



NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 33: The Density Matrix

Hartree-Fock-Roothan Equations

HF Equation with molecular orbitals

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

$$\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_b^{N/2} 2\hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$$

molecular orbitals as a linear combination of basis functions (Roothan)

$$\psi_a(i) = \sum_{\nu=1}^K C_{\nu a} \Theta_{\nu}(i) \text{ for } a = 1, 2, \dots, K$$

Hartree-Fock-Roothan Equations

$$\sum_{\nu=1}^K \mathcal{F}_{\mu\nu} C_{\nu a} = \varepsilon_a \sum_{\nu=1}^K S_{\mu\nu} C_{\nu a} \text{ for } a = 1, 2, \dots, K$$

$$\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon}$$



The charge density

Consider a closed-shell system,

$$\begin{aligned}\rho(r) &= 2 \sum_a^{N/2} \psi_a^*(i) \psi_a(i) = 2 \sum_a^{N/2} \sum_{\nu} C_{\nu a}^* \Theta_{\nu}^*(i) \sum_{\mu} C_{\mu a} \Theta_{\mu}(i) \\ &= \sum_{\mu\nu} \left(2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \right) \Theta_{\mu}(i) \Theta_{\nu}^*(i) \\ &= \sum_{\mu\nu} P_{\mu\nu} \Theta_{\mu}(i) \Theta_{\nu}^*(i)\end{aligned}$$

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$$

density matrix

Total Charge Density

$$\int dr \rho(r) = 2 \sum_a^{N/2} \int dr |\psi_a(r)|^2 = 2 \sum_a^{N/2} 1 = N$$



Matrix Representation of the Fock Operator: Fock Matrix

$$F_{\mu\nu} = \langle \Theta_\mu | \hat{\mathcal{F}}(i) | \Theta_\nu \rangle$$

$$\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_b^{N/2} 2\hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$$

$$= \langle \Theta_\mu | \hat{h}_i | \Theta_\nu \rangle + \sum_b^{N/2} \langle \Theta_\mu | 2\hat{\mathcal{J}}_b(i) | \Theta_\nu \rangle - \langle \Theta_\mu | \hat{\mathcal{K}}_b(i) | \Theta_\nu \rangle$$

$$\hat{\mathcal{J}}_b(i) | \Theta_\nu(i) \rangle = \int dr_j \psi_b^*(j) r_{ij}^{-1} \psi_b(j) | \Theta_\nu(i) \rangle$$

$$\hat{\mathcal{K}}_b(i) | \Theta_\nu(i) \rangle = \int dr_j \psi_b^*(j) r_{ij}^{-1} \psi_b(i) | \Theta_\nu(j) \rangle$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_b^{N/2} 2 \langle \Theta_\mu(i) \psi_b(j) | r_{ij}^{-1} | \psi_b(j) \Theta_\nu(i) \rangle - \langle \Theta_\mu(i) \psi_b(j) | r_{ij}^{-1} | \psi_b(i) \Theta_\nu(j) \rangle$$



Fock Matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_b^{N/2} 2 \langle \Theta_\mu(i) \psi_b(j) | r_{ij}^{-1} | \psi_b(j) \Theta_\nu(i) \rangle - \langle \Theta_\mu(i) \psi_b(j) | r_{ij}^{-1} | \psi_b(i) \Theta_\nu(j) \rangle$$

$$\psi_b = \sum_\sigma C_{\sigma b} \Theta_\sigma = \sum_\lambda C_{\lambda b} \Theta_\lambda$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_b 2 \left\langle \Theta_\mu(i) \sum_\lambda C_{\lambda b} \Theta_\lambda(j) | r_{ij}^{-1} | \sum_\sigma C_{\sigma b} \Theta_\sigma(j) \Theta_\nu(i) \right\rangle$$

$$- \sum_b \left\langle \Theta_\mu(i) \sum_\lambda C_{\lambda b} \Theta_\lambda(j) | r_{ij}^{-1} | \sum_\sigma C_{\sigma b} \Theta_\sigma(i) \Theta_\nu(j) \right\rangle$$

$$= h_{\mu\nu} + \sum_{\lambda, \sigma} \left(2 \sum_b C_{\sigma b} C_{\lambda b}^* \right) \left(\langle \Theta_\mu(i) \Theta_\lambda(j) | r_{ij}^{-1} | \Theta_\nu(i) \Theta_\sigma(j) \rangle - \frac{1}{2} \langle \Theta_\mu(i) \Theta_\lambda(j) | r_{ij}^{-1} | \Theta_\sigma(i) \Theta_\nu(j) \rangle \right)$$

$$= h_{\mu\nu} + \sum_{\sigma, \lambda} P_{\sigma\lambda} \left((\mu\lambda | \nu\sigma) - \frac{1}{2} (\mu\lambda | \sigma\nu) \right)$$



Components of Fock Matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

One-electron integrals

$$\begin{aligned} h_{\mu\nu} &= \left\langle \Theta_{\mu}(i) \left| \hat{h}_i \right| \Theta_{\nu}(i) \right\rangle \\ &= \left\langle \Theta_{\mu}(i) \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{1}{r_{iA}} \right| \Theta_{\nu}(i) \right\rangle \\ &= T_{\mu\nu} + V_{\mu\nu}^{\text{eN}} \end{aligned}$$

- Two-electron integrals
- Four-center integrals
 - For K basis functions #of 2-e integrals: K^4

Permutational symmetry

$$\begin{aligned} (\mu\lambda|\nu\sigma) &= (\lambda\mu|\nu\sigma) = (\mu\lambda|\sigma\nu) = (\lambda\mu|\sigma\nu) \\ (\nu\sigma|\mu\lambda) &= (\nu\sigma|\lambda\mu) = (\sigma\nu|\mu\lambda) = (\sigma\nu|\lambda\mu) \end{aligned}$$

$K^4/8$
unique integrals!

Nonlinear Roothan Equations

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

Fock matrix depends on density matrix (thereby, on expansion coefficients)

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

Roothan Equations (nonlinear) require iterative solution:

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

When basis functions are orthonormal,

$$\mathbf{F} \mathbf{C} = \mathbf{C} \varepsilon$$

Typically the basis functions are normalized but not orthogonal. In that case, orthogonalization of the basis is carried out. The transformed (orthonormal) basis functions result in a transformed Fock matrix, where Roothan Equation appears as eigenvalue problem.



Hartree-Fock Energy in basis representation

Molecular Orbital Energy

$$\varepsilon_a = (a|h|a) + \sum_b^{N/2} 2(ab|ab) - (ab|ba) = h_{aa} + \sum_b^{N/2} 2J_{ab} - K_{ab}$$

Hartree-Fock Energy (with spatial orbitals)

$$E_{\text{HF}} = 2 \sum_a^{N/2} h_{aa} + \sum_{a,b}^{N/2} 2J_{ab} - K_{ab}$$

Hartree-Fock Energy

$$\begin{aligned} E_{\text{HF}} &= \sum_a^{N/2} h_{aa} + \varepsilon_a \\ &= \frac{1}{2} \sum_{\mu,\nu} P_{\nu\mu} (h_{\mu\nu} + F_{\mu\nu}) \end{aligned}$$

The last relation can be derived by inserting basis expansion in the energy expression.





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Lecture 34: Evaluation of Molecular Properties

Hartree-Fock-Roothan Equations

$$\psi_a(i) = \sum_{\nu=1}^K C_{\nu a} \Theta_{\nu}(i)$$

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

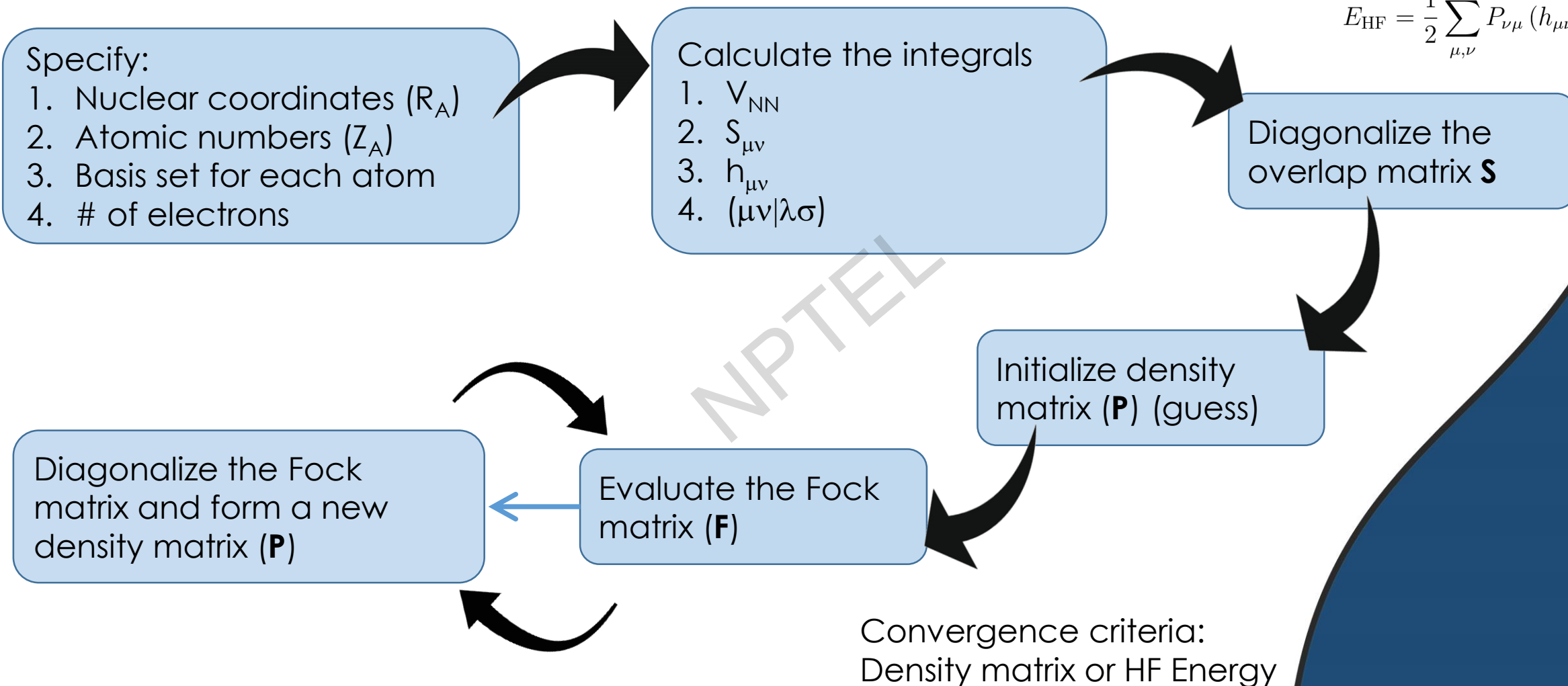
$$\mathbf{F} \mathbf{C} = \mathbf{C} \mathbf{\varepsilon}$$

$$E_{\text{HF}} = \frac{1}{2} \sum_{\mu,\nu} P_{\nu\mu} (h_{\mu\nu} + F_{\mu\nu})$$

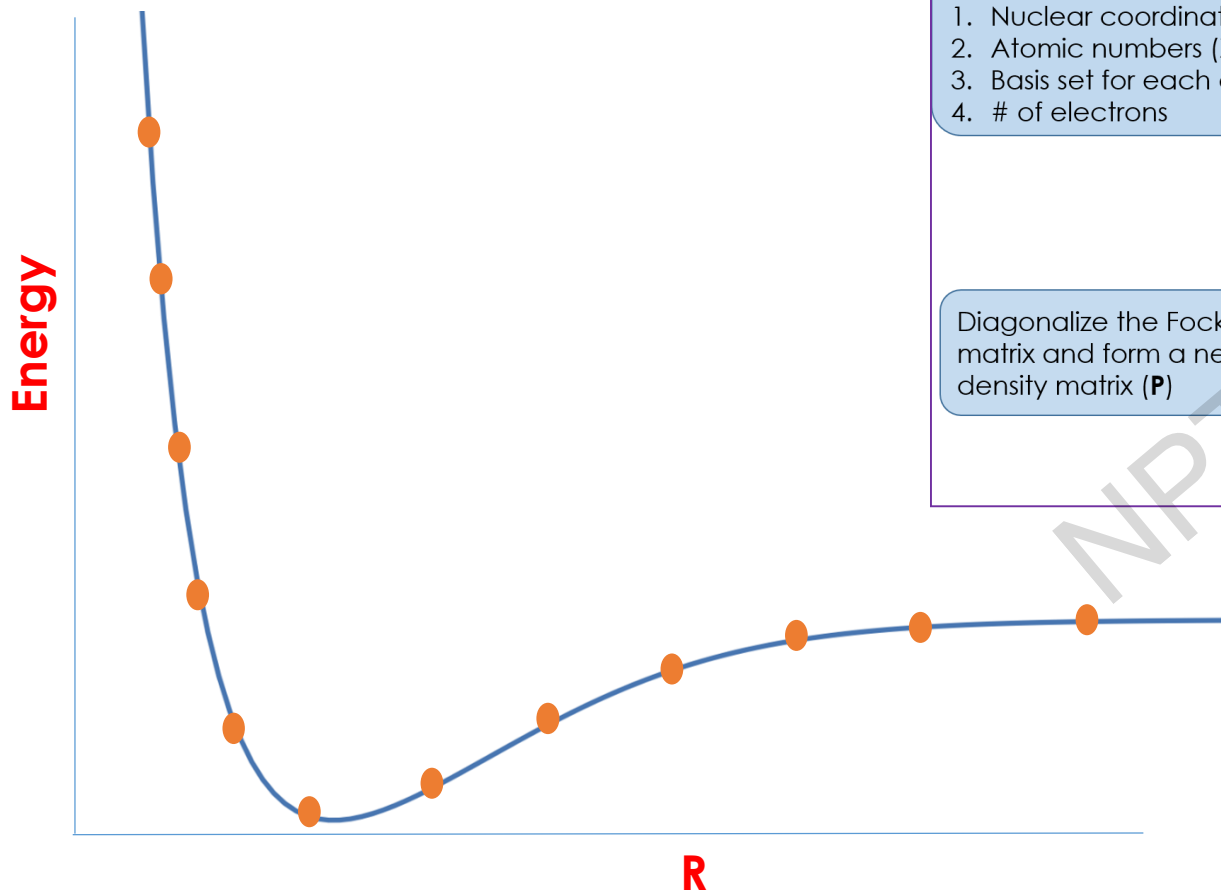
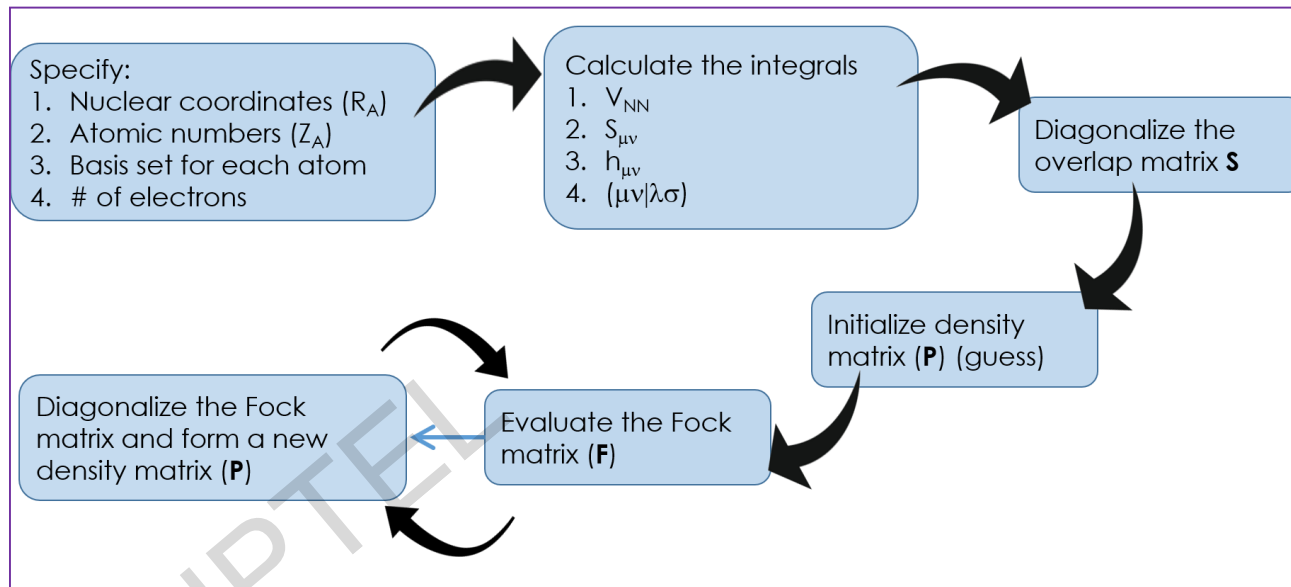


A typical HF-SCF Calculation:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$
$$\mathbf{F} \mathbf{C} = \mathbf{C} \boldsymbol{\varepsilon}$$
$$E_{\text{HF}} = \frac{1}{2} \sum_{\mu,\nu} P_{\nu\mu} (h_{\mu\nu} + F_{\mu\nu})$$



Potential Energy Surface



- 3N-6 (5) Dimensional PE Surfaces
- Geometry optimization
- Reaction mechanism

Molecular properties from the HF wavefunction

Expectation value of any 1-electron operator

$$\hat{O}_1 = \sum_i^N \hat{o}_i$$

$$\begin{aligned}\langle \hat{O}_1 \rangle &= \langle \Phi_{\text{HF}} | \hat{O}_1 | \Phi_{\text{HF}} \rangle \\&= 2 \sum_a^{N/2} (\psi_a(i) | \hat{o}_i | \psi_a(i)) \\&= 2 \sum_a^{N/2} \left(\sum_{\mu} C_{\mu a} \Theta_{\mu}(i) | \hat{o}_i | \sum_{\nu} C_{\nu a} \Theta_{\nu}(i) \right) \\&= \sum_{\mu, \nu} \left(\sum_a^{N/2} 2 C_{\nu a} C_{\mu a}^* \right) (\Theta_{\mu}(i) | \hat{o}_i | \Theta_{\nu}(i)) \\&= \sum_{\mu \nu} P_{\nu \mu} (\mu | \hat{o}_i | \nu) \\&= \sum_{\mu \nu} P_{\nu \mu} o_{\mu \nu}\end{aligned}$$

Some examples:

- Dipole moment
- Quadrupole moment
- Field gradient at a nucleus
- Diamagnetic susceptibility



Population Analysis

$$\begin{aligned}
 \int dr \rho(r) &= 2 \sum_a^{N/2} \int dr_i \psi_a^*(i) \psi_a(i) \\
 &= \sum_{\mu\nu} P_{\mu\nu} \int dr_i \Theta_\nu^*(i) \Theta_\mu(i) \\
 &= \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = \sum_\mu (\mathbf{PS})_{\mu\mu} = \text{tr } \mathbf{PS} = N \text{ (Total \# of electrons)}
 \end{aligned}$$

$(\mathbf{PS})_{\mu\mu}$ Number of 'electrons' associated with the basis function μ

$e_A = \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$ Number of 'electrons' associated with an atom A

$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$ Partial charge on atom A
Mulliken partial charge



Population Analysis

Mulliken population analysis

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{P} \mathbf{S})_{\mu\mu}$$

$$N = \sum_{\mu} (\mathbf{P} \mathbf{S})_{\mu\mu} = \sum_{\mu} (\mathbf{S}^{\alpha} \mathbf{P} \mathbf{S}^{1-\alpha})_{\mu\mu}$$

Löwdin population analysis

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{\mu\mu}$$



Some Popular Population Analysis Schemes

Methods from wavefunction partitioning:

- **Mulliken** Population Analysis
- **Löwdin** Population Analysis
- **Natural** Population Analysis

From molecular electrostatic potential:

- **CHELPG** (CHarges from ELectrostatic Potentials using a Grid-based method)
- **MSK** (Merz-Singh-Kollman Scheme)
- **RESP** (Restrained Electrostatic Potential)

From electron density distribution:

- **Bader's AIM** (atoms in molecules analysis)
- **Hirshfeld analysis**
- **Voronei deformation density**





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Approximate Methods in Quantum Chemistry

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Lecture 35: Basis Sets - I

Basis functions

Should

- have analytical form
- form a 'complete set' with less number of functions
- be easily orthogonalizable
- allow fast integral evaluation



Choice of basis functions

Hydrogenic functions

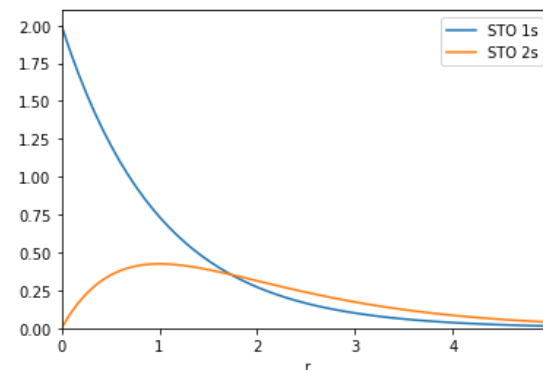
$$\Psi_{nlm} = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+1)!}} \left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1} \left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right) Y_{lm}(\theta, \phi)$$

Slater Type Orbitals

$$\Psi_{nlm}^{\text{STO}} = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} \exp(-\zeta r) Y_{lm}(\theta, \phi)$$

$$\langle \hat{r} \rangle = \frac{2n+1}{2\zeta}$$

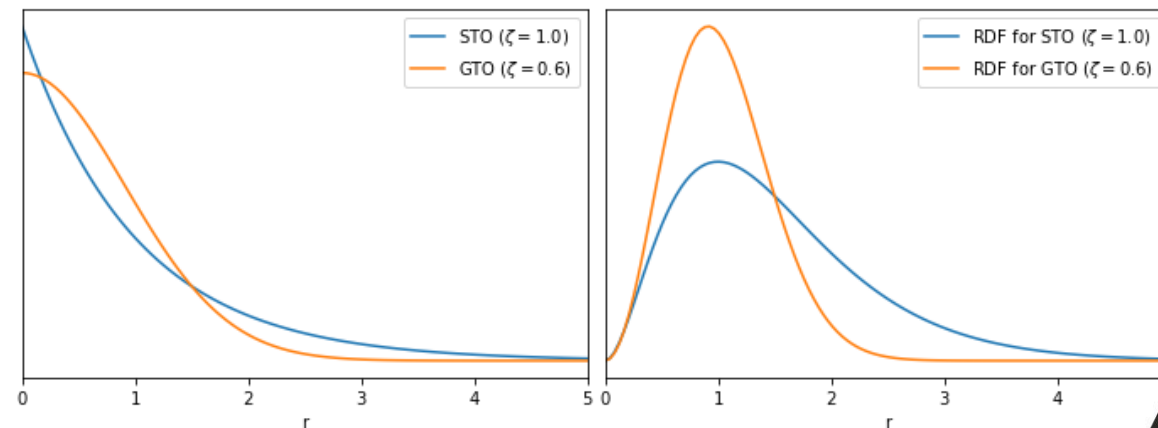
$$\langle \hat{r} \rangle = \frac{3n^2 - l(l+1)}{2Z}$$



Gaussian-type Orbitals (GTOs)

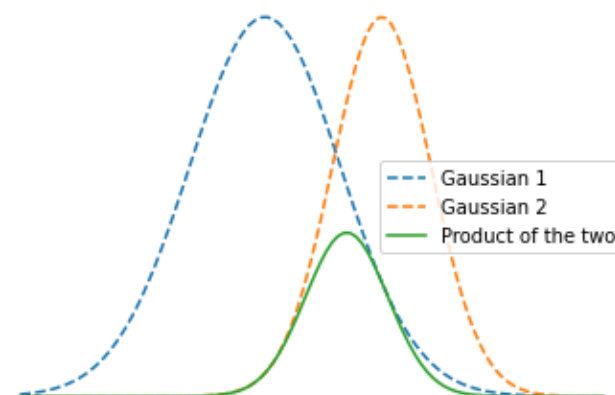
$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} r^{2n-2-l} \exp(-\zeta r^2) Y_{lm}(\theta, \phi)$$

$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} x^i y^j z^k \exp(-\zeta r^2), \quad i + j + k = l$$

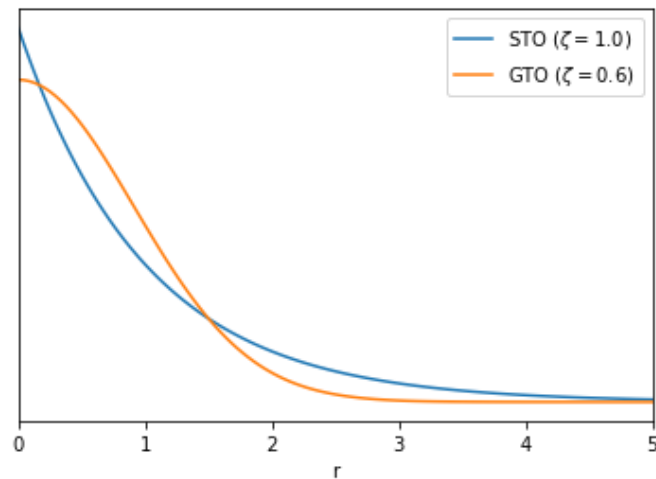
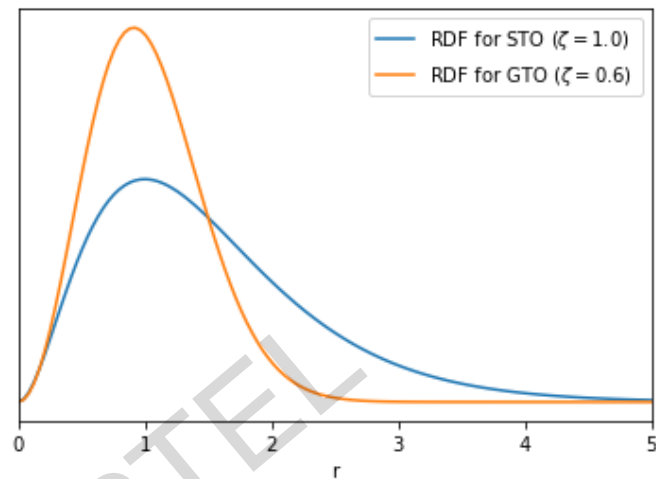
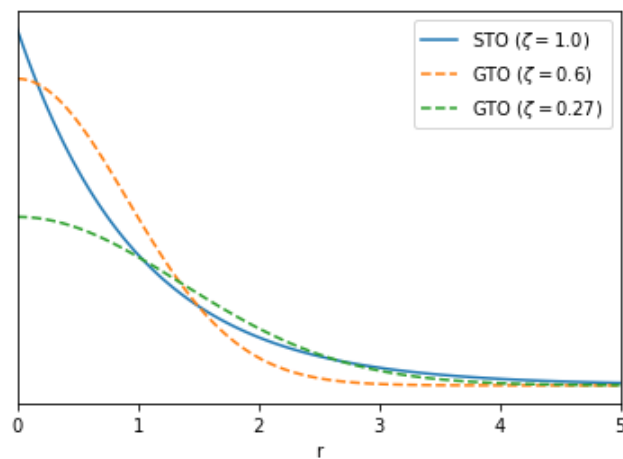
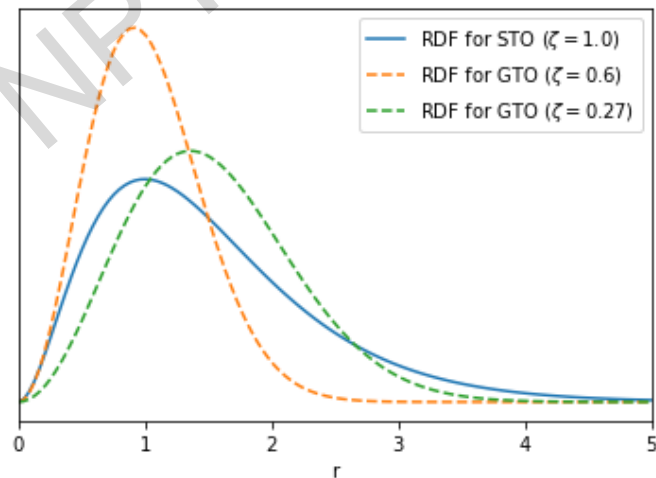


Product of two Gaussians is a Gaussian

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$



Gaussian-type Orbitals (GTOs)



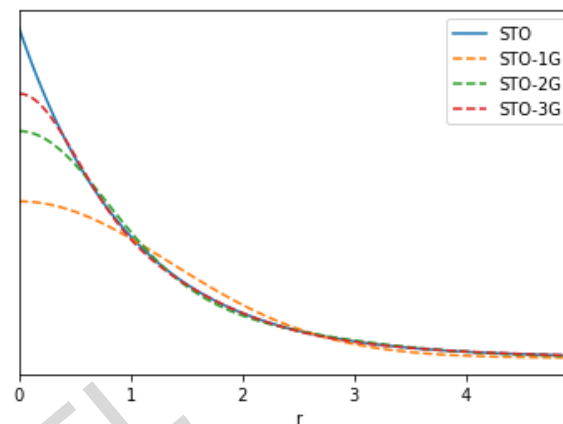
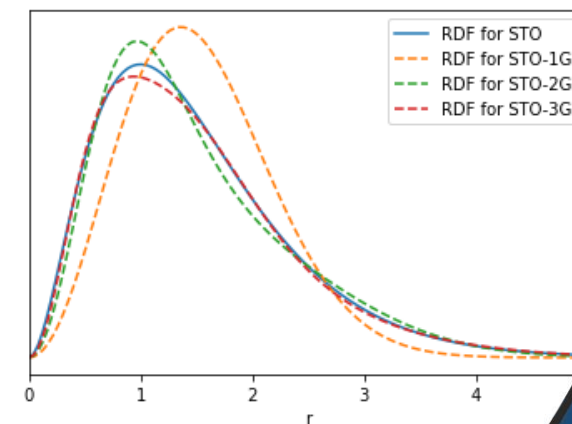
Radial Distribution Function (RDF)

$$= 4\pi r^2 |\psi(r)|^2$$

Contracted Gaussian Type Functions

$$\Psi^{\text{cGTO}} = \mathcal{N} \sum_i^n c_i \Psi_{\text{primitive}}^{\text{GTO}}$$

$$\Psi^{\text{cGTO}} = \mathcal{N} \sum_i^n c_i x^i y^j z^k \exp(-\zeta_i r^2)$$



$$\Psi_{1\text{G}}^{\text{cGTF}}(\zeta = 1.0) = \Psi_{1\text{G}}^{\text{GTO}}(\zeta = 0.27)$$

$$\Psi_{2\text{G}}^{\text{cGTF}}(\zeta = 1.0) = 0.67 \Psi_{2\text{G}}^{\text{GTO}}(\zeta = 0.151) + 0.43 \Psi_{2\text{G}}^{\text{GTO}}(\zeta = 0.851)$$

$$\Psi_{3\text{G}}^{\text{cGTF}}(\zeta = 1.0) = 0.44 \Psi_{3\text{G}}^{\text{GTO}}(\zeta = 0.109) + 0.53 \Psi_{3\text{G}}^{\text{GTO}}(\zeta = 0.405) + 0.15 \Psi_{3\text{G}}^{\text{GTO}}(\zeta = 2.227)$$

name	ζ	c_i
STO-1G	0.270	1.0
	0.851	0.43
STO-2G	0.151	0.67
	0.405	0.53
	2.227	0.15
STO-3G	0.109	0.44
	0.405	0.53
	2.227	0.15



Library of basis functions

← → ↻ 🔒 basissetexchange.org ☆

Basis Set Exchange

[Download](#) [GitHub](#) [Feedback](#) [About](#) [Help](#) [Request a Basis set](#)

Orbital basis: All

- 6-311+G*
- 6-311+G*-J
- 6-311+G**
- 6-311G
- 6-311G(2df,2pd)
- 6-311G(d,p)
- 6-311G-J
- 6-311G*
- 6-311G**
- 6-311xxG(d,p)
- 6-31G
- 6-31G(2df,p)
- 6-31G(3df,3pd)
- 6-31G(d,p)
- 6-31G-J
- 6-31G*
- 6-31G**
- 6ZaPa-NR
- 7ZaPa-NR
- AHGBS-9
- AHGBSP1-9
- AHGBSP2-9
- AHGBSP3-9
- Ahlrichs pVDZ

Total found: 328 basis sets

[Select All](#) [Reset Selection](#)



<https://www.basissetexchange.org/>



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Lecture 36: Basis Sets - II

Contracted Gaussian Functions

STO-3G for Carbon

C S

71.61683735	0.1543289673
13.04509632	0.5353281423
3.530512160	0.4446345422

STOs: 1s, 2s, 2p [2s,1p] # 5 functions

GTOs: 1s(3), 2s(3), 2p(3) (6s,3p)

Contraction Scheme: (6s,3p) -> [2s,1p]

C SP

2.941249355	-0.0999672291	0.1559162750
0.683483096	0.3995128261	0.6076837186
0.222289915	0.7001154689	0.3919573931

ζ_i

C_i

C_i

$$\psi_{1s}^{\text{STO}} = 0.15e^{-71.61r^2} + 0.53e^{-13.04r^2} + 0.44e^{-3.53r^2}$$

$$\psi_{2s}^{\text{STO}} = -0.09e^{-2.94r^2} + 0.39e^{-0.68r^2} + 0.70e^{-0.22r^2}$$

$$\psi_{2p}^{\text{STO}} = 0.15e^{-2.94r^2} + 0.60e^{-0.68r^2} + 0.39e^{-0.22r^2}$$

Single zeta – Double zeta – Triple zeta ...



Split-Valence Basis

3-21G basis for Nitrogen

#BASIS SET: (6s,3p) -> [3s,2p]

N S

242.7660000	0.0598657005
36.48510000	0.3529550030
7.814490000	0.7065130060

N SP

5.425220000	-0.4133000774
1.149150000	1.2224417267

N SP

0.2832050000	1.0000000000
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ζ_i

C_i

C_i

K GTOs to describe 1
STO of core orbital

$l/m/n$ GTOs to describe the
1st/2nd/3rd STO of valence
orbital

K-ImnG

core-valence
separation

of digits = # of
STOs for each
valence orbital



Split-Valence Basis

6-31G for Carbon

#BASIS SET: (10s,4p) -> [3s,2p]

C S

3047.524880	0.1834737132E-02
457.3695180	0.1403732281E-01
103.9486850	0.6884262226E-01
29.21015530	0.2321844432E+00
9.286662960	0.4679413484E+00
3.163926960	0.3623119853E+00

core

C SP

7.868272350	-0.1193324198E+00	0.6899906659E-01
1.881288540	-0.1608541517E+00	0.3164239610E+00
0.544249258	0.1143456438E+01	0.7443082909E+00

cGTF 1

valence

C SP

0.1687144782	0.1000000000E+01	0.1000000000E+01
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cGTF 2

ζ_i

C_i

C_i

	1s	2s	2p	#K
#STOs	1	2	2	9
#GTOs	6	3+1	3+1	



Further improvements

❑ Polarization functions

- Basis function with angular momentum l is mixed with basis function of angular momentum $l+1$

$K-lmnG^*$

❑ Diffuse functions

- Small zeta exponent of same l
- Necessary for anions, electronegative atoms, Rydberg states, weakly bound complexes

$K-lmn+G$

❑ Correlation Consistent

- Basis sets are optimized using correlated wavefunctions (not HF wavefunctions)

$cc-pVDZ$

❑ Effective Core Potentials (ECP)

- For heavy elements core electrons are treated as ECP with relativistic corrections

$LANL2DZ$

❑ Plane wave basis

- For periodic materials – valence electrons are modelled as free electrons





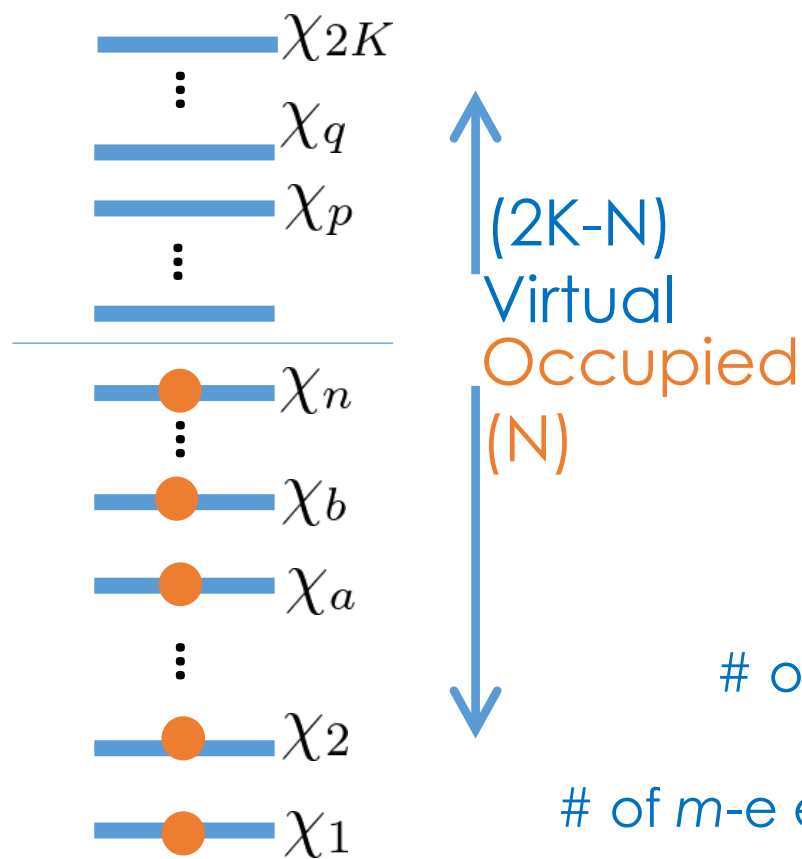
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Lecture 37: Electron Correlation and Post HF Methods

Slater Determinants from HF wavefunction



$$|\Phi\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_a(i) \chi_b(j) \cdots \chi_n(N)\rangle$$

$$|\Phi_a^p\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_p(i) \chi_b(j) \cdots \chi_n(N)\rangle$$

$$|\Phi_{ab}^{pq}\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_p(i) \chi_q(j) \cdots \chi_n(N)\rangle$$

of ground states = 1

of 1-e excitations = $(2K - N) N$

of 2-e excitations = $(N(N-1)/2) ((2K-N)(2K-N-1)/2)$

$$\text{\# of } m\text{-e excitations} = \binom{N}{m} \binom{2K - N}{m}$$

$$\text{Total \# of Slater Determinants} = \binom{2K}{N} \quad \binom{N}{m} = \frac{N!}{m!(N-m)!}$$

Configuration Interaction

$$|\Phi\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_a(i) \chi_b(j) \cdots \chi_n(N)\rangle$$

$$|\Phi_a^p\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_p(i) \chi_b(j) \cdots \chi_n(N)\rangle$$

$$|\Phi_{ab}^{pq}\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_p(i) \chi_q(j) \cdots \chi_n(N)\rangle$$

$$\begin{aligned} |\Psi_{\text{CI}}\rangle &= C_0 |\Phi_{\text{HF}}\rangle + \sum_{a \ p} C_a^p |\Phi_a^p\rangle + \sum_{a>b \ p>q} C_{ab}^{pq} |\Phi_{ab}^{pq}\rangle + \sum_{a>b>c \ p>q>r} C_{abc}^{pqr} |\Phi_{abc}^{pqr}\rangle + \cdots \\ &= C_0 |\Phi_{\text{HF}}\rangle + C_S |S\rangle + C_D |D\rangle + C_T |T\rangle + \cdots \end{aligned}$$

n-tuply excited determinants

$$E_{\text{CI}} = \langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle$$



Configuration Interaction

$$|\Psi_{\text{CI}}\rangle = C_0|\Phi_{\text{HF}}\rangle + \sum_{a\ p} C_a^p|\Phi_a^p\rangle + \sum_{a>b\ p>q} C_{ab}^{pq}|\Phi_{ab}^{pq}\rangle + \sum_{a>b>c\ p>q>r} C_{abc}^{pqr}|\Phi_{abc}^{pqr}\rangle + \dots$$

$$= C_0|\Phi_{\text{HF}}\rangle + C_S|S\rangle + C_D|D\rangle + C_T|T\rangle + \dots$$

$$E_{\text{CI}} = \langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle$$

$$E_{\text{correlation}} = E_{\text{CI}} - E_{\text{HF}}$$

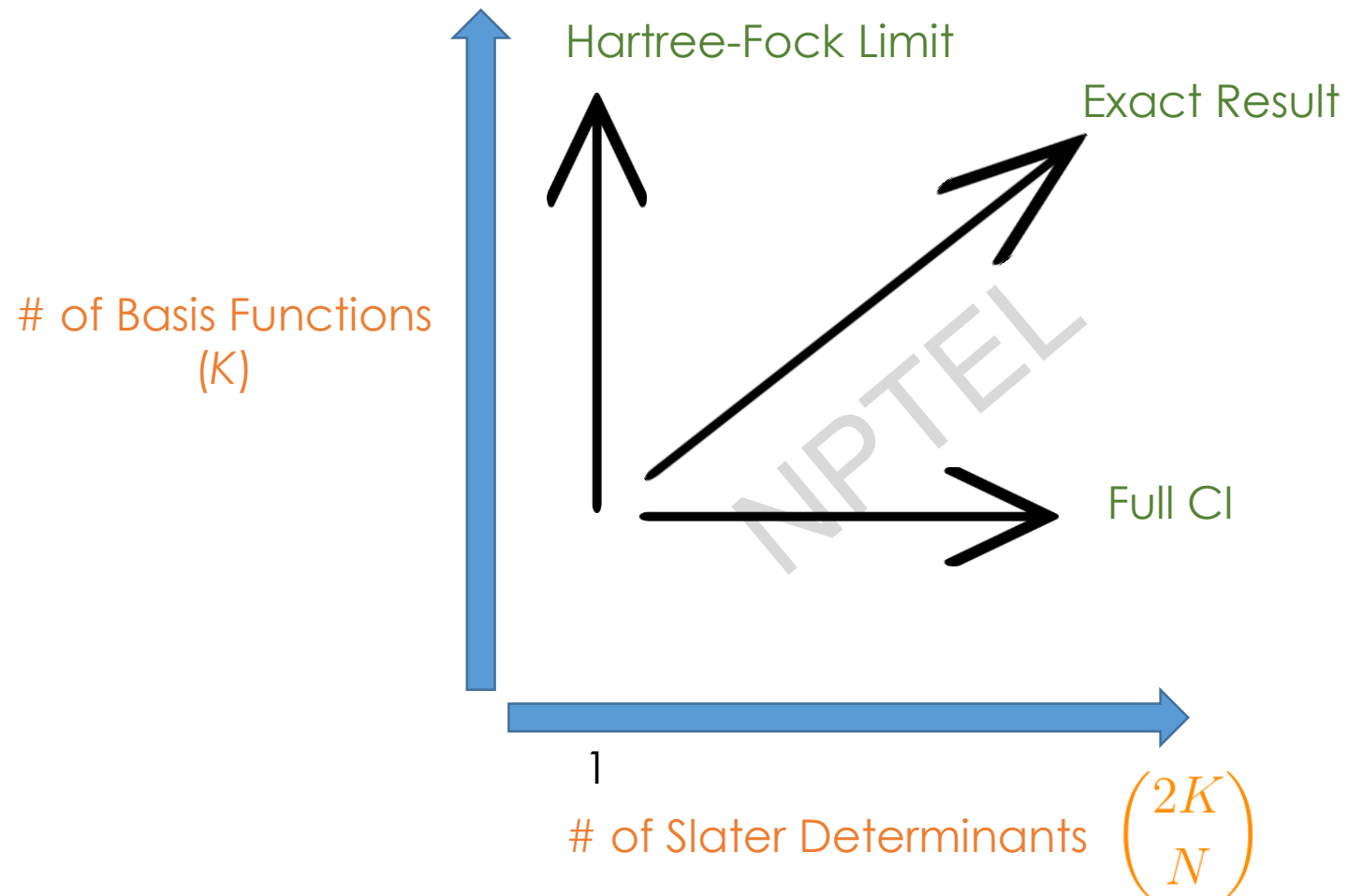
Structure of a CI Matrix

	$ \Phi_{\text{HF}}\rangle$	$ S\rangle$	$ D\rangle$	$ T\rangle$	$\dots$
$\langle \Phi_{\text{HF}} $	$\langle \Phi_{\text{HF}} \hat{H} \Phi_{\text{HF}} \rangle$	$\langle \Phi_{\text{HF}} \hat{H} S \rangle$	$\langle \Phi_{\text{HF}} \hat{H} D \rangle$	$\langle \Phi_{\text{HF}} \hat{H} T \rangle$	$\dots$
$\langle S $		$\langle S \hat{H} S \rangle$	$\langle S \hat{H} D \rangle$	$\langle S \hat{H} T \rangle$	$\dots$
$\langle D $			$\langle D \hat{H} D \rangle$	$\langle D \hat{H} T \rangle$	$\dots$
$\langle T $				$\langle T \hat{H} T \rangle$	$\dots$
$\vdots$					$\ddots$

- Full CI
- Truncated CI
 - DCI
 - SDCI



Path to Exact Result



Perturbation Treatment: MP2

N-electron Hamiltonian
and its true solution

$$\hat{H} = \sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}} \quad \hat{H}\Psi = E\Psi$$

Comparison of Molecular Hamiltonian and HF Hamiltonian

$$\begin{aligned}\hat{H}_{\text{HF}} &= \sum_i^N \hat{\mathcal{F}}_i \\ &= \sum_i^N \left(\hat{h}_i + \sum_j \hat{\mathcal{J}}_j(i) - \hat{\mathcal{K}}_j(i) \right) \\ &= \sum_i^N \left(\hat{h}_i + \hat{v}_{\text{HF}}(i) \right)\end{aligned}$$

$$\begin{aligned}\hat{H} - \hat{H}_{\text{HF}} &= \sum_{i>j} \frac{1}{r_{ij}} - \sum_i \hat{v}_{\text{HF}}(i) \\ &= H'\end{aligned}$$

$$E_{\text{correlation}} = E_0^{(1)} + E_0^{(2)}$$



Other popular approximate methods ...

- Multiconfiguration SCF Method
- Coupled Cluster Method
- Density Functional Methods

