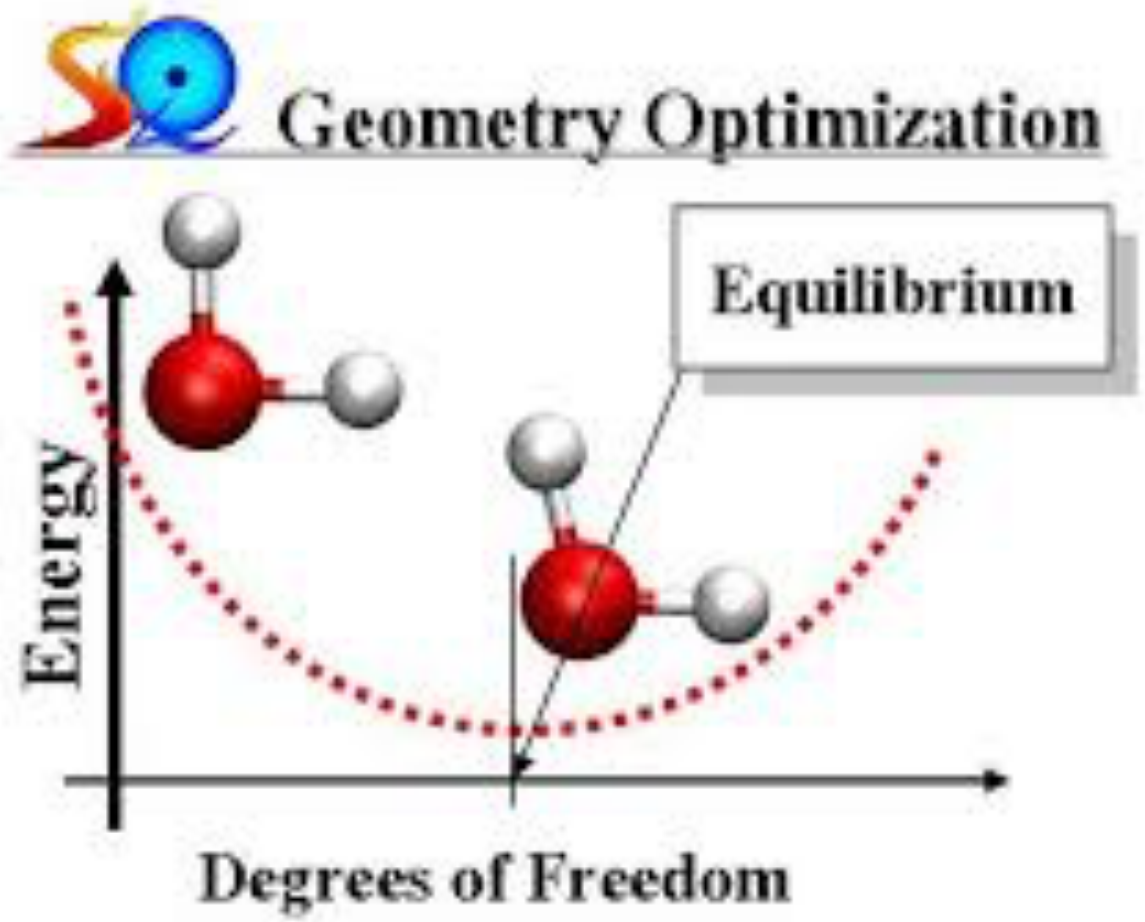
电子结构

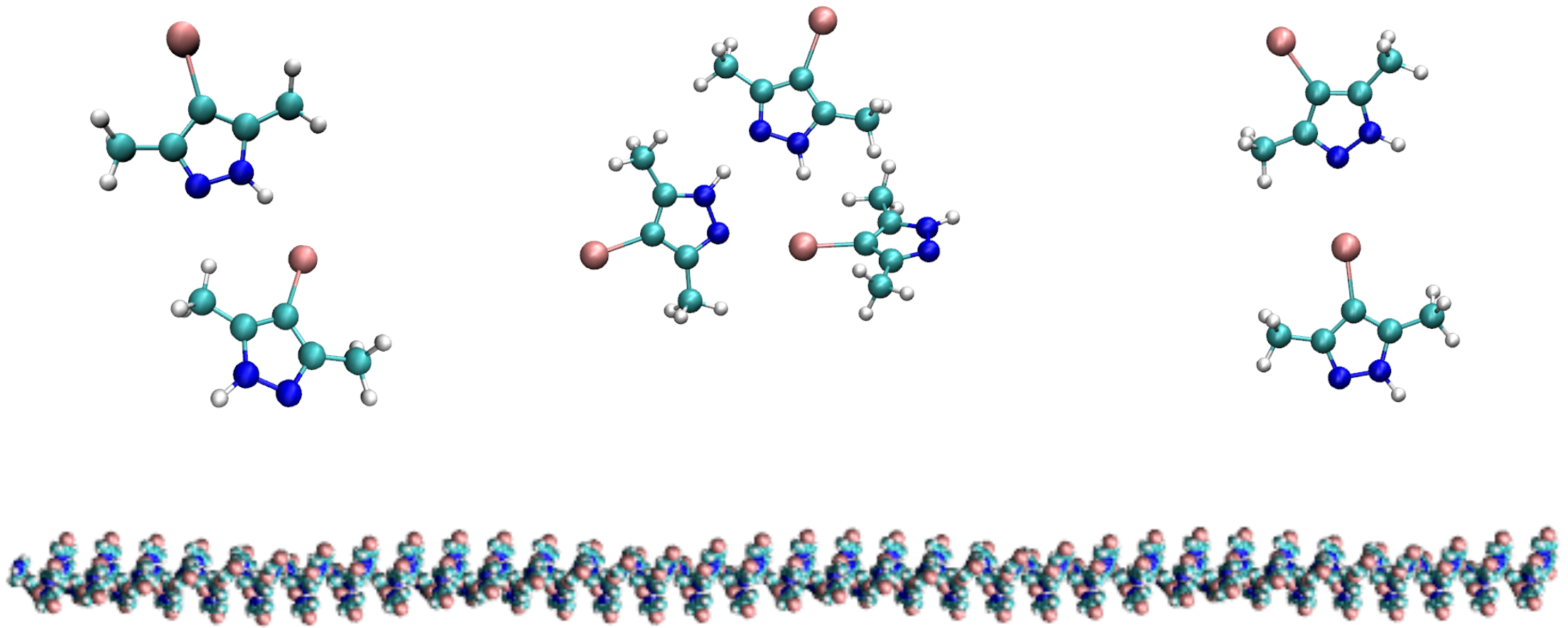


结构优化

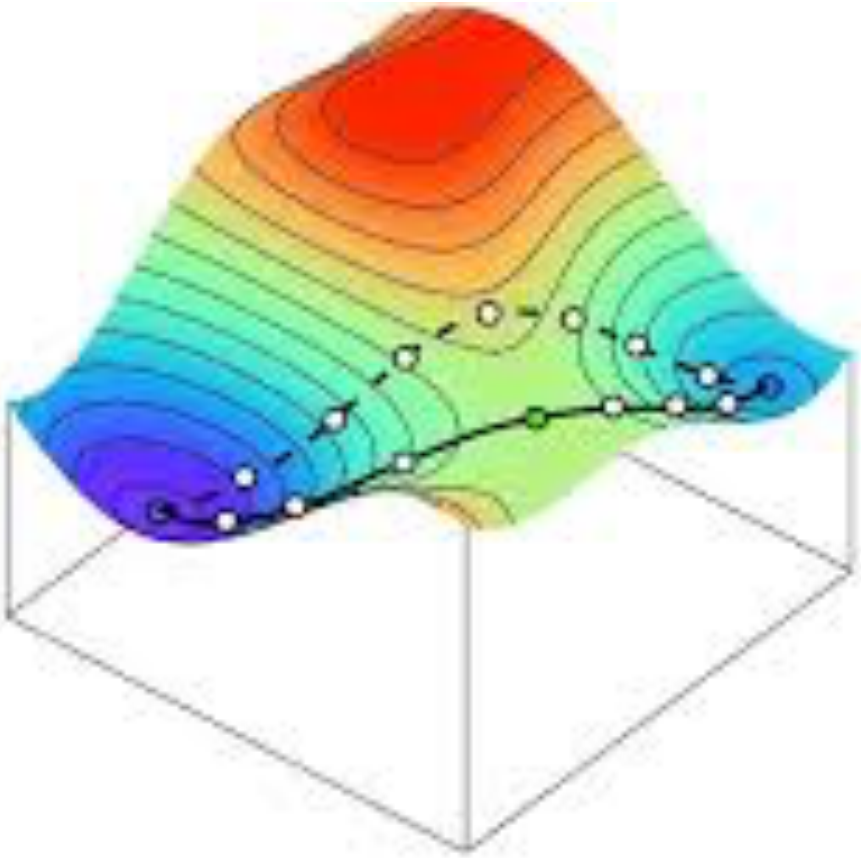

Transition Structure A
Second Order Saddle Point
Transition
Structure B
Minimum for
Product A
Minimum
for Product B
Second Order
Saddle Point
Minimum for Reactant
Valley-Ridge
Inflection Point

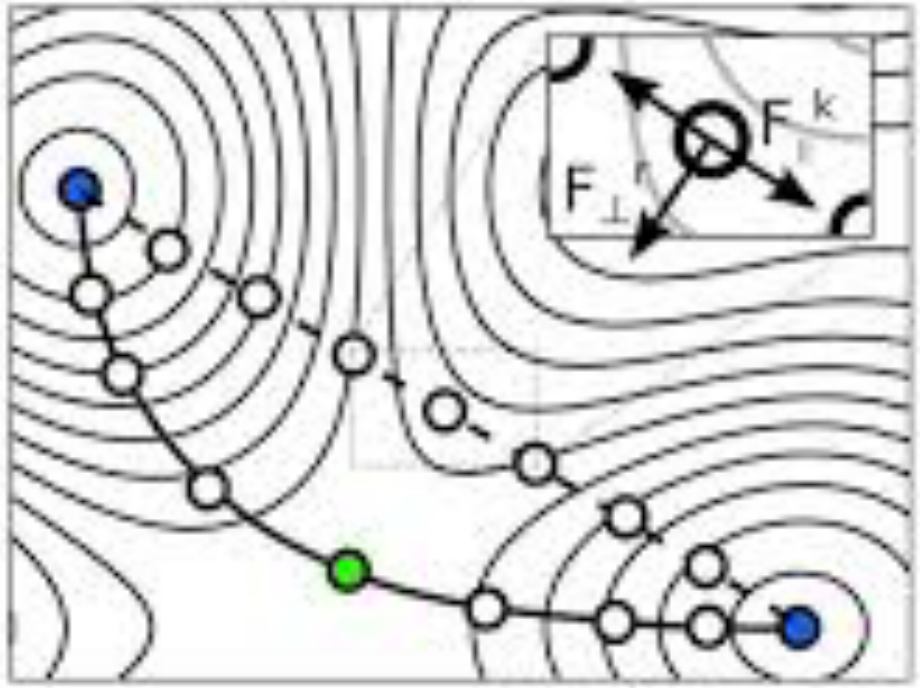
Stationary state





Transition State





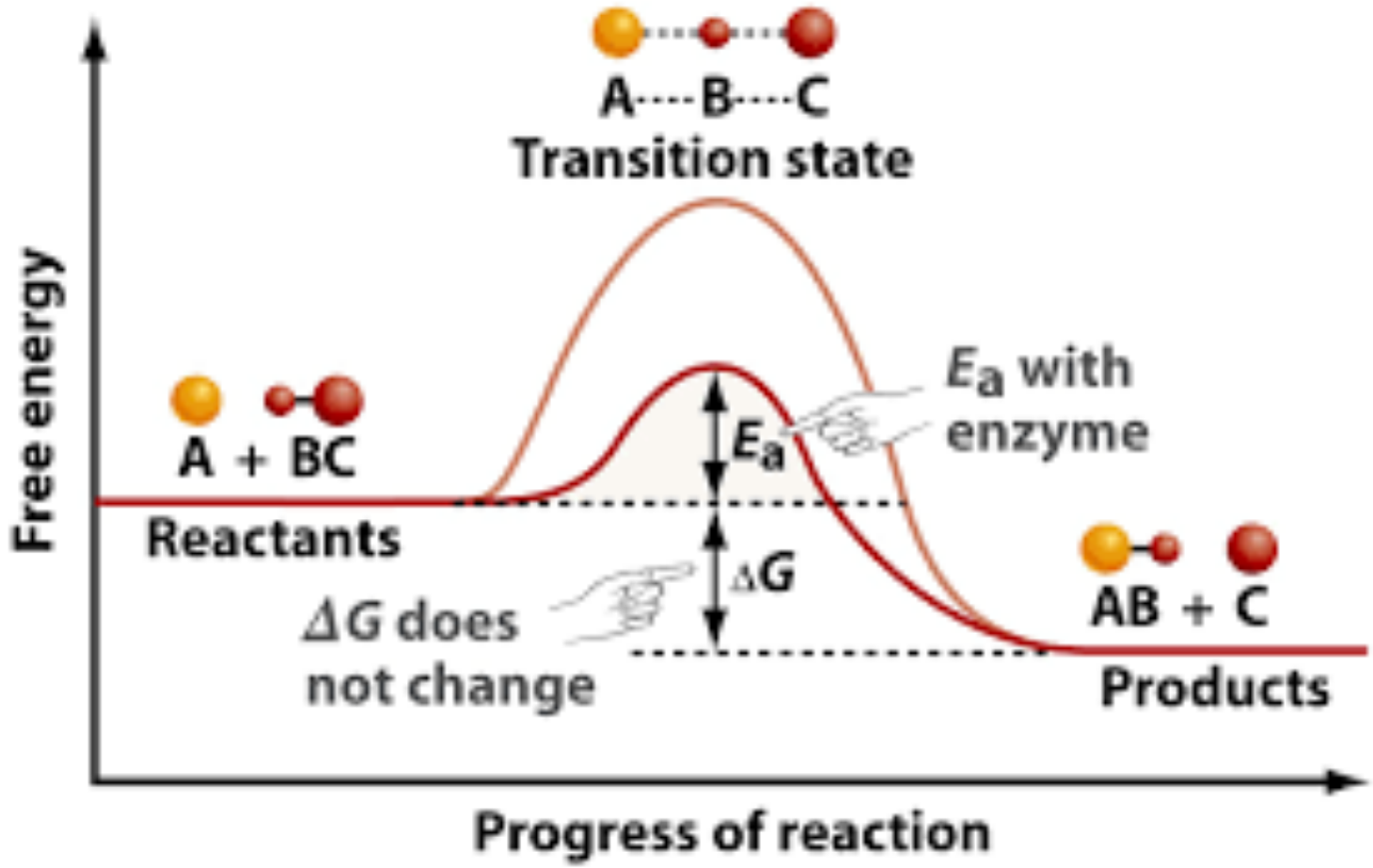
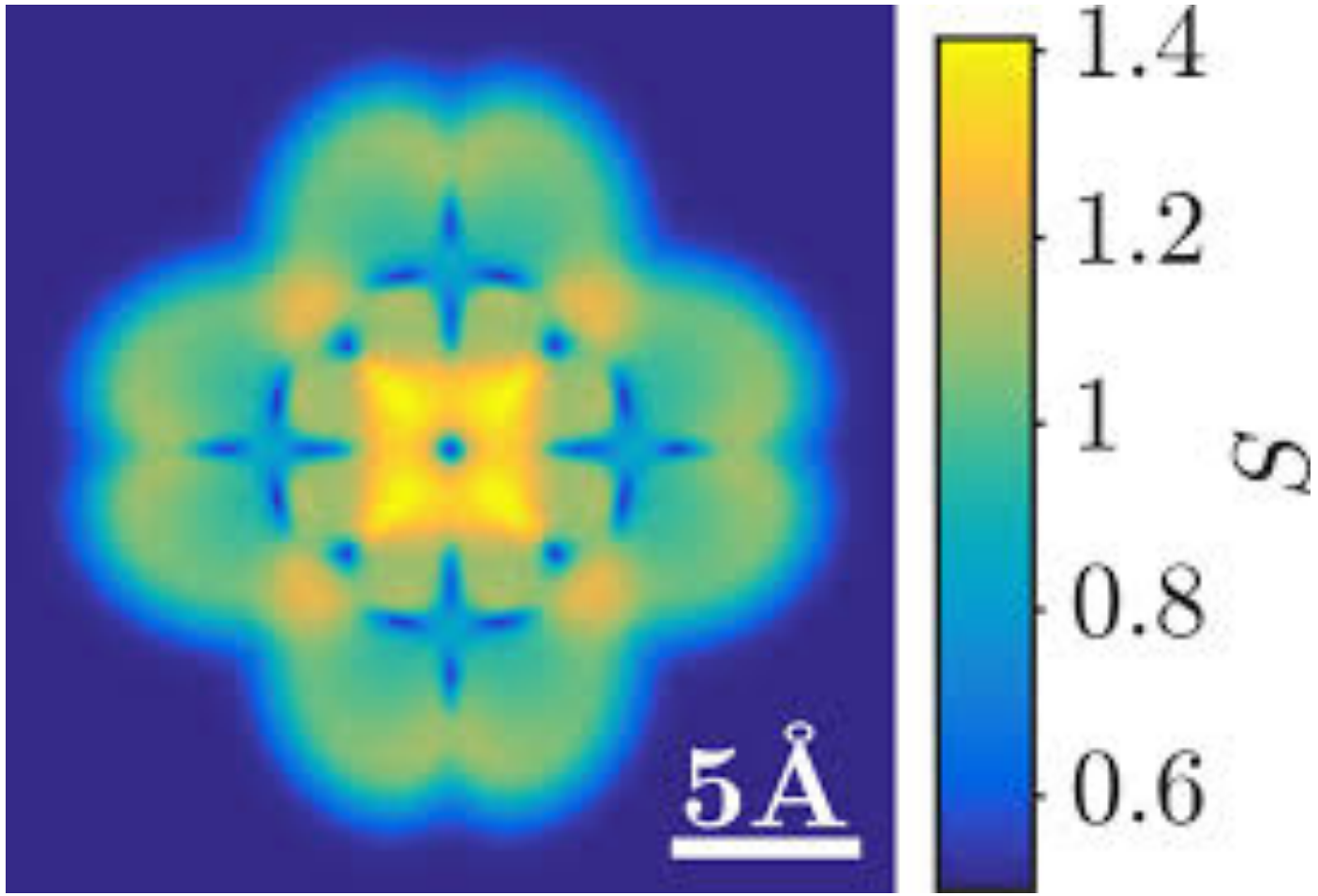


Figure 3-21 Biological Science, 2/e

STM simulation



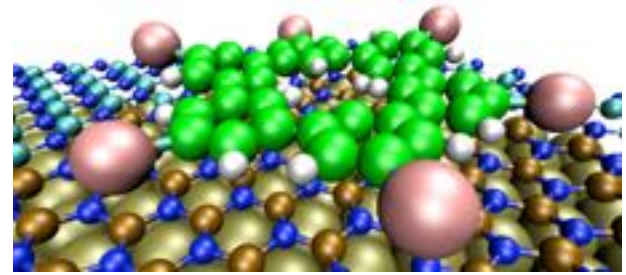
Density Difference

Changes in the electronic density due to interactions, e.g., molecule adsorbed on substrate

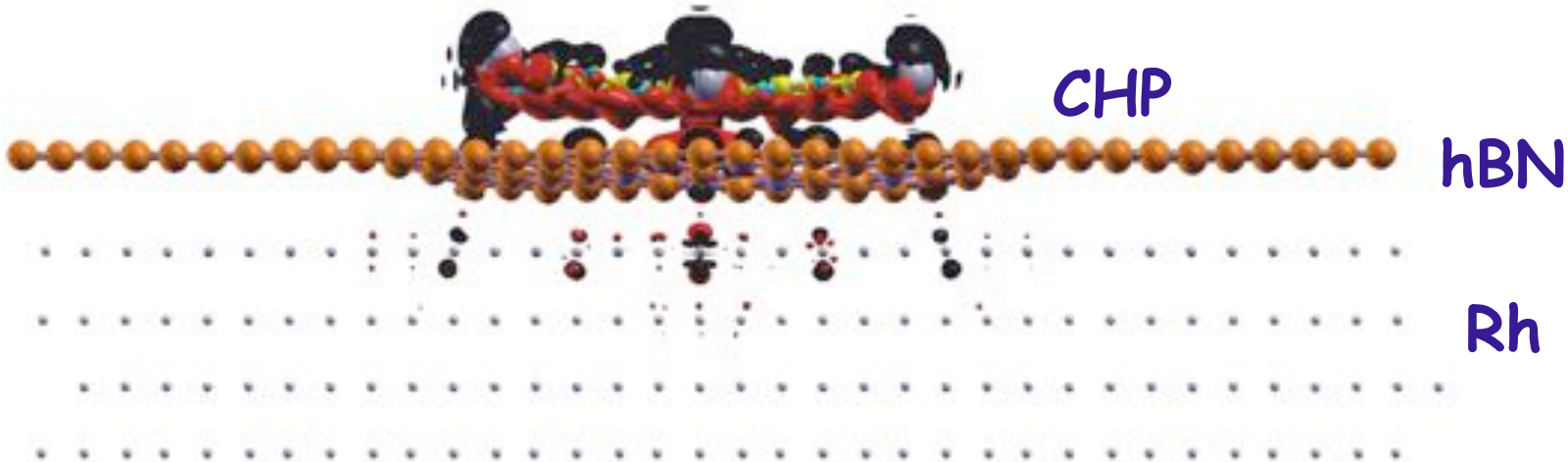
$$E_{\mathrm{ads}} = E_{\mathrm{tot}} - (E^{o}_{\mathrm{sub}} + E^{o}_{\mathrm{mol}})$$

$$E_{\mathrm{int}} = E_{\mathrm{tot}} - \left(E^{f}_{\mathrm{sub}} + E^{f}_{\mathrm{mol}}\right)$$

CHP on hBN/Rh (5 eV)



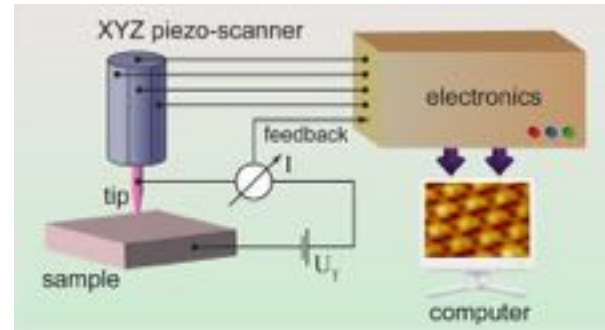
$$\Delta n_{\mathrm{int}}(\mathbf{r}) = n_{\mathrm{tot}}(\mathbf{r}) - \left(n^{f}_{\mathrm{sub}}(\mathbf{r}) + n^{f}_{\mathrm{mol}}(\mathbf{r})\right)$$



STM images

Tersoff-Hamann approximation to mimic the iso-current topography

$$n_b(\mathbf{r}) = \sum_{i:\varepsilon_i \in [E_f - V_b : E_f]} \left[\sum_{\mu\nu} C^*_{\mu i} C_{\nu i} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) \right] \rightarrow n_b(\mathbf{R})$$

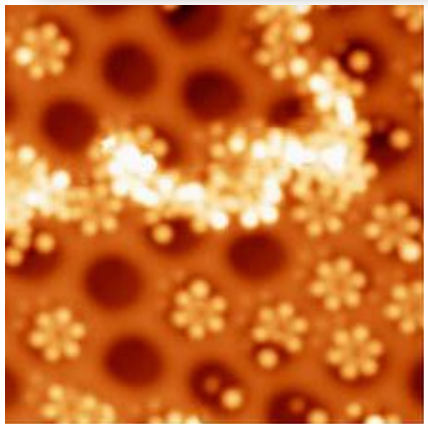


Find height at constant energy projected density

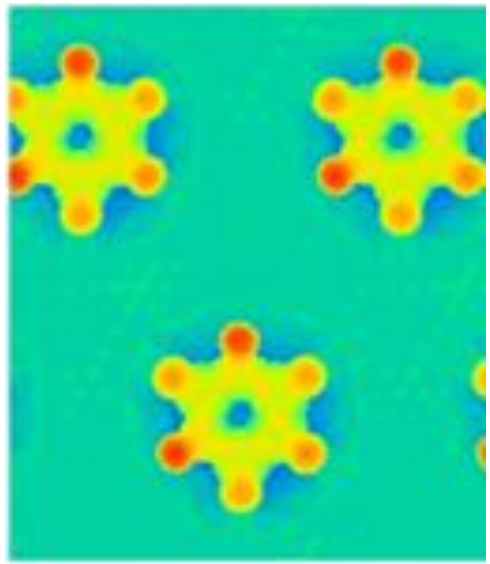
$$z : n_b(X, Y, z)\ e^{-2kR_0\sqrt{\Phi(X,Y,z)}}$$

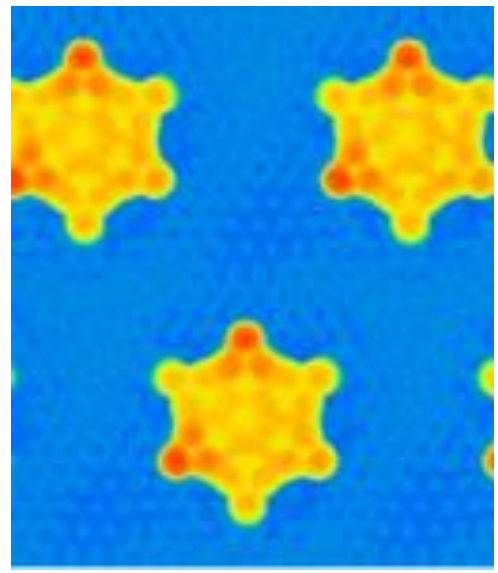
CHP on hBN/Rh (5 eV)

Vb=-1310 mV

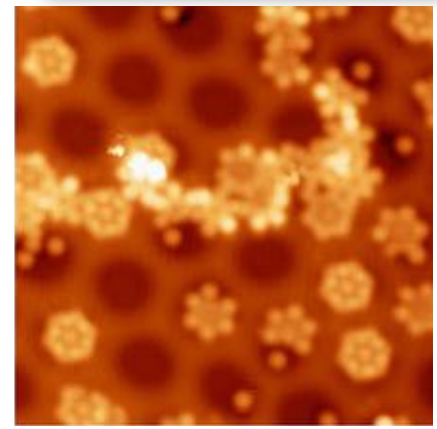


occupied states





Vb=+1480 mV



unoccupied states

Core-hole Creation and Decay

XES/NEXAFS local probes for electronic and geometric properties

Unoccupied levels, symmetry resolved

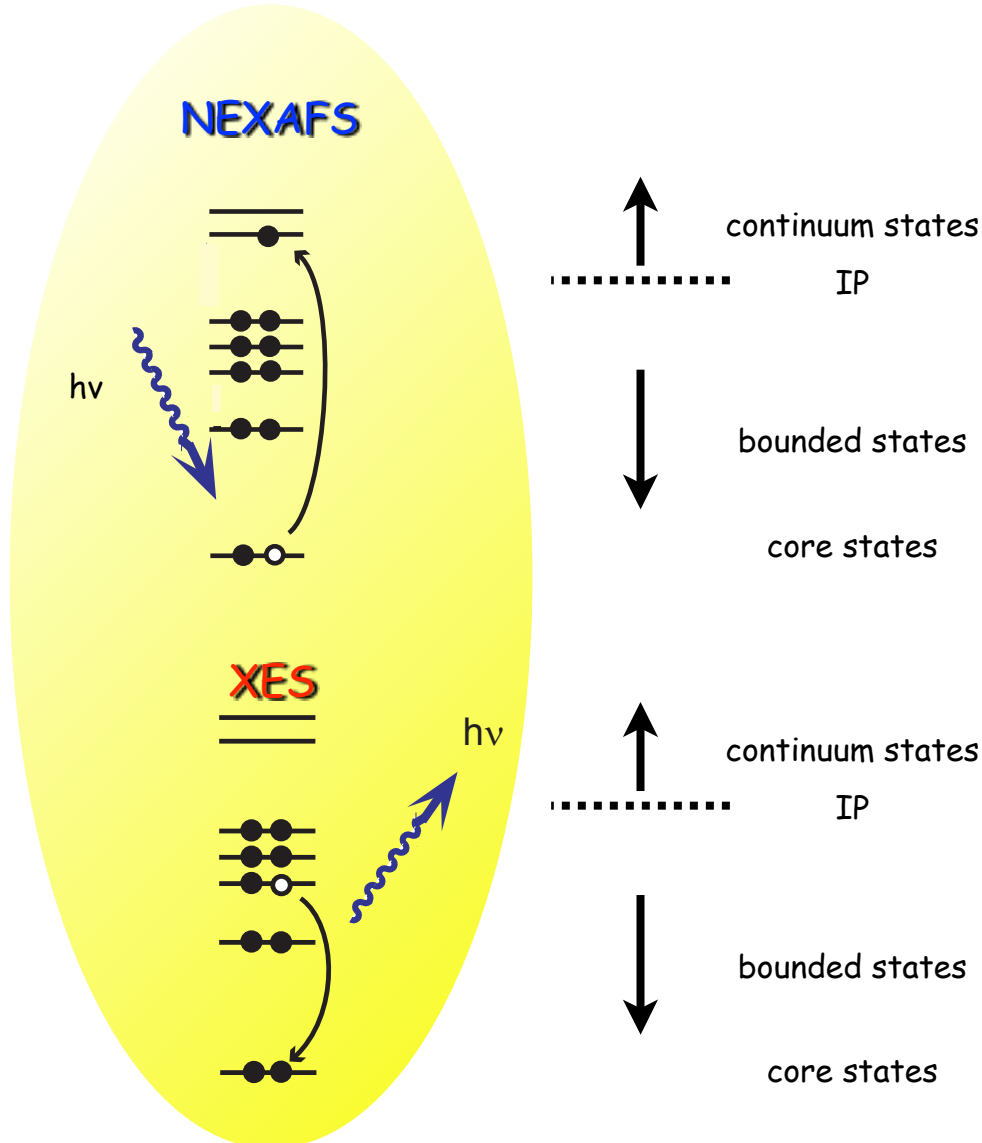
One step process
Finale state: core-hole

Instantaneous configuration in dynamic systems

Occupied orbitals

Two step process
Final state : valence-hole

Binding of adsorbed molecules

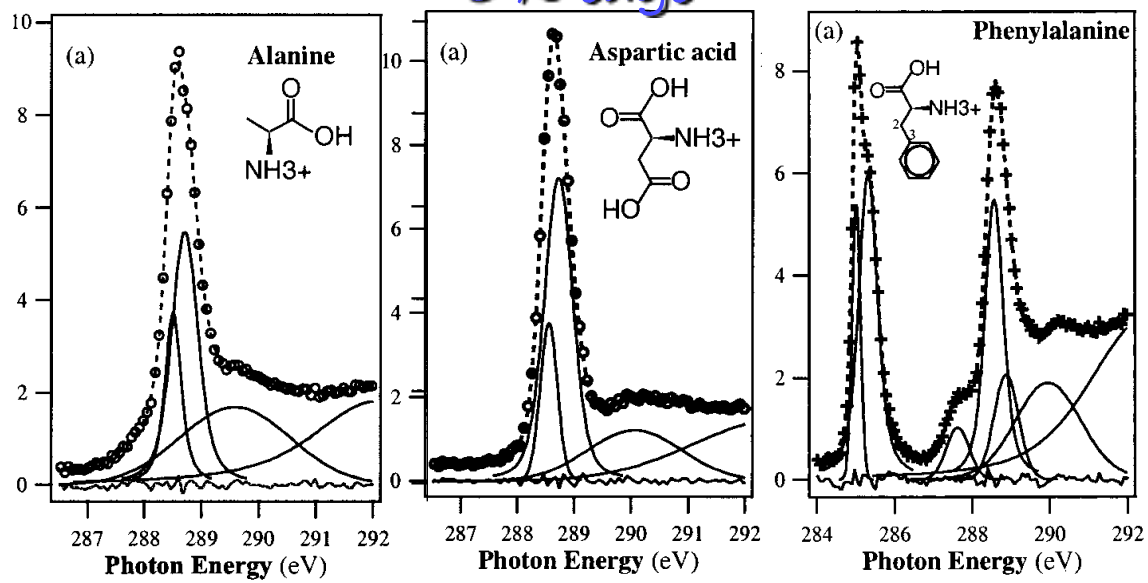


X-ray Absorption Simulations

Interpretation of experiment,
structures refinement (signal assignment),
understanding of physical-chemical properties of materials.

XAS of amino-acid series

C K-edge



Kaznacheyev et al,
JPC A, **106**, 3153 (2002)

Computational spectroscopy (inner-shell, NMR, ..) often requires approaches beyond cluster model or PP approximation:

Efficient scheme for AE in condensed matter

AE linear response theory

PDOS 和 Band Structure

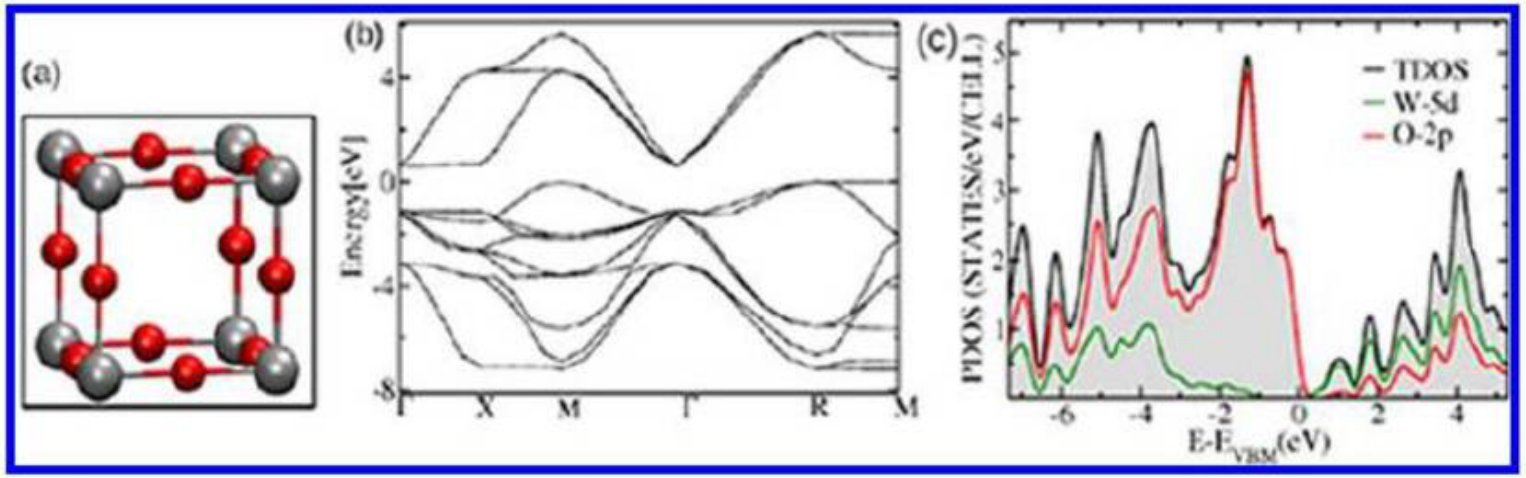
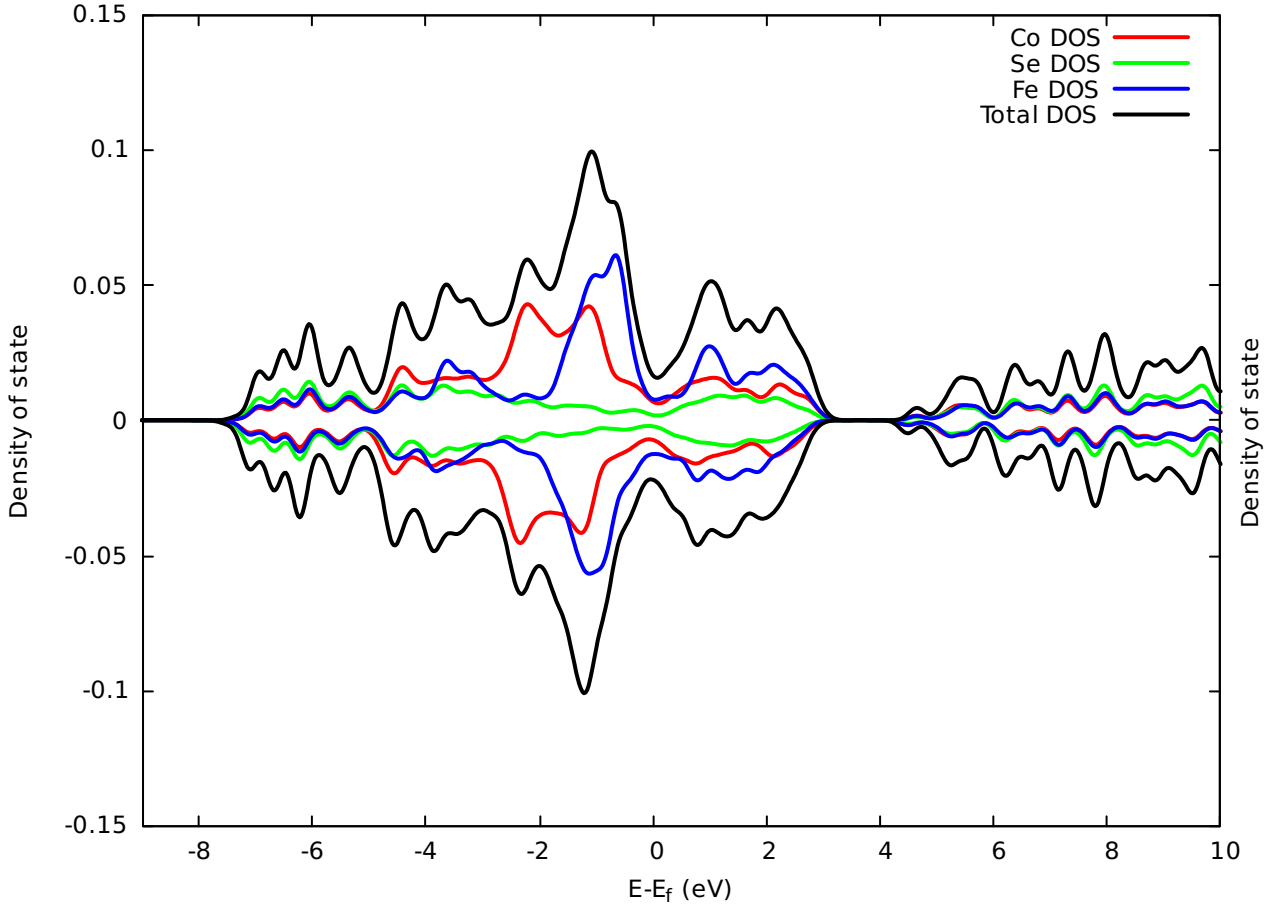
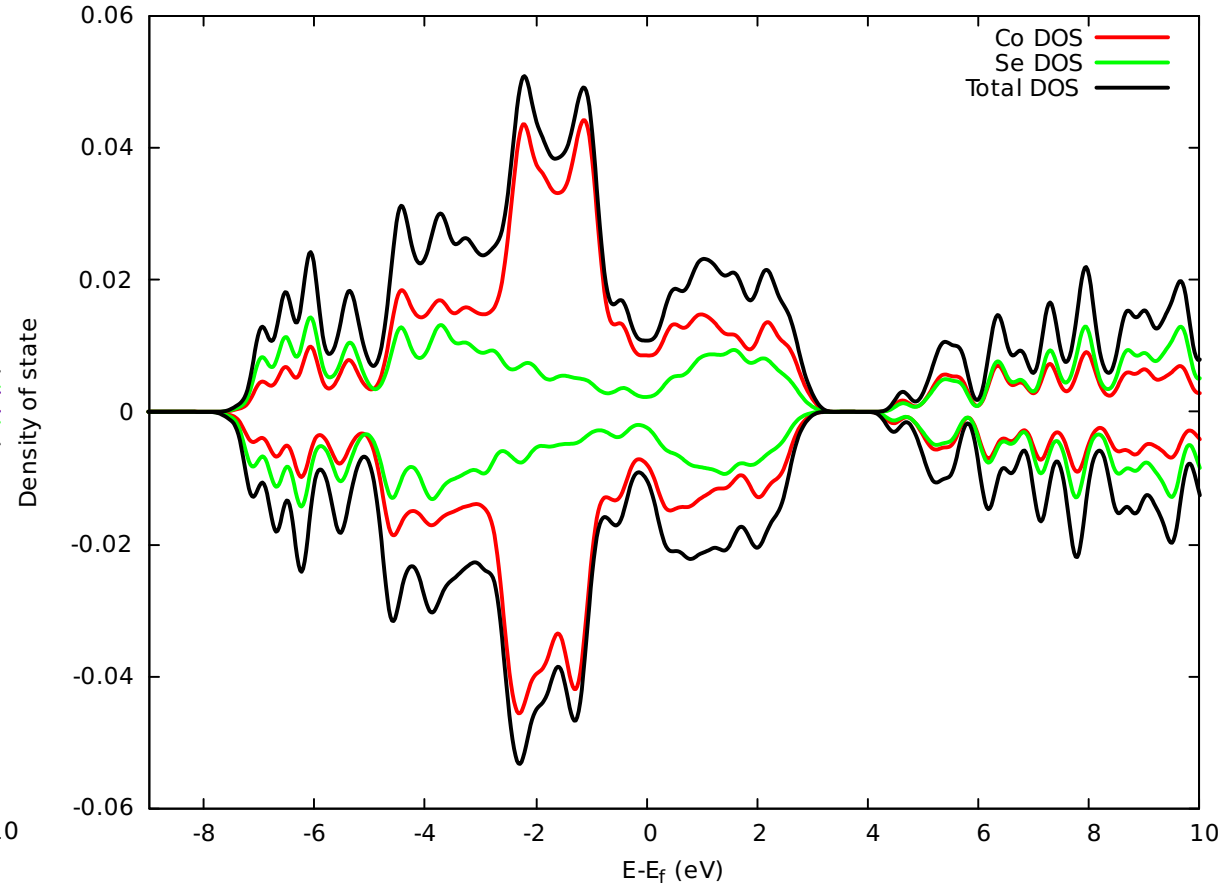


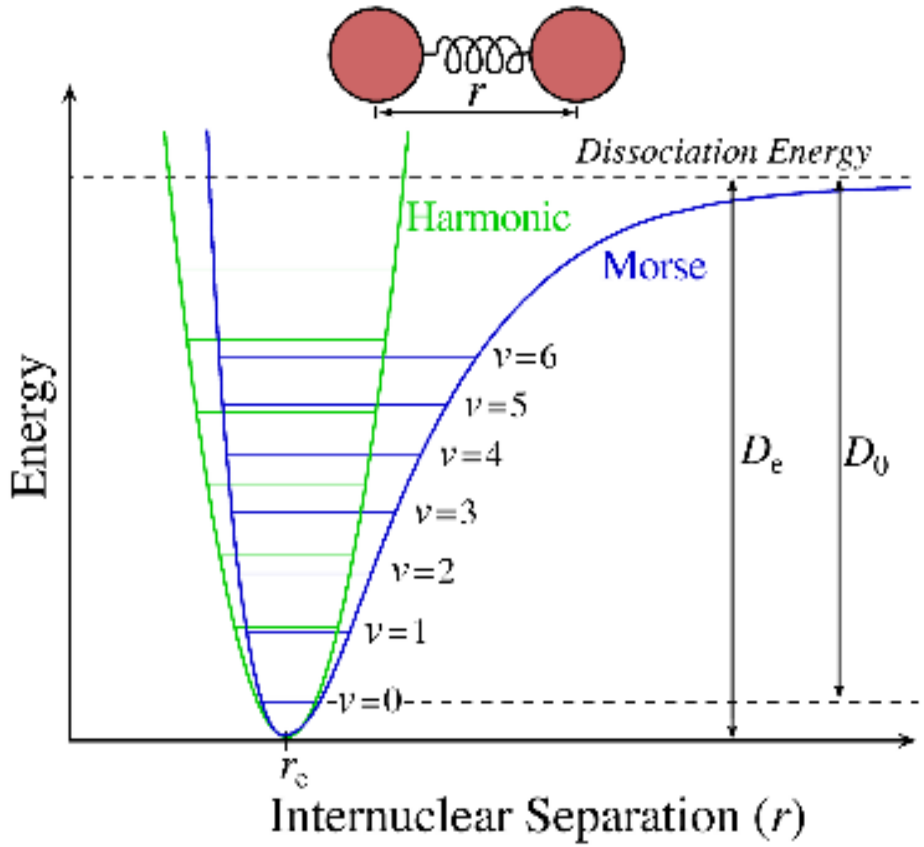
Figure 1. Band structure (b) and projected density of states (PDOS) and total density of states (TDOS) (c) of simple cubic WO_3 as obtained with DFT/LDA calculations. In panel c, the zero of energy has been chosen at the VBM (E_{VBM}). The crystal structure is shown in part a.

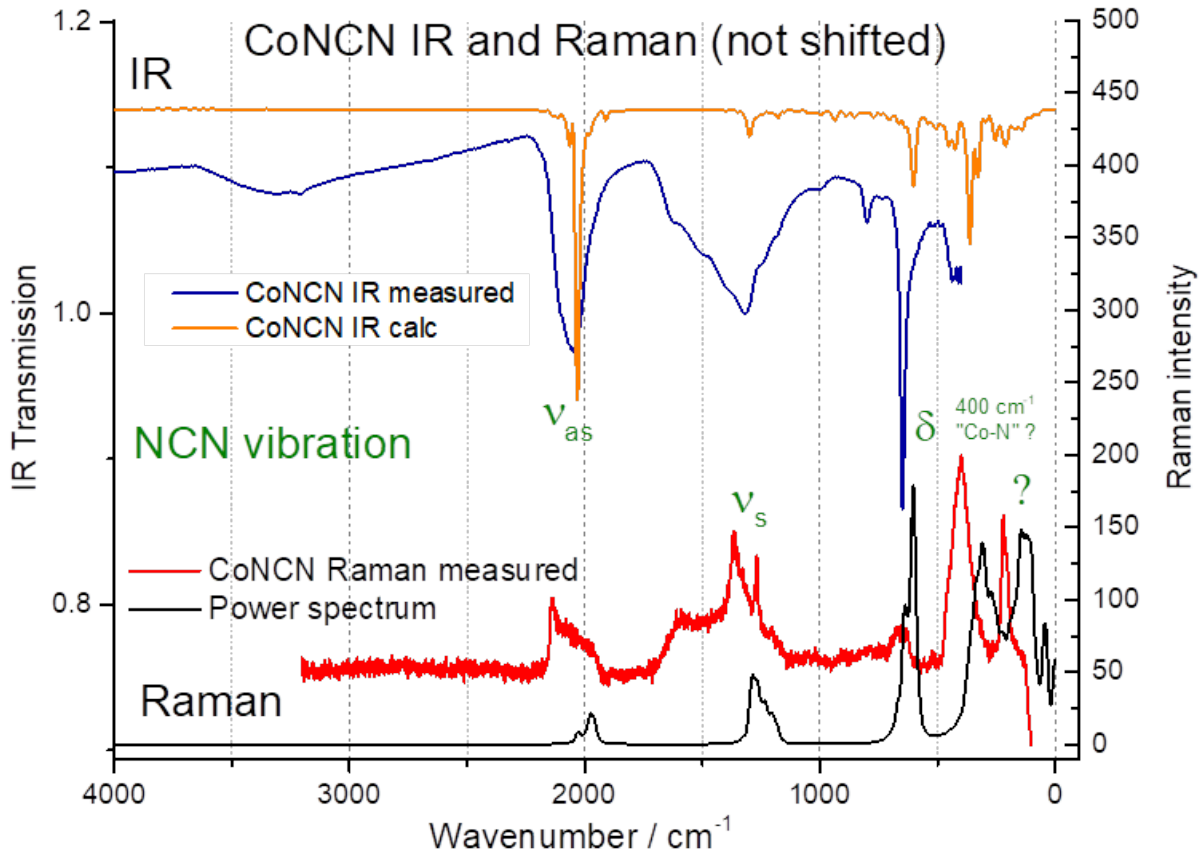
Doping bulk


Co DOS
Se DOS
Fe DOS
Total DOS
Density of state
E-E$_f$ (eV)
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-8
-6
-4
-2
0
2
4
6
8
10


Co DOS
Se DOS
Total DOS
Density of state
E-E$_f$ (eV)
0.06
0.04
0.02
0
-0.02
-0.04
-0.06
-8
-6
-4
-2
0
2
4
6
8
10

IR


r
Dissociation Energy
Harmonic
Morse
v=6
v=5
v=4
v=3
v=2
v=1
v=0
D_e
D_0
Energy
r_e
Internuclear Separation (r)

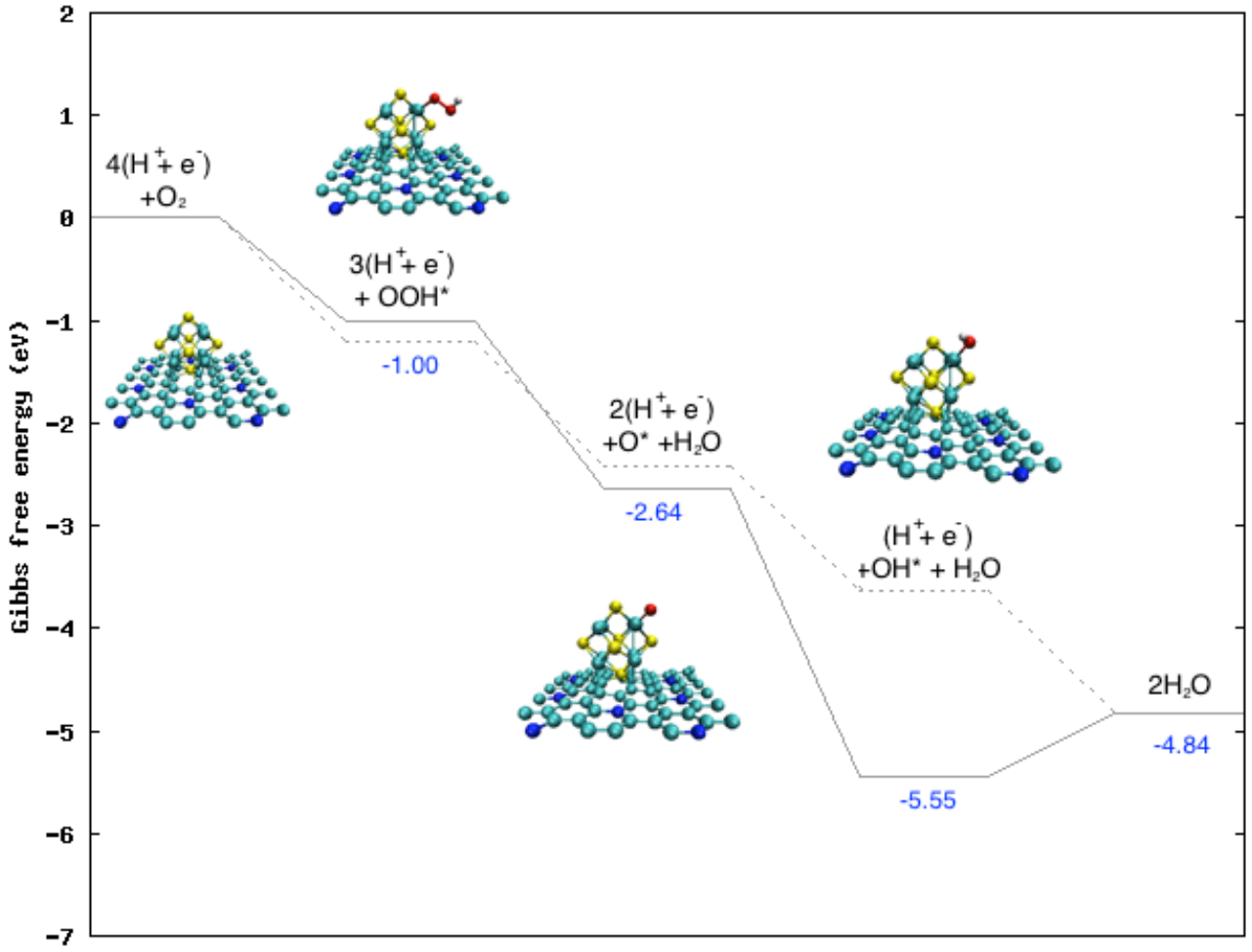

CoNCN IR and Raman (not shifted)
IR
Raman
CoNCN IR measured
CoNCN IR calc
CoNCN Raman measured
Power spectrum
NCN vibration
ν_{as}
ν_s
δ
400 cm^{-1}
"Co-N" ?
?
IR Transmission
Raman intensity
Wavenumber / cm^{-1}
1.2
1.0
0.8
500
450
400
350
300
250
200
150
100
50
0
4000
3000
2000
1000
0

电化学计算 – OER ORR

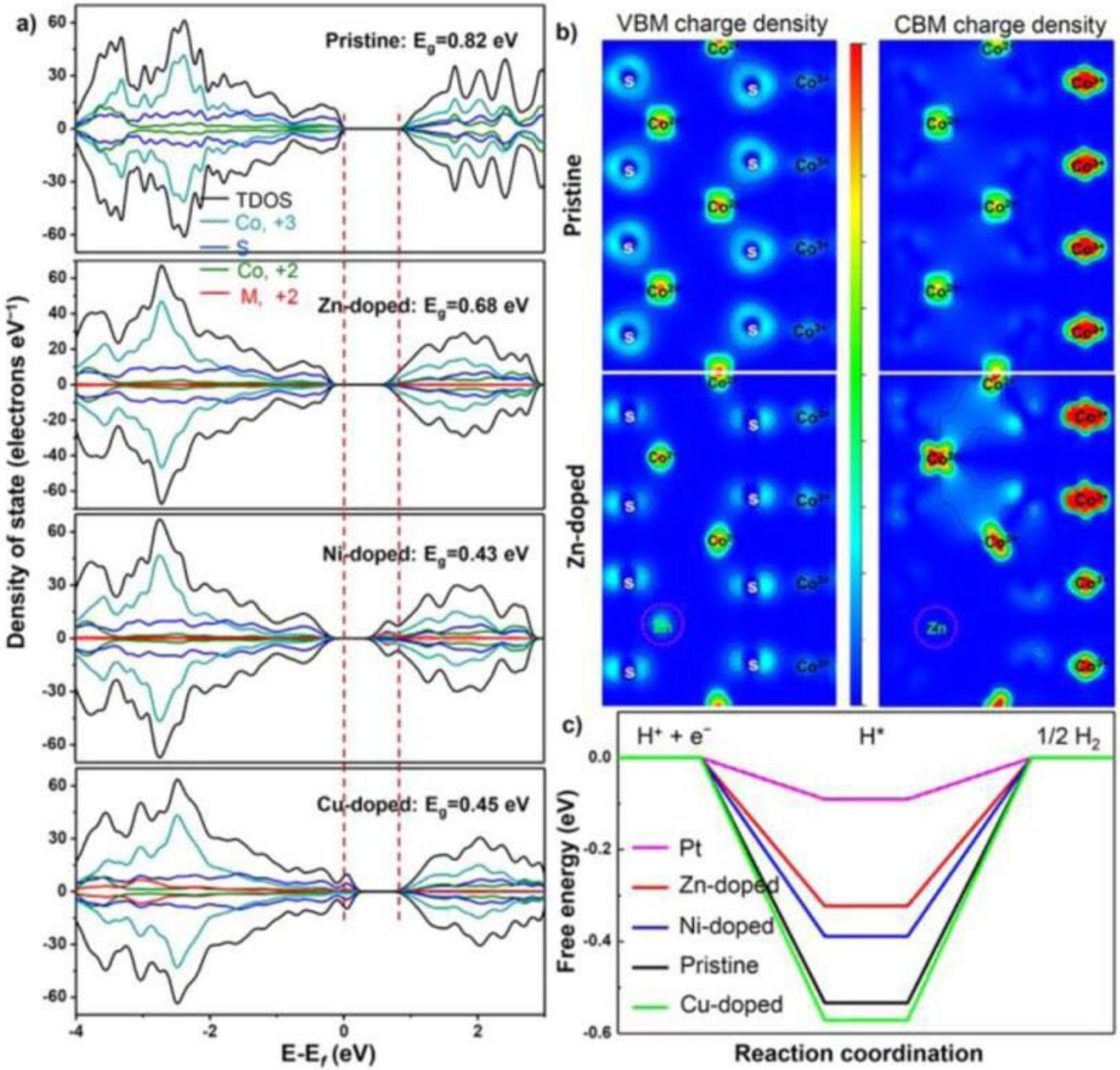
- 表面的吸附计算

O2(g) *O *OH *OOH H2O(g)

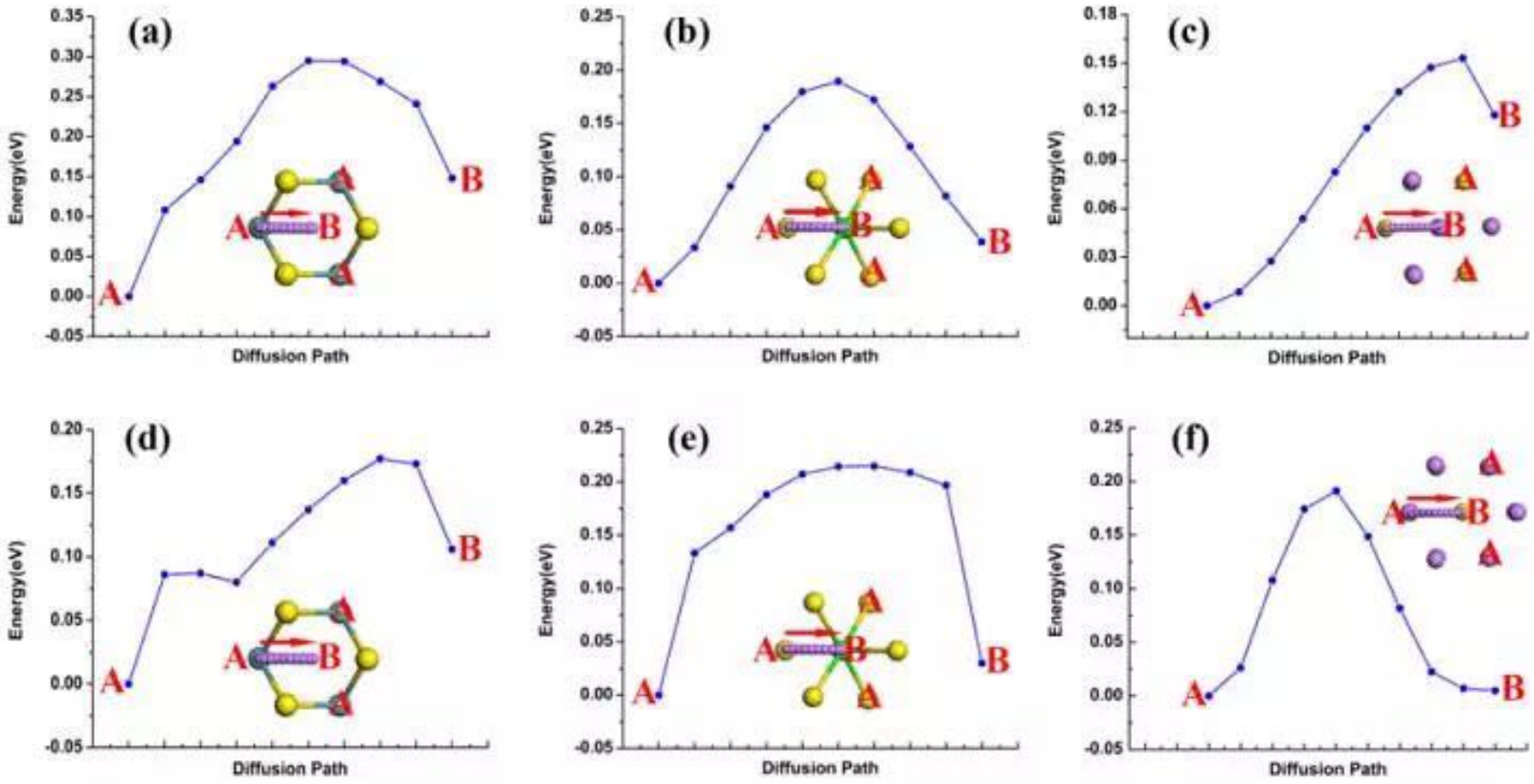
H_2 H* $H^+ + e^-$



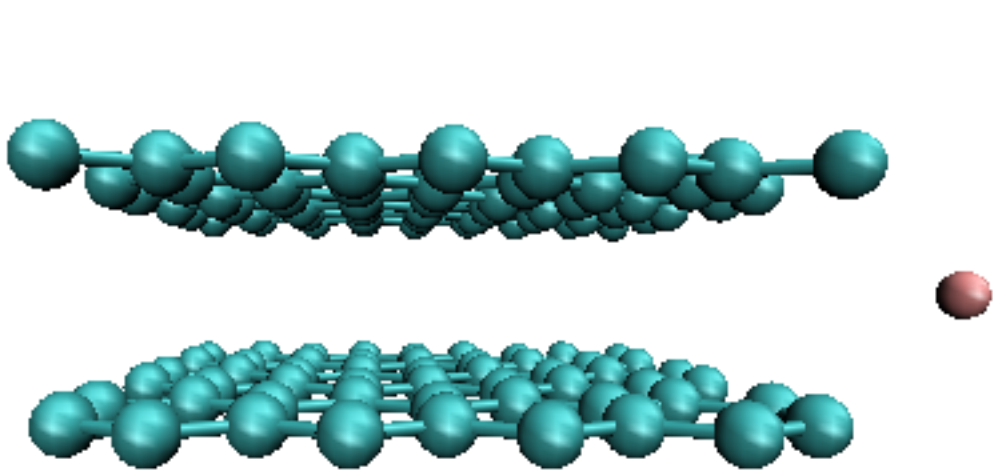
电化学 - HER

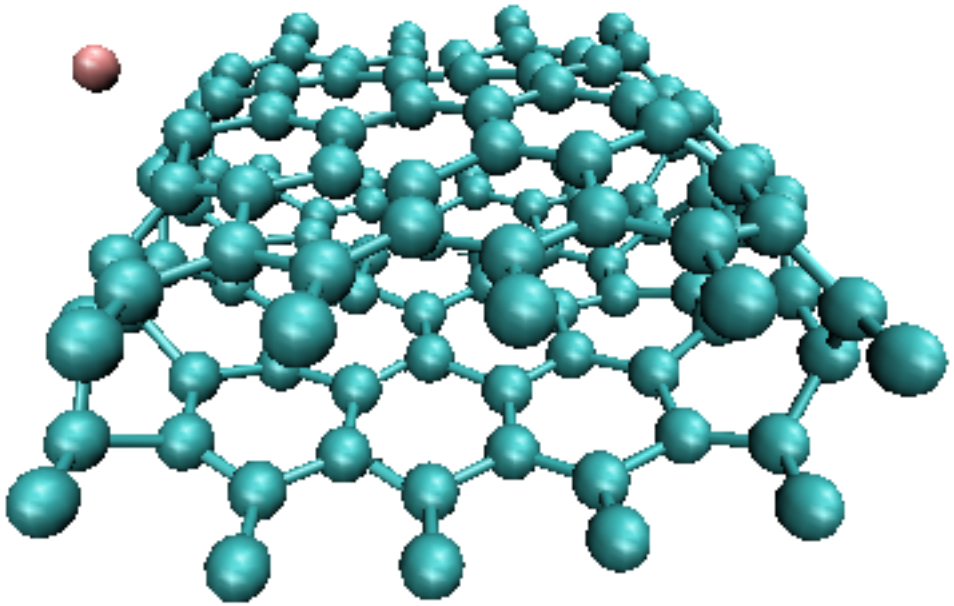

a)
Pristine: E_g=0.82 eV
TDOS
Co, +3
S
Co, +2
M, +2
Zn-doped: E_g=0.68 eV
Ni-doped: E_g=0.43 eV
Cu-doped: E_g=0.45 eV
Density of state (electrons eV^{-1})
E-E$_f$ (eV)
b)
VBM charge density
CBM charge density
Pristine
Zn-doped
c)
H$^+$ + e$^-$
H*
1/2 H$_2$
Free energy (eV)
Pt
Zn-doped
Ni-doped
Pristine
Cu-doped
Reaction coordination

锂电池

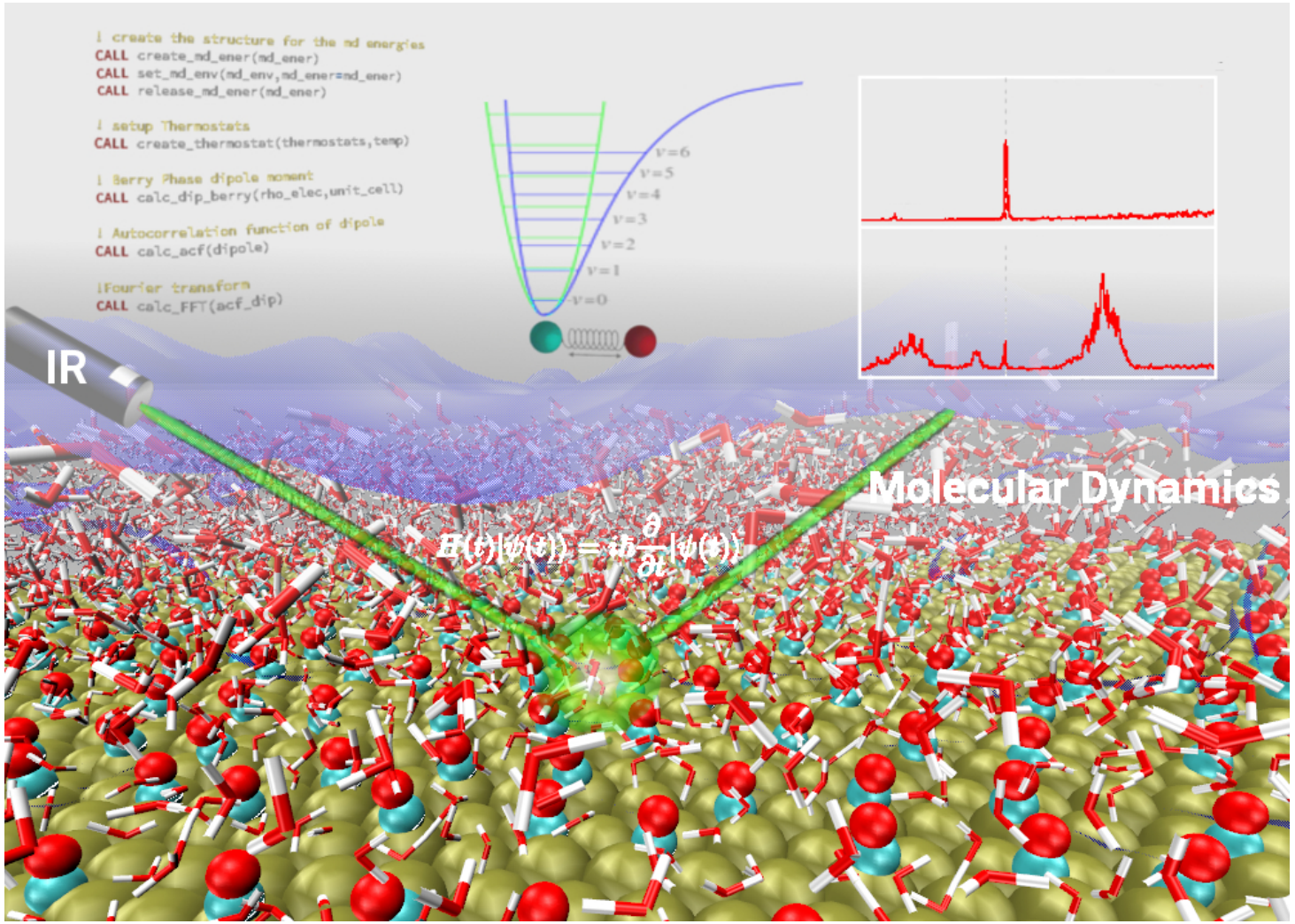


分子动力学





VMD 制图


! create the structure for the md energies
CALL create_md_ener(md_ener)
CALL set_md_env(md_env,md_ener=md_ener)
CALL release_md_ener(md_ener)
! setup Thermostats
CALL create_thermostat(thermostats,temp)
! Berry Phase dipole moment
CALL calc_dip_berry(rho_elec,unit_cell)
! Autocorrelation function of dipole
CALL calc_acf(dipole)
!Fourier transform
CALL calc_FFT(acf_dip)
v=6
v=5
v=4
v=3
v=2
v=1
v=0
IR
Molecular Dynamics