Computational Materials Theory and Methods

Lecture 3:
Quantum Mechanics

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Basics of the Molecular Orbital Theory

Basis set expansion

$$\phi_i = \sum_{a=1}^{N_{bas}} \chi_a c_{a,i}$$

Orbitals:
Molecular, crystal, etc.

N_{mo}

N_{bas}

=

N_{mo}

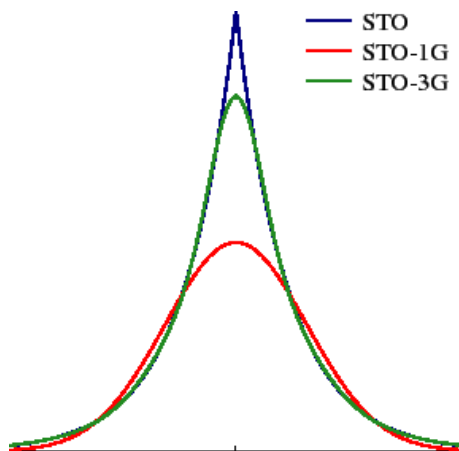N_{bas}

Basis functions:
Atomic orbitals, plane-waves, etc.

In general

$$N_{bas} \geq N_{mo}$$

Atomic orbitals

Slater-type orbitals (STO):
$$\chi_{\zeta,n,l,m}(r,\theta,\phi) = NY_l^m(\theta,\phi)r^{l-1}e^{-\zeta r}$$

Gaussian-type orbitals (GTO):
$$\chi_{\zeta,n,l,m}(r,\theta,\phi) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2}$$

where $l_x + l_y + l_z = l$

STO-2G: $\psi_{STO} = c_1\psi_{GTO_1} + c_2\psi_{GTO_2}$

$$\psi_{GTO_1} = \left(\frac{2\alpha_1}{\pi}\right)^{3/4}e^{-\alpha_1 r^2} \qquad \psi_{GTO_2} = \left(\frac{2\alpha_2}{\pi}\right)^{3/4}e^{-\alpha_2 r^2}$$

STO-2G	α_1	c_1	α_2	c_2
1s (C)	0.151623	0.678914	0.851819	0.430129
2s (C)	0.0974545	0.963782	0.384244	0.0494718
2p (C)	0.0974545	0.61282	0.384244	0.511541

Just for the radial component of wavefunction

Energy of electron in H atom

Basis set	Energy [hartree]
STO-3G	-0.49491
STO-4G	-0.49848
STO-5G	-0.49951
STO-6G	-0.49983
Exact	-0.5

Atomic orbitals

Where to get

https://bse.pnl.gov/bse/portal

Potential problems

Basis set superposition error
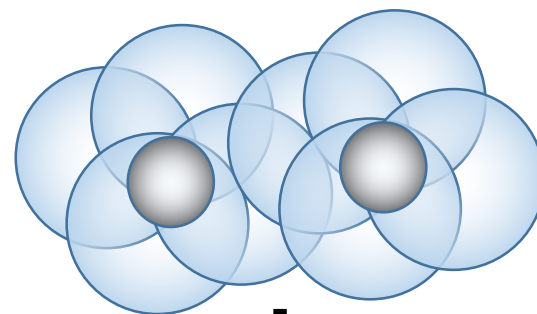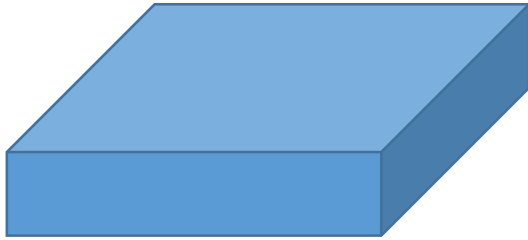

Dissociation
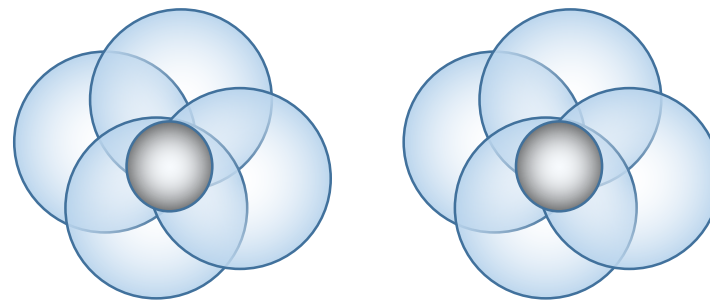
Linear dependence

Pulay forces

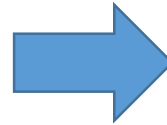# Plane waves (PW)

Real space unit cell

Reciprocal space unit cell
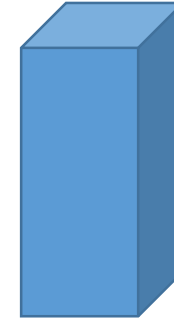
The bigger the size in real space, the smaller its counterpart in the reciprocal

Unit cell volume
$$\Omega = a\,(b \times c)$$

Real space coordinate

k-point vector (crystal momentum vector)

$$\psi_{k,i}(r) = \frac{1}{\sqrt{\Omega}} \sum_G c_n(G) e^{i(k+G)r}$$

Reciprocal space grid points

Band ("orbital") index

5

Plane waves (PW)

k-points convergence

In DFT, many properties are given by:

$$A = \sum_k w_k \, A_k$$

$$k$$

$$k$$
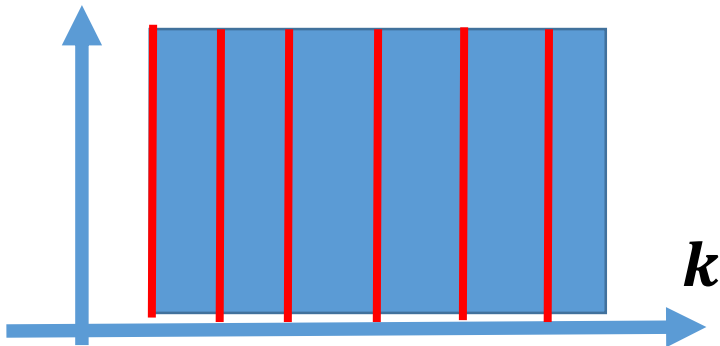
pw convergence

Kinetic energy of free electrons

$$E_{kin} = \frac{|G + k|^2}{2}$$

$$E_{kin} \leq E_{cut}$$
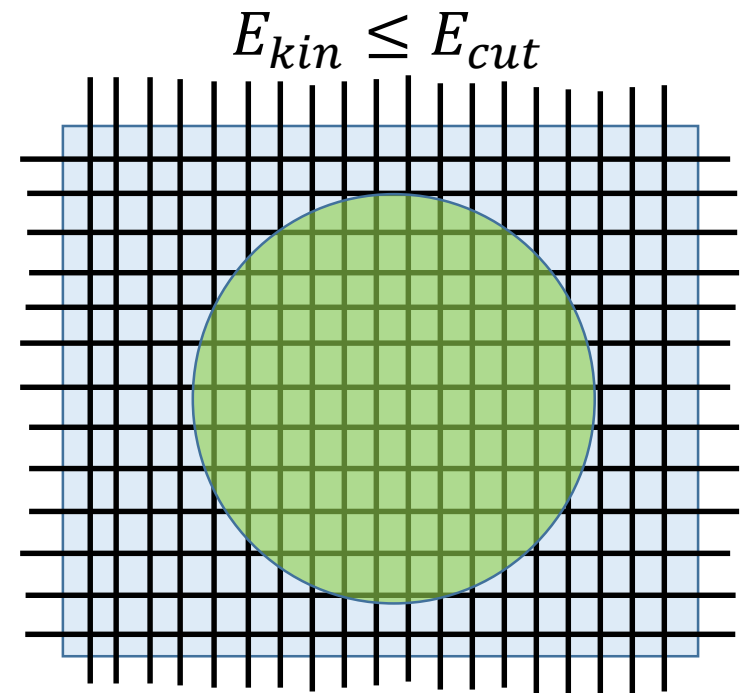
Basis set comparisons

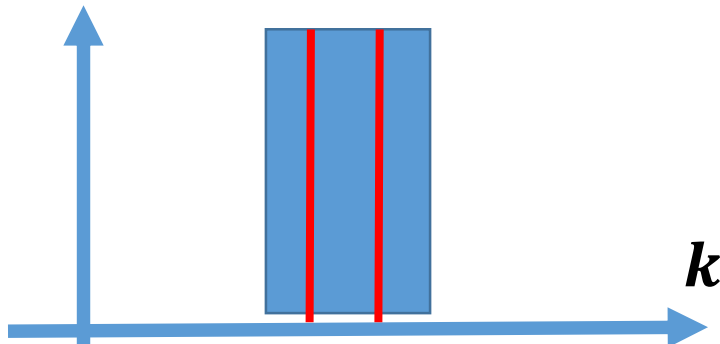## Atomic basis

Doesn't depend on the unit cell size
Good for finite systems (clusters/molecules)

Analytic integrals

All-electron

Basis set superposition error

Not systematically controllable

Linear dependence for large sets

Pulay forces

PW basis

Depends on the unit cell size, not the number of atoms
Good for periodic systems

Massive linear algebra

Needs a pseudopotential

No BSSE

Systematically controllable via k-points and
$$E_{cut}$$

No problems with linear dependence

No Pulay forces

Schrodinger equation

$$\hat{H}\boldsymbol{\phi} = \boldsymbol{E}\boldsymbol{\phi}$$

$$\sum_{b=1}^{N} \langle \chi_a | \hat{H} | \chi_b \rangle c_{b,i} = \sum_{b=1}^{N} \langle \chi_a | \chi_b \rangle c_{b,i} E_i \ , b = 1,2, \dots N$$

Variational principle

$$H \quad C \quad = \quad S \quad C \quad E$$

N_{bas} N_{mo}

Diabatic Hamiltonian
(non-interacting basis)

Adiabatic Hamiltonian
(interacting basis)
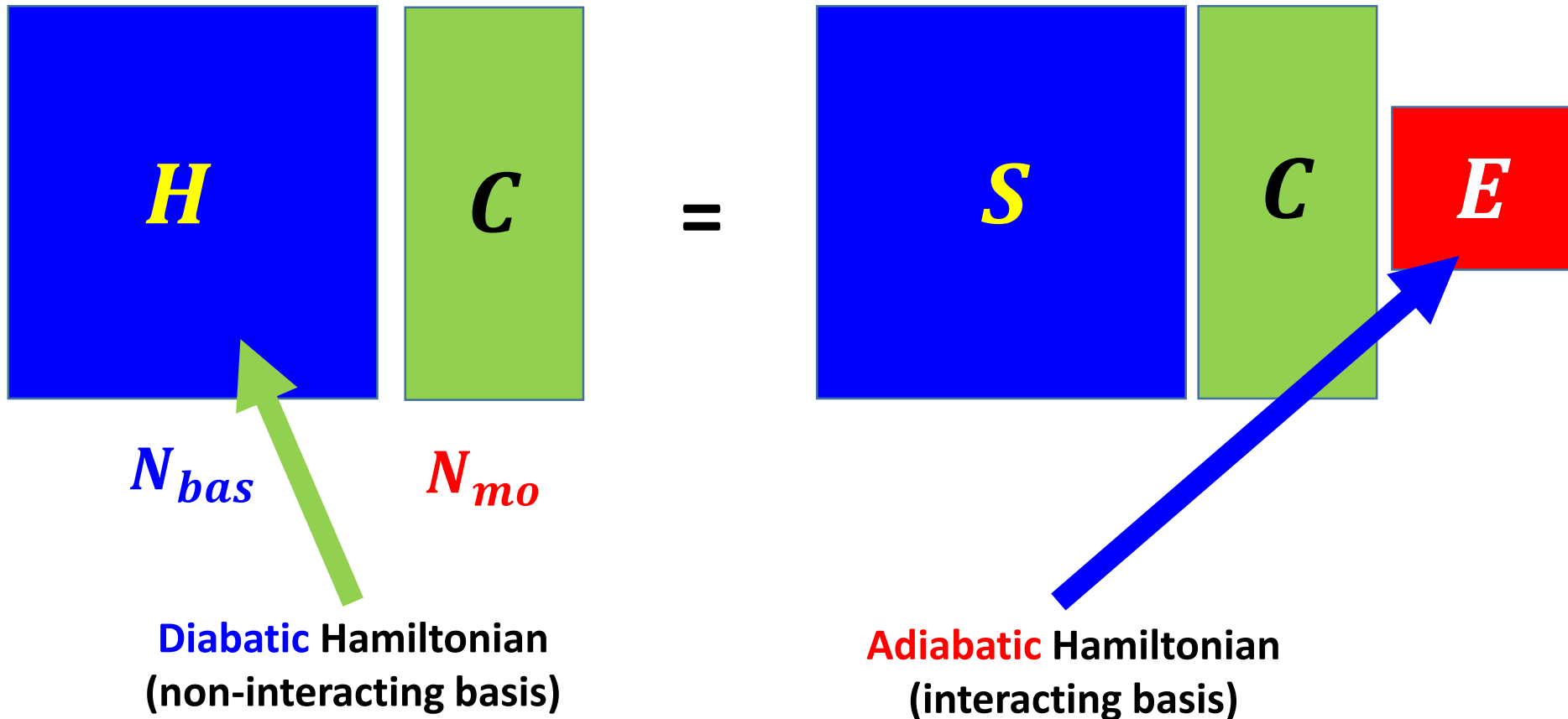
Hierarchy of wavefunctions

AO or PW (χ_i)

Primitive mathematical basis

MO or Crystal orbitals:

$$\psi_i = \sum_a \chi_a c_{a,i}$$

Solution to the mean-filed SE
(1-electron functions)

Slater determinants:

$$\Phi_i = \left| \psi_{i_1} \dots \psi_{i_N} \right|$$

Account for anti-symmetry
(exchange/fermionic statistics)

Configuration interaction (CI), SAC-CI, MR-CI: $\Psi_I = \sum_I \Phi_I c_I$

Account for correlation,
proper spin symmetry

Constructing the Hamiltonian

(in the AO basis)

Fock (mean-filed) Hamiltonian

$$F_{ab,\sigma} = H_{ab} + G_{ab,\sigma}$$

Core Hamiltonian

Coulomb and Exchange Hamiltonian

(does not depend on charge/spin density)

(depends on charge/spin density)

$$G_{ab,\sigma} = \sum_{cd} P_{cd}(ab|cd) - P_{cd,\sigma}(ad|cb)$$

$$P = COC^T$$ Density matrix

Molecular integrals

(depends on the solution of SE)

Dealing with the complexity of SE

Scaling considerations

Solution of the eigenvalue problem: $O(N_{bas}^3)$

Construction of the integrals: $O(N_{bas}^4)$

Approximations

Keep only the core part

⬇

Replace the core with a special formula
(TB- or extended Hückel)
One-shot solution

⬇

Semiempirical methods:
Simplify the 2-electron 4-center integrals, neglect some
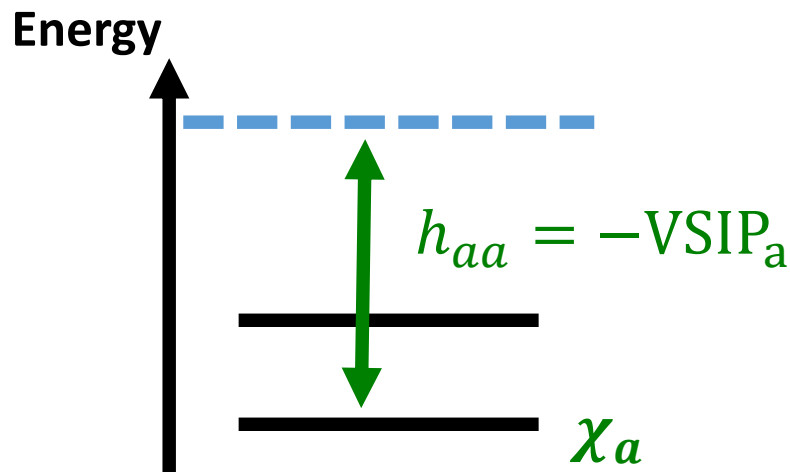(CNDO, INDO, MNDO, etc. PMn)
Need self-consistent solution

Akimov, A. V.; Prezhdo, O. V. *Chem. Rev.* **2015**, *115*, 5797–5890.

Extended Hückel theory (EHT)

Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412.

$$\chi_a = c_1 N_1 \exp(-\textcolor{red}{\zeta_1} r) + c_2 N_2 \exp(-\textcolor{red}{\zeta_2} r)$$

$$S_{ab} = \langle \chi_a | \chi_b \rangle$$

$$H_{ab} = \frac{\textcolor{blue}{K_{ab}}}{2} S_{ab}(\textcolor{green}{h_{aa}} + \textcolor{green}{h_{bb}})$$

- Simple math, efficient
- Clear meaning of parameters
- Consider it a Tight-Binding
- General-purpose (analog of UFF)
- No SCF required: 1-shot

Fancier schemes: SC-EHT
Charge-dependent VSIP

$$h_{aa} = h_{aa}^0 - A q_a$$

Energy

$$h_{aa} = -\text{VSIP}_a$$

$$\chi_a$$
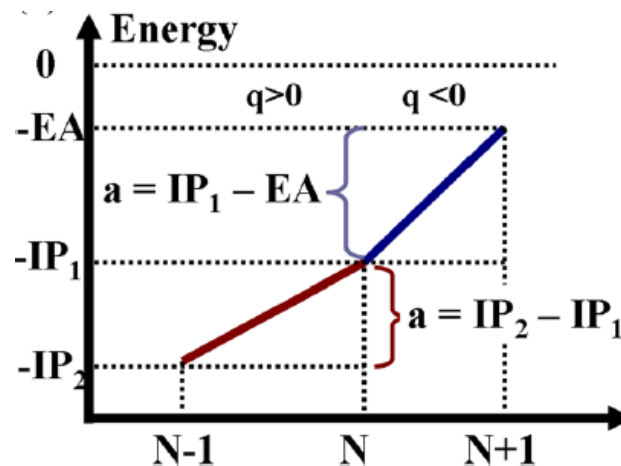
Akimov, A. V.; Prezhdo, *J. Math. Chem.* **2015**, *53*, 528–550.

Self-consistent field (SCF)

Guess density matrix, P_0
Core Hamiltonian, H
Overlap matrix, S
Pre-compute integrals in AO basis

Density matrix, P_n

Construct the Fock matrix
$$F_n = H + G(P_n)$$

Solve the eigenvalue problem:
$$F_n C_n = S C_n \epsilon_n$$

Update density matrix:
$$P_{n+1} = C_n O_n C_n^T$$

Compute the total energy :
$$E_n = tr[\, (H_n + F_n) P_n]$$

Check the convergence:
$$|P_{n-1} - P_n| < \eta_{dens}$$
$$|E_{n-1} - E_n| < \eta_{en}$$

Done