

Electronic structure

Hartree-Fock method in molecules and solids (2)

Attila Szabo & Neil Ostlund, *Modern Quantum Chemistry*, Dover, 1996

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Collection of known results (1)

$$\left[\hat{h}(1) + \sum_{b \neq a} \hat{\mathcal{J}}_b(1) - \sum_{b \neq a} \hat{\mathcal{K}}_b(1) \right] \chi_a(1) = \varepsilon_a \chi_a(1)$$

$$\hat{\mathcal{J}}_b(1) \chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1) \quad \hat{\mathcal{K}}_b(1) \chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

$$\langle a | \hat{\mathcal{J}}_b(1) | a \rangle = \langle ab | ab \rangle$$

$$\langle a | \hat{\mathcal{K}}_b(1) | a \rangle = \langle ab | ba \rangle$$

$$\langle a | \hat{\mathcal{J}}_b(1) | a \rangle - \langle a | \hat{\mathcal{K}}_b(1) | a \rangle = \langle ab | ab \rangle - \langle ab | ba \rangle$$

$$\langle b | \hat{\mathcal{J}}_b(1) | b \rangle - \langle b | \hat{\mathcal{K}}_b(1) | b \rangle = \langle bb | bb \rangle - \langle bb | bb \rangle = 0$$

$$\hat{\mathcal{F}} = \left[\hat{h}(1) + \sum_b \left(\hat{\mathcal{J}}_b(1) - \hat{\mathcal{K}}_b(1) \right) \right]$$

Collection of known results (2)

$$\hat{\mathcal{F}} = \left[\hat{h}(1) + \sum_b \left(\hat{\mathcal{J}}_b(1) - \hat{\mathcal{K}}_b(1) \right) \right]$$

Core Hamiltonian

Hartree-Fock potential

$$\hat{h}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}}$$

$$\hat{v}^{\text{HF}}(1) = \sum_b \left[\hat{\mathcal{J}}_b(1) - \hat{\mathcal{K}}_b(1) \right]$$

$$\hat{\mathcal{F}}(1)\chi_a(1) = \varepsilon_a\chi_a(1)$$

Collection of known results (3)

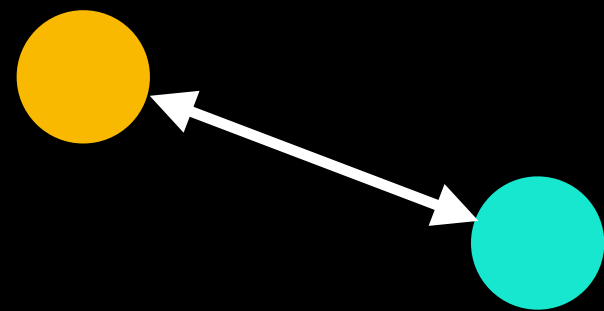
$$\hat{\mathcal{F}}(1)\chi_a(1) = \varepsilon_a\chi_a(1)$$

$$\hat{\mathcal{F}}(1)|a\rangle = \varepsilon_a|a\rangle$$

$$\langle a|\hat{h}|a\rangle + \sum_b \langle ab||ab\rangle = \varepsilon_a$$

$$E_0 = \langle \Psi_0|\hat{H}|\Psi_0\rangle = \sum_a^N \langle a|\hat{h}|a\rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab||ab\rangle \neq \sum_a \varepsilon_a$$

$$\varepsilon_a = T_a + V_{Na} + V_{ab}$$



$$\begin{aligned} \varepsilon_b &= T_b + V_{Nb} + V_{ba} \\ &= T_b + V_{Nb} + V_{ab} \end{aligned}$$

$$E_0 = T_a + T_b + V_{Na} + V_{Nb} + V_{ab}$$

$$\varepsilon_a + \varepsilon_b = T_a + T_b + V_{Na} + V_{Nb} + 2V_{ab}$$

Koopman's theorem

$$|^{N-1}\Psi_c\rangle = a_c |^N\Psi_0\rangle$$

$$\text{IP} = ^{N-1}E_c - ^NE_0$$

$$= -\langle c|\hat{h}|c\rangle - \frac{1}{2}\sum_{a[b=c]}\langle ab||ba\rangle - \frac{1}{2}\sum_{[a=c]b}\langle ab||ab\rangle$$

$$= -\langle c|\hat{h}|c\rangle - \frac{1}{2}\sum_a\langle ac||ac\rangle - \frac{1}{2}\sum_b\langle cb||cb\rangle$$

$$\langle ac|ac\rangle = \langle ca|ca\rangle$$

$$= -\langle c|\hat{h}|c\rangle - \sum_b\langle cb||cb\rangle$$

$$= -\varepsilon_c$$

$$\text{EA} = ^NE_0 - ^{N+1}E^r = -\varepsilon_r$$

Closed shell H-F

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle = |1\bar{1}2\bar{2}\cdots\frac{N}{2}\bar{\frac{N}{2}}\rangle$$

$$\hat{\mathcal{F}}|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$$

$$\hat{\mathcal{F}}|\psi_a\alpha(1)\rangle = \varepsilon_a|\psi_a\alpha(1)\rangle$$

$$\langle\alpha|\hat{\mathcal{F}}|\alpha\rangle|\psi_a\rangle = \varepsilon_a|\psi_a\rangle$$

$$\langle\alpha|\hat{h}(1)|\alpha\rangle = \int d\omega_1 \alpha^*(\omega_1)\hat{h}(1)\alpha(\omega_1) = \hat{h}(1)$$

$$\langle\alpha|\hat{h}(1)|\alpha\rangle = \hat{h}(1)$$

$$\langle\alpha|\hat{\mathcal{J}}_b|\alpha\rangle = \int d\omega_1 \alpha^*(\omega_1) \sum_{b=1}^N \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \alpha(\omega_1) = 2 \sum_b^{N/2} \left[\int d\mathbf{r}_2 \psi_b^*(2) r_{12}^{-1} \psi_b(2) \right]$$

$$\langle\alpha|\hat{\mathcal{J}}_b|\alpha\rangle = 2 \sum_b^{N/2} J_b$$

$$\begin{aligned}
 \langle \alpha | \hat{\mathcal{K}}_b | \alpha \rangle &= \int d\omega_1 \alpha^*(\omega_1) \sum_{b=1}^N \left[\int d\mathbf{x}_2 \psi_b^*(2) \sigma(\omega_2) r_{12}^{-1} \psi_c(2) \alpha(\omega_2) \right] \sigma(\omega_1) \\
 &= \sum_b^{N/2} \left[\int d\mathbf{r}_2 \psi_b^*(2) r_{12}^{-1} \psi_c(2) \right] \quad \text{There are only } \frac{N}{2} \text{ terms of } \sigma(\omega_2) = \alpha(\omega_2).
 \end{aligned}$$

$$\langle \alpha | \hat{\mathcal{K}}_b | \alpha \rangle = \sum_b^{N/2} K_b$$

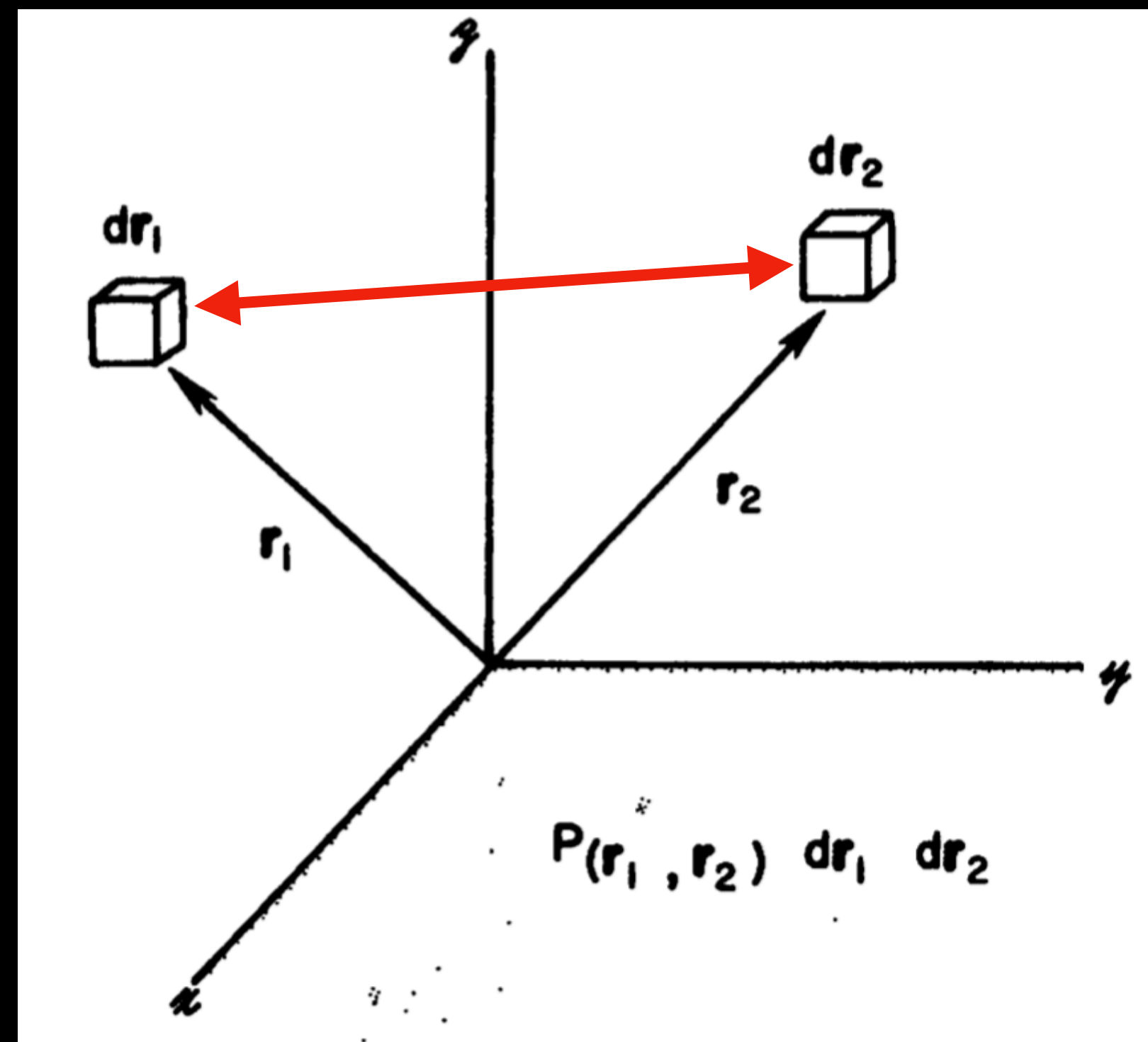
$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_b^{N/2} [2J_a(1) - K_a(1)]$$

$$E_0^{\text{closed}} = 2 \sum_a^{N/2} h_{aa} + \sum_a^{N/2} \sum_b^{N/2} [2J_{ab} - K_{ab}]$$

Self interaction

$$E_0^{\text{closed}} = 2 \sum_a^{N/2} h_{aa} + \sum_a^{N/2} \sum_b^{N/2} [2J_{ab} - K_{ab}]$$

When $a = b$, there is non-physical effect named self-interaction:



Since the electron contains -1 charge, when $a = b$, there is non-zero Coulomb interaction between the electron r_1 part and r_2 part.

$$J_{aa} = \langle aa | aa \rangle \neq 0$$

But fortunately, the exchange term can precisely counter the self-interaction. So the exchange term from H-F is also called **exact exchange**.

$$K_{aa} = \langle aa | aa \rangle \equiv J_{aa}$$

Atomic orbitals



LCAO

Molecular orbitals

Operators:

$$\hat{h}, \hat{J}, \hat{K}, \hat{\mathcal{F}}$$

Solve the eigenvalue problem:

$$\hat{\mathcal{F}} |a\rangle = \varepsilon_a |a\rangle$$

Closed shell:

$$\hat{J}_b, \hat{K}_b$$

$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_b^{N/2} [2J_a(1) - K_a(1)]$$

$$\hat{\mathcal{F}} |a\rangle = \varepsilon_a |a\rangle$$

Problem: Atomic orbitals
always too complicated to
use.

For numerical calculation: Roothaan equation



Clemens C. J. Roothaan, 1918-2019



After retiring from UChicago in 1988, he worked for Hewlett-Packard, where he developed the mathematical co-processor routines for the Itanium chip and served as a liaison for the computing needs of the Large Hadron Collider in Europe.

Introduce a set of known functions

$$\left\{ \phi_{\mu}(\mathbf{r}) \mid \mu = 1, 2, \dots, K \right\}$$

In principle, this expansion needs to use infinite number of basis functions.

Expand each molecular orbital in the linear expansion

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu}, \quad i = 1, 2, \dots, K \quad N \times N \text{ unknown parameters}$$

$$\hat{\mathcal{F}} \psi_i = \varepsilon_i \psi_i \quad \hat{\mathcal{F}} \sum_{\nu} C_{\nu i} \phi_{\nu} = \varepsilon_i \sum_{\nu} C_{\nu i} \phi_{\nu} \quad \int d\mathbf{r}_1 \phi_{\mu}^* \hat{\mathcal{F}} \sum_{\nu} C_{\nu i} \phi_{\nu} = \int d\mathbf{r}_1 \phi_{\mu}^* \varepsilon_i \sum_{\nu} C_{\nu i} \phi_{\nu}$$

$$\sum_{\nu} C_{\nu i} \int d\mathbf{r}_1 \phi_{\mu}^* \hat{\mathcal{F}} \phi_{\nu} = \varepsilon_i \sum_{\nu} C_{\nu i} \int d\mathbf{r}_1 \phi_{\mu}^* \phi_{\nu}$$

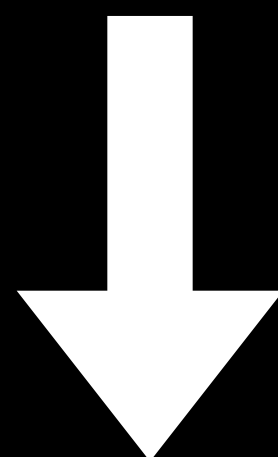
$$S_{\mu\nu} = \int d\mathbf{r}_1 \phi_{\mu\nu}^*(1) \phi_\nu(1)$$

$$F_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^* \hat{\mathcal{F}} \phi_\nu$$

$$\sum_\nu C_{\nu i} \int d\mathbf{r}_1 \phi_\mu^* \hat{\mathcal{F}} \phi_\nu = \varepsilon_i \sum_\nu C_{\nu i} \int d\mathbf{r}_1 \phi_\mu^* \phi_\nu$$



$$\sum_\nu F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_\nu S_{\mu\nu} C_{\nu i} \quad i = 1, 2, \dots, K$$



$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

$$\hat{\mathcal{F}} = \hat{h}(1) + \sum_a^{N/2} [2J_a(1) - K_a(1)]$$

$$\mathbf{F}_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^* \hat{\mathcal{F}} \phi_\nu$$

$$= \int d\mathbf{r}_1 \phi_\mu^* \hat{h}(1) \phi_\nu + \sum_a^{N/2} \int d\mathbf{r}_1 \phi_\mu^* [2\hat{J}_a - \hat{K}_a] \phi_\nu$$

$$= H_{\mu\nu}^{\text{core}} + \sum_{a=1}^{N/2} \sum_{\lambda,\sigma}^{K,K} C_{\lambda a} C_{\sigma a}^* [2\langle \mu\sigma | \nu\lambda \rangle - \langle \mu\sigma | \lambda\nu \rangle]$$

$$= H_{\mu\nu}^{\text{core}} + \sum_{\lambda,\sigma}^{K,K} P_{\lambda\sigma} [2\langle \mu\sigma | \nu\lambda \rangle - \langle \mu\sigma | \lambda\nu \rangle]$$

$$\mathbf{F}_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu}$$

$$\begin{aligned} H_{\mu\nu}^{\text{core}} &= \int d\mathbf{r}_1 \phi_\mu^* \left[-\frac{1}{2} \nabla_1^2 \right] \phi_\nu \\ &+ \int d\mathbf{r}_1 \phi_\mu^* \left[-\sum_A^M \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} \right] \phi_\nu \\ &= T_{\mu\nu} + V_{\mu\nu}^{\text{nucl}} \end{aligned}$$

$$J_a = \int d\mathbf{r}_2 \psi_a^* r_{12}^{-1} \psi_a$$

$$= \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* \int d\mathbf{r}_2 \phi_\sigma^* r_{12}^{-1} \phi_\lambda$$

$$K_a \phi_\nu = \left[\int d\mathbf{r}_2 \psi_a^* r_{12}^{-1} \phi_\nu \right] \psi_a$$

$$= \left[\int d\mathbf{r}_2 \sum_\sigma C_{\sigma a}^* \phi_\sigma^* r_{12}^{-1} \phi_\nu \right] \sum_\lambda C_{\lambda a} \phi_\lambda$$

$$= \sum_{\lambda\sigma} C_{\sigma a}^* C_{\lambda a} \left[\int d\mathbf{r}_2 \phi_\sigma^* r_{12}^{-1} \phi_\nu \right] \phi_\lambda$$

$$\mathbf{F}_{\mu\nu} = H^{\text{core}} + G_{\mu\nu}$$

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon$$

$$\mathbf{F} = \mathbf{F}(\mathbf{C})$$

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}$$

So if we choose: $\mathbf{X} = \mathbf{S}^{-1/2} \rightarrow \mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{S}^{-1/2} \mathbf{S} \mathbf{S}^{-1/2} = \mathbf{1}$

$$\mathbf{C} = \mathbf{X} \mathbf{C}'$$

$$\Rightarrow$$

$$\mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{S} \mathbf{X} \mathbf{C}' \epsilon$$

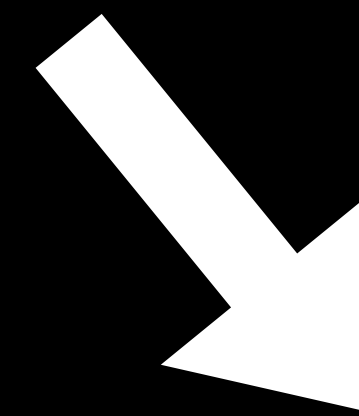
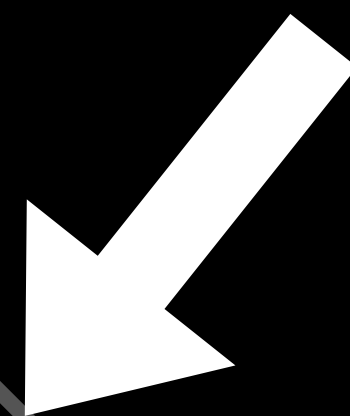
$$\mathbf{X}^\dagger \mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{X}^\dagger \mathbf{S} \mathbf{X} \mathbf{C}' \epsilon$$

$$(\mathbf{X}^\dagger \mathbf{F} \mathbf{X}) \mathbf{C}' = \mathbf{C}' \epsilon$$

$$\mathbf{F}' \mathbf{C}' = \mathbf{C}' \epsilon$$

Choose the matrix \mathbf{X}

First, diagonalize the overlap matrix: $\mathbf{S} = \mathbf{U}\mathbf{s}\mathbf{U}^\dagger$



Symmetric

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$$

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$$

Non-symmetric

PySCF

The Python-based Simulations of Chemistry Framework

PySCF is an open-source collection of electronic structure modules powered by Python. The package aims to provide a simple, lightweight, and efficient platform for quantum chemistry calculations and methodology development.

currently v.1.7.1

Get Started

```
# set up the H2 molecule
import numpy as np
import scipy.linalg
from pyscf import gto, scf
r=1.4
# Set up H2 molecular geometry and basis
mol = gto.M(
    atom = [['H', (0, 0, 0)],
            ['H', (r, 0, 0)]],
    basis = "sto-3g", unit="bohr")
```



Psi4: OPEN-SOURCE QUANTUM CHEMISTRY

Usage of basis

Pople Style Basis Sets

STO-nG basis sets:

Minimum basis set.
Slater type orbital
consisting of n PGTOs.



K-nlmG basis sets:

Split valence type,

- K (in front of '-'): how many PGTOs are used for representing the core orbitals.
- nlm (after '-'): how many functions the valence orbitals are split into, how many PGTOs are used.
- nl: a doublet split valence.
- nlm: a triplet split valence.

(s- and p- functions) G (polarization functions)

The outer part of valence orbitals, represented by 1 PGTO.

3-21G

The core orbitals are a contraction of three PGTOs.

The inner part of valence orbitals is a contraction of 2 PGTOs.

The outer part of valence orbitals, represented by 1 PGTO.

6-31G

The core orbitals are a contraction of 6 PGTOs.

The inner part of valence orbitals is a contraction of 3 PGTOs.

$$6-31G^* = 6-31G(d)$$

Add a set of d-type basis functions
to the heavy atoms.

$$6-31G^{**}=6-31G(d,p)$$

Add a set of d-type basis functions to the heavy atoms, and add a single set of p-type function to H.

The number of 6-31G** basis functions:

H: $2+3=5$

(1s, 1s'), (2ps, 2py, 2pz)

Li to F: $1+2+2*3+6=15$

(1s, core), (2s, 2s') (2p, 2p') (2d, 6 functions in Cartesian coordinate)

Add diffuse functions (+)

The first '+': One set of diffuse s- and p-functions on heavy atoms.

The second '+': a diffuse s-function is added to hydrogen atoms.

6-31+G(d)

6-311++G(2df,2pd)

6-311++G(3df,3pd)

Beyond Hartree-Fock

Correlation energy

$$E_{\text{corr}} = E_{\text{non-rel}} - E_{\text{HF}}$$

Static correlation

Weak or broken bonds involving a large occupation of antibonding orbitals cannot be described by a single determinant.

Dynamic correlation

Remaining correlation associated with the instantaneous short-range electron-electron interactions.

Configuration Interaction (CI)

$$|\psi\rangle = C_0 |\psi_0\rangle + \sum_a^{\text{vir}} \sum_i^{\text{occ}} C_i^a |\psi_i^a\rangle + \sum_{a<b}^{\text{vir}} \sum_{i<j}^{\text{occ}} C_{ij}^{ab} |\psi_{ij}^{ab}\rangle + \dots$$

CIS,CISD...

$$\hat{a}_a^\dagger \hat{a}_i |\psi_0\rangle = |\psi_i^a\rangle$$

MR CI

CASSCF

Manybody Perturbation, MP

$$\hat{H}^{(0)} = \sum_i \hat{f}_i \quad \psi_0^{(0)} = \psi_{HF}$$

$$\hat{H}^{(0)} \psi_0^{(0)} = \sum_{m=1}^N \epsilon_m \psi_0^{(0)}$$

$$E_0^{(0)} + E_0^{(1)} = E_{HF}$$

$$E_0^{(2)} = \sum_{s \neq 0} \frac{|\langle \psi_s^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_s^{(0)}}$$

$$= \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{i=j+1}^n \sum_{j=1}^{n-1} \frac{|\langle ab | r_{12}^{-1} | ij \rangle - \langle ab | r_{12}^{-1} | ji \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

CASPT2

MP2 does not work well at geometries far from equilibrium.
Not variational.

Coupled Cluster, CC

CC wavefunction ansatz

$$\begin{aligned}\psi &= e^{\hat{T}} \psi_{HF} & \hat{T} &= \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n & \hat{T}_1 \psi_0 &= \sum_{a=n+1}^{\infty} \sum_{i=1}^n t_i^a \psi_i^a \\ \langle \psi_0 | \hat{H} | e^{\hat{T}} \psi_0 \rangle &= E \langle \psi_0 | e^{\hat{T}} \psi_0 \rangle = E \\ \langle \psi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \psi_0 \rangle &= \langle \psi_0 | \hat{H} | e^{\hat{T}} \psi_0 \rangle \langle \psi_{ij}^{ab} | e^{\hat{T}} \psi_0 \rangle\end{aligned}$$

CCD

$$\langle \psi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2) \psi_0 \rangle = (E_{\text{HF}} + \langle \psi_0 | \hat{H} | \hat{T}_2 \psi_0 \rangle) \langle \psi_{ij}^{ab} | \hat{T}_2 \psi_0 \rangle$$