

Chapter 7. Ab initio Theory

Ab initio: from the first principles.

I. Roothaan-Hall approach

Assuming Born-Oppenheimer approximation, the electronic Hamiltonian:

$$\begin{aligned}\hat{H} &= \hat{T}_e + V_{en} + V_{ee} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_a \frac{Z_a}{r_{ia}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}\end{aligned}$$

Wavefunction (Slater determinant):

$$|\Psi\rangle = |\chi_1 \chi_2 \dots \chi_N|$$

where $|\chi_i\rangle = |\psi_i\rangle \otimes |\alpha, \beta\rangle$ is the MO spin-orbitals. Substituting it to the Schrödinger equation leads to the single-electron Hartree-Fock eq.

$$\hat{F}_i |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

where the Fock operator for a close-shell singlet is

$$\hat{F}_i = -\frac{1}{2} \nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}} + \sum_{j=1}^{N/2} [2\hat{J}_j(i) - \hat{K}_j(i)]$$

It is difficult to solve because of its integro-differential nature.

Roothaan-Hall equations

$$|\psi_i\rangle = \sum_{\nu=1}^K c_{\nu i} |\phi_{\nu}\rangle \quad (\text{LCAO-MO})$$

in which $|\phi_{\nu}\rangle$ are the atomic basis functions. Substituting back to H-F equation, and multiplying $\langle\phi_{\mu}|$ on the left and integrate:

$$\sum_{\nu=1}^K c_{\nu i} \langle\phi_{\mu}(i)|\hat{F}_i|\phi_{\nu}(i)\rangle = \varepsilon_i \sum_{\nu=1}^K c_{\nu i} \langle\phi_{\mu}(i)|\phi_{\nu}(i)\rangle$$

The overlap matrix

$$S_{\mu\nu} = \langle\phi_{\mu}(i)|\phi_{\nu}(i)\rangle$$

The Fock matrix:

$$\begin{aligned} F_{\mu\nu} &= \langle\phi_{\mu}(i)|\hat{F}_i|\phi_{\nu}(i)\rangle \\ &= \left\langle\phi_{\mu}(i)\left|-\frac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}}\right|\phi_{\nu}(i)\right\rangle \\ &\quad + \sum_{j=1}^{N/2} \langle\phi_{\mu}(i)|2\hat{J}_j(i) - \hat{K}_j(i)|\phi_{\nu}(i)\rangle \\ &= h_{\mu\nu} + 2J_{\mu\nu} - K_{\mu\nu} \end{aligned}$$

where the Coulomb and exchange integrals:

$$J_{\mu\nu} = \sum_j \sum_{\lambda\sigma} c_{j\lambda} c_{j\sigma} \left\langle\phi_{\mu}(1)\phi_{\nu}(1)\left|\frac{1}{r_{12}}\right|\phi_{\lambda}(2)\phi_{\sigma}(2)\right\rangle$$

$$K_{\mu\nu} = \sum_j \sum_{\lambda\sigma} c_{j\lambda} c_{j\sigma} \left\langle \phi_\mu(1) \phi_\lambda(1) \left| \frac{1}{r_{12}} \right| \phi_\nu(2) \phi_\sigma(2) \right\rangle$$

Since the charge density matrix

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{N/2} c_{i\lambda} c_{i\sigma}$$

The integrals can be simplified as

$$J_{\mu\nu} = \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu | \lambda\sigma)$$

$$K_{\mu\nu} = \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\lambda | \nu\sigma)$$

So, the Fock matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma)]$$

The matrix form of R-H eq.

FC=SCE

Roothaan-Hall equation is nonlinear since the Fock matrix depends on the LCAO coefficients. In other words, an electron experience an average field of other electrons and nuclei.

Solution: self-consistent field (SCF)

- initial guess of single electron field
- solve R-H eq. for new LCAO coefficients
- iterate until convergence

SCF Procedure:

- P** from initial guess of LCAO coefficients **C**.
- construct Fock matrix from **P** and integrals
- construct overlap matrix and diagonalize it to obtain $\mathbf{S}^{-1/2}$:

$$\mathbf{U}^{-1}\mathbf{S}\mathbf{U} = \mathbf{D} \quad (\mathbf{D} \text{ is diagonal})$$

$$\mathbf{S}^{-1/2} = \mathbf{U}\mathbf{D}^{-1/2}\mathbf{U}^{-1}, \quad \text{so} \quad \mathbf{S}^{-1/2}\mathbf{S}\mathbf{S}^{-1/2} = \mathbf{I}$$

- transform R-H eq. to an eigenequation

$$\mathbf{S}^{-1/2}\mathbf{F}\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{S}\mathbf{C}\mathbf{E}$$

$$\mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}\mathbf{S}^{1/2}\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C}\mathbf{E}$$

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}, \quad \text{where} \quad \mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}, \quad \mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C}$$

- diagonalizing \mathbf{F}' for energies and coefficients
- calculate new **P** from **C**.
- check convergence to determine if to stop or reiterate.

II. Basis sets

The atomic basis used in LCAO can be of Slater or Gauss-type.

Slater-type orbitals (STO):

$$|\phi^{STO}\rangle \propto r^{n-1} e^{-\zeta r} Y_{lm_l}(\theta, \varphi)$$

Faithful representation of AOs, but difficult to evaluate integrals.

Gauss-type orbitals (GTO):

$$|\phi^{GTO}\rangle = x^a y^b z^c e^{-\alpha r^2}$$

0th-order GTO:

$$g_s \propto e^{-\alpha r^2}$$

1st-order GTOs:

$$g_x \propto x e^{-\alpha r^2}, \quad g_y \propto y e^{-\alpha r^2}, \quad g_z \propto z e^{-\alpha r^2}$$

2nd-order GTOs:

$$g_{xx}, g_{yy}, g_{zz}, g_{xy}, g_{yz}, g_{xz}, \quad (6)$$

Lost clear AO characters, but easy for integration as product of Gaussians is also a Gaussian.

Compromise:

$$|\phi_\mu\rangle = \sum_p d_{\mu p} |\phi_p^{GTO}\rangle$$

The expansion coefficients and Gaussian exponents are chosen to mimic the corresponding STO. These parameters are often fixed in contraction.

Types of basis set

i. minimal basis, STO- n G

Use n primitive GTO to fit a STO.

Higher n is not necessarily better.

ii. split-valence or double-zeta basis: 3-21G, 4-31G, 6-31G

1 STO for core orbitals and 2 STOs for valence orbitals for better description of chemical bonds.

3-21G: core orbitals with 3 GTOs per STO, valence orbitals with 2 contracted GTOs for one STO and 1 GTO for a diffuse STO with a different ζ .

iii. triple-zeta basis, 6-311G

1 STO for core orbitals and 3 STOs for valence orbitals.

Higher # of zeta possible

iv. polarized functions, 6-31G*, 6-31G**

Adding polarization (p, d, f) functions improves results, particularly anisotropy.

6-31G*: DZ+P, add polarization (d) functions to non-H atoms. (**: add p to H as well)

6-31G(kp, ld), 6-31G** =(p, d),

v. diffuse functions, 6-31+G, 6-31++G

Adding GTO with very small α improves description of weak bonds.

+: add to non-H atoms (++: add to H as well)

Example: 6-311G** for H₂O

H: 3 s -type STOs with 5 (311) GTOs,
3 p -type polarization functions.

O: 1 1s-core STO with 6 GTOs
3 s -type STOs with 5 (311) GTOs
9 p -type STOs with 15 (311) GTOs,
5 d -type polarization functions with 6 primitive GTOs.

total: 30 basis functions, 48 primitive GTOs

Increasing basis set leads to more costly calculations.

The Hartree-Fock limit:

As the basis size increases, the electronic energy and geometry converge to the Hartree-Fock limit.

The H-F limit:

- good equilibrium geometry (0.05 Å)
- 10-15% higher vibrational frequencies (0.89 scaling)
- dissociation energy and barrier height ~50% or more.

Spin restricted and unrestricted HF

RHF: use one set of MOs for both α and β electrons

May lead to problems with open-shell molecules such as NO and O₂.

UHF: use two different sets of MO for the α and β electrons.

More general and flexible, but different equation.

More accurate for close-shell molecules as well, particularly at dissociation asymptotes.

III. Electronic correlation

Because of the mean field approximation, H-F ignores the interactions between individual electrons. The energy difference is the correlation energy.

Correlation energy important for quantitative results.

Correlation energy can be captured by either variational or perturbative methods

Configuration interaction (CI):

Example: H₂, in the 2-MO approximation, two electrons can be placed in the following combinations:

$$\sigma_g(1)\sigma_g(2), \sigma_g(1)\sigma_u(2), \sigma_u(1)\sigma_g(2), \sigma_u(1)\sigma_u(2)$$

parity: *g* *u* *u* *g*

CI wavefunction:

$$|\Psi_g\rangle = c_1|\sigma_g(1)\sigma_g(2)\rangle + c_2|\sigma_u(1)\sigma_u(2)\rangle$$

Varying c_1, c_2 lowers energy.

Configuration state functions (CSF):

For K spin-orbitals, the H-F configuration fills the lowest N .

Excited configurations possible by moving e^- to higher virtual orbitals.

Single excitations: 1 electron is excited.

$$\left| \Phi_a^p \right\rangle = \left| \chi_1 \chi_2 \cdots \chi_p \chi_b \cdots \chi_N \right|$$

Double excitations: 2 electrons are excited.

$$\left| \Phi_{ab}^{pq} \right\rangle = \left| \chi_1 \chi_2 \cdots \chi_p \chi_q \cdots \chi_N \right|$$

...

Illustration:

CSF: linearly combined determinants that have correct electronic symmetry.

CI wavefunction:

$$\left| \Psi^{CI} \right\rangle = C_0 \left| \Phi \right\rangle + \sum_{a,p} C_a^p \left| \Phi_a^p \right\rangle + \sum_{a < b} \sum_{p < q} C_{ab}^{pq} \left| \Phi_{ab}^{pq} \right\rangle + \dots$$

The coefficients are variationally determined to lower E .
Numerically, solving eigenequation

$$\mathbf{HC}=\mathbf{EC}$$

Note: the MO coefficients are already determined in the H-F calculations and fixed in CI.

S/D/T/CI: CI with singles/doubles/triples excitations. SDCI preferred.

Full CI: include all CFSs, very expansive ($\propto K^N / N!$)

Problem: size inconsistency, energy and energy error do not increase with the size of molecule.

CI vs. HF

Multiconfiguration SCF

MCSCF: optimize both MO coefficients and CI coefficients, more accurate.

MCSCF-CI: MCSCF followed by CI.

CASSCF (complete active space SCF): spin-orbitals divided into three classes:

- inactive orbitals: low energy doubly occupied spin-orbitals
- virtual orbitals: high energy empty spin-orbitals
- active orbitals: spin-orbitals in between

CFSs in CASSCF arise from all possible ways of distributing electrons among the active spin-orbitals.

Better for bond forming/breaking processes involving the active electrons

Multi-reference CI

Generate CFSs not only from the H-F configuration, but also excited ones as well.

Good for excited states and dissociation limits.

Coupled-cluster (CC) methods

$$|\Psi_{CC}\rangle = (e^{\hat{T}_1 + \hat{T}_2 + \dots})|\Phi_{HF}\rangle$$

where the operators in the exponent represent single, double, triple excitations, etc.

Better than CI because it includes excitations in all orders and is better in capturing more correlation energy.

CCSD: coupled-cluster with single and double excitations.

Møller-Plesset (MP) perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

where at H-F limit they are

$$\hat{H}_0 = \sum_i \hat{F}_i$$

$$\hat{H}' = \hat{H} - \sum_i \hat{F}_i$$

Energy corrections to $E^0 = \langle \Phi_0 | \hat{H}_{HF} | \Phi_0 \rangle$

$$E^{(1)} = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle \quad 1^{\text{st}} \text{ order}$$

It can be shown that

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

so MP1 is not effective in including correlation energy.

$$E^{(2)} = \sum_J \frac{\langle \Phi_0 | \hat{H}' | \Phi_J \rangle \langle \Phi_J | \hat{H}' | \Phi_0 \rangle}{E^0 - E_J} \quad 2^{\text{nd}} \text{ order}$$

MP2: includes double excitations.

MP3/4 better, include higher excitations, but much more expensive.

Pros and cons of CI and MP approaches:

CI:

- variational
- provide info for excited states
- size-inconsistence
- can be quite expansive, and converge slowly

MP:

- size-consistent
- good for molecular properties
- often used for single point calculations
- difficult to do high-order perturbation calculations
- non-variational, energy can be lower than true energy
- not good for geometry far from equilibrium
- not applicable to excited states

Protocol for accurate determination of important properties such as atomization energy, ionization energy, electronic and proton affinities etc.

G3:

- HF/6-31G* geometry optimization
- MP2/6-31G* geometry optimization
- Single point MP4
- Corrections