Chimica Computazionale

Fundamentals of Quantum Chemistry

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PhotoInduced Quantum Dynamics (PIQD) Group



Nobel Prize in Chemistry in 1998

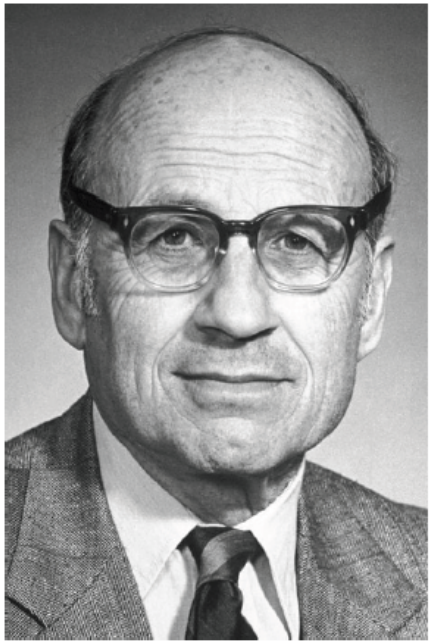


Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2

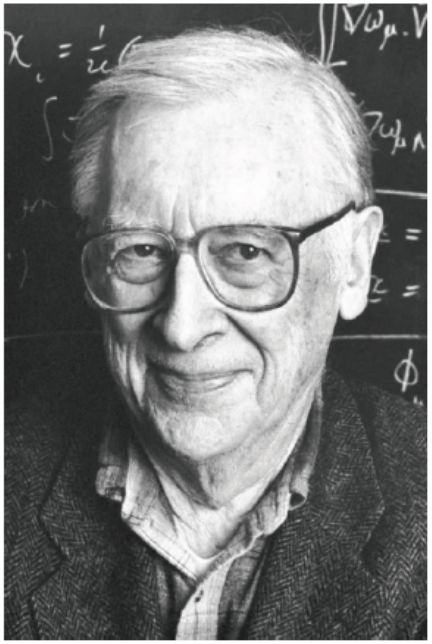


Photo from the Nobel Foundation archive.

John A. Pople

Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry"

Fundamentals of quantum mechanics

Postulates of quantum mechanics

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4. Probability to find a particle in $d\tau$ is proportional to $|\Psi|^2$
5. Ψ evolves in time according to

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

Hamiltonian operator

- Hamiltonian operator $\hat{H}$

$$\hat{H}_{\text{tot}} = \hat{T}_e + \hat{T}_N + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN}$$

$$\hat{T}_e = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 \quad \text{electron kinetic energy}$$

$$\hat{T}_N = -\sum_k \frac{\hbar^2}{2m_k}\nabla_k^2 \quad \text{nuclear kinetic energy}$$

$$\hat{V}_{eN} = -\sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} \quad \text{electron-nucleus attraction}$$

$$\hat{V}_{ee} = \sum_{i<j} \frac{e^2}{r_{ij}} \quad \text{electron-electron repulsion}$$

$$\hat{V}_{NN} = \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \quad \text{nucleus-nucleus repulsion}$$

Variational principle

- An approximate wave function has an energy W above or equal to the exact energy E_0

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- **Proof**:
- Assume that a complete basis is given

$$\begin{aligned} \hat{H}\Psi_I &= E_I\Psi_I \quad I = 0, 1, 2, ..., \infty \\ \langle\Psi_I|\Psi_J\rangle &= \delta_{IJ} \end{aligned}$$

- Approximate wave function

$$\Phi = \sum_{I=0}^{\infty} a_I\Psi_I$$

- And its energy W

$$\begin{aligned} W &= \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \\ &= \frac{\sum_{I,J=0}^{\infty} a_I a_J\langle\Psi_I|\hat{H}|\Psi_J\rangle}{\sum_{I,J=0}^{\infty} a_I a_J\langle\Psi_I|\Psi_J\rangle} \end{aligned}$$

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- $W \geq E_0$ or $(W - E_0) \geq 0$

$$W - E_0 = \frac{\sum_{I=0}^{\infty} a_I^2 E_I}{\sum_{I=0}^{\infty} a_I^2} - E_0 = \frac{\sum_{I=0}^{\infty} a_I^2 (E_I - E_0)}{\sum_{I=0}^{\infty} a_I^2} \geq 0$$

- E_0 is the lowest energy
- Since $a_I^2 \geq 0$ and $(E_I - E_0) \geq 0$, this completes the proof

Born-Oppenheimer approximation

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- Exceptions: conical intersection, photochemistry... (not treated here)

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\hat{H}_e &= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} \\
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- From here on, $\Psi \equiv \Psi_e$, $\hat{H} \equiv \hat{H}_e$ and $E \equiv E_e$

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- Neglect of the nuclear-electron coupling is usually only a minor approximation compared with other (numerical) errors
- Error in H_2 is about 10^{-4} Hartree
- Even better for heavier nuclei

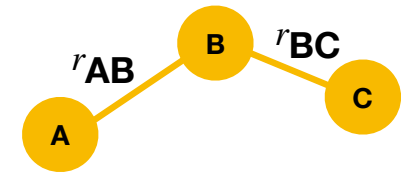
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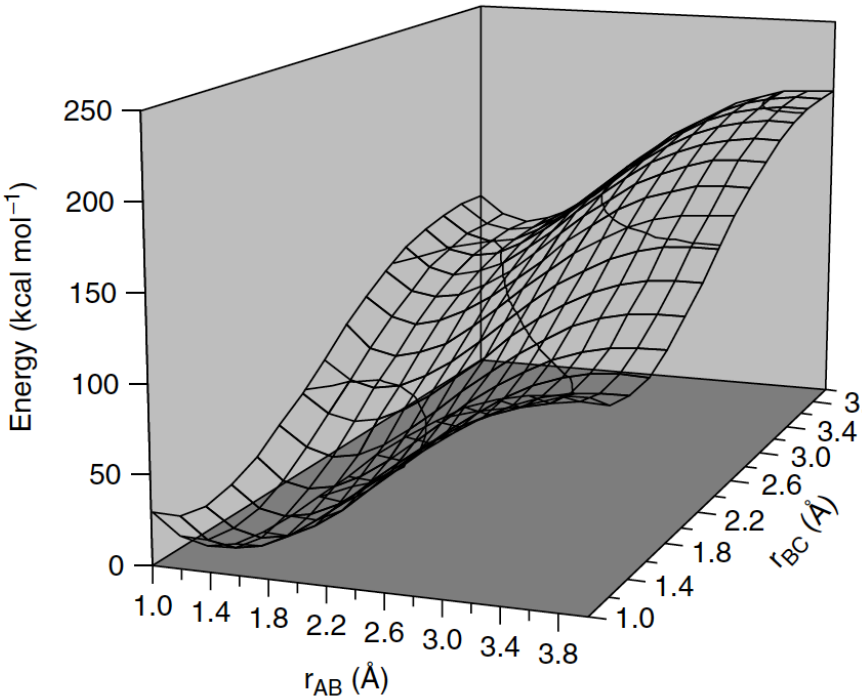
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- $\hat{V}_{NN}$ is an additive constant to $E(\mathbf{R})$

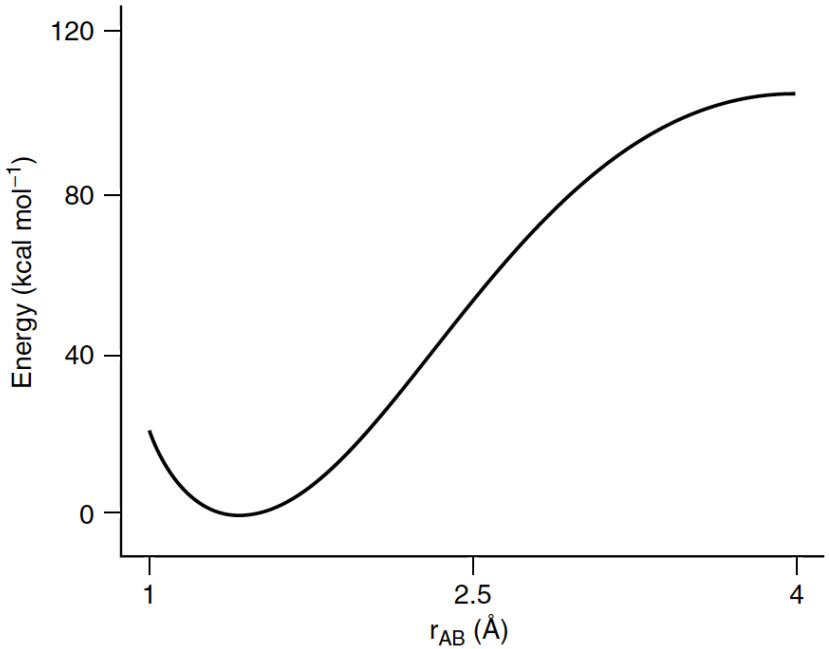
Potential energy surface

- PES: hypersurface of the potential energy of a collection of atoms over all possible arrangements
- In general, $3K - 6$ degrees of freedom (K number of nuclei)
- Chemically interesting regions of the PES

ABC molecule

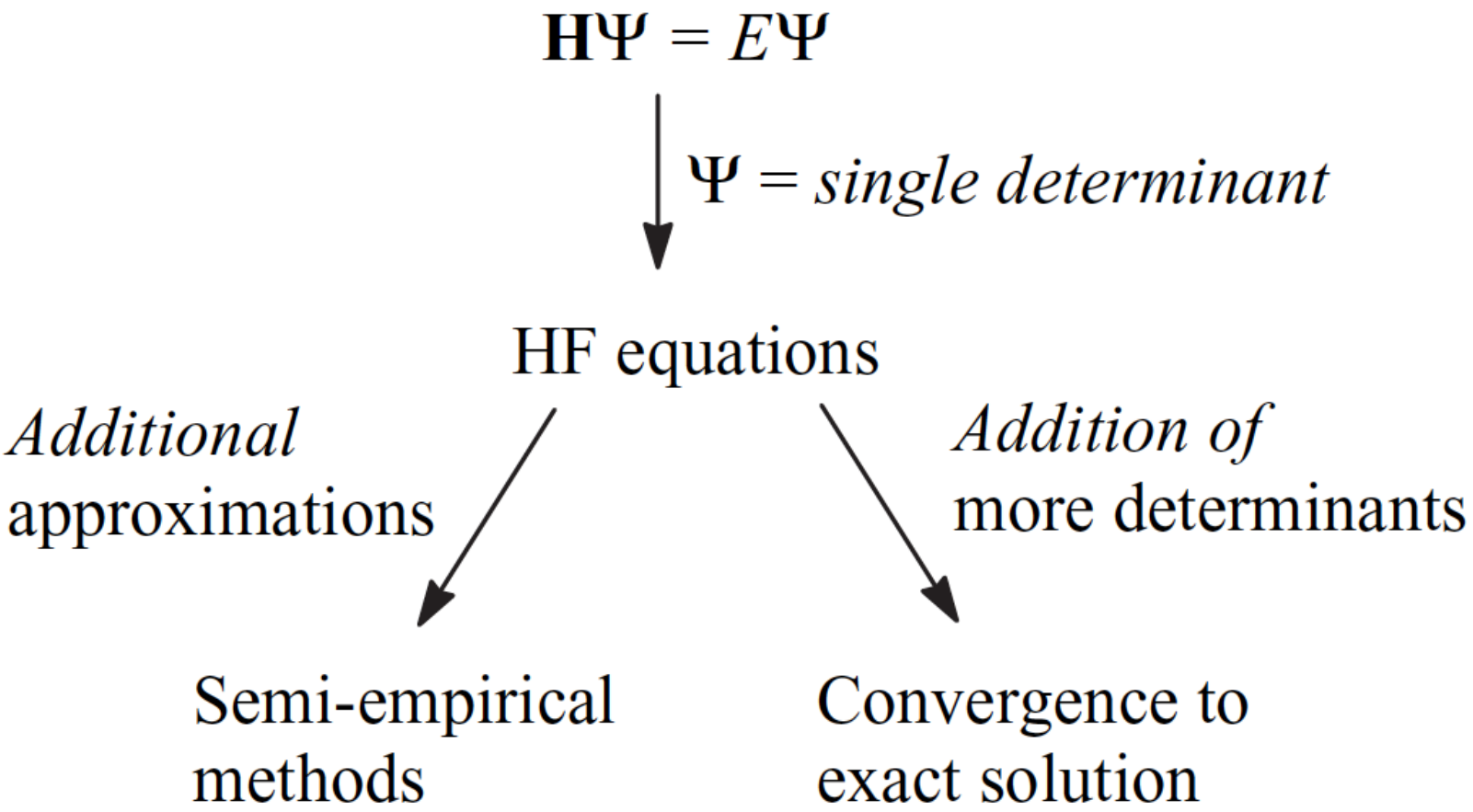




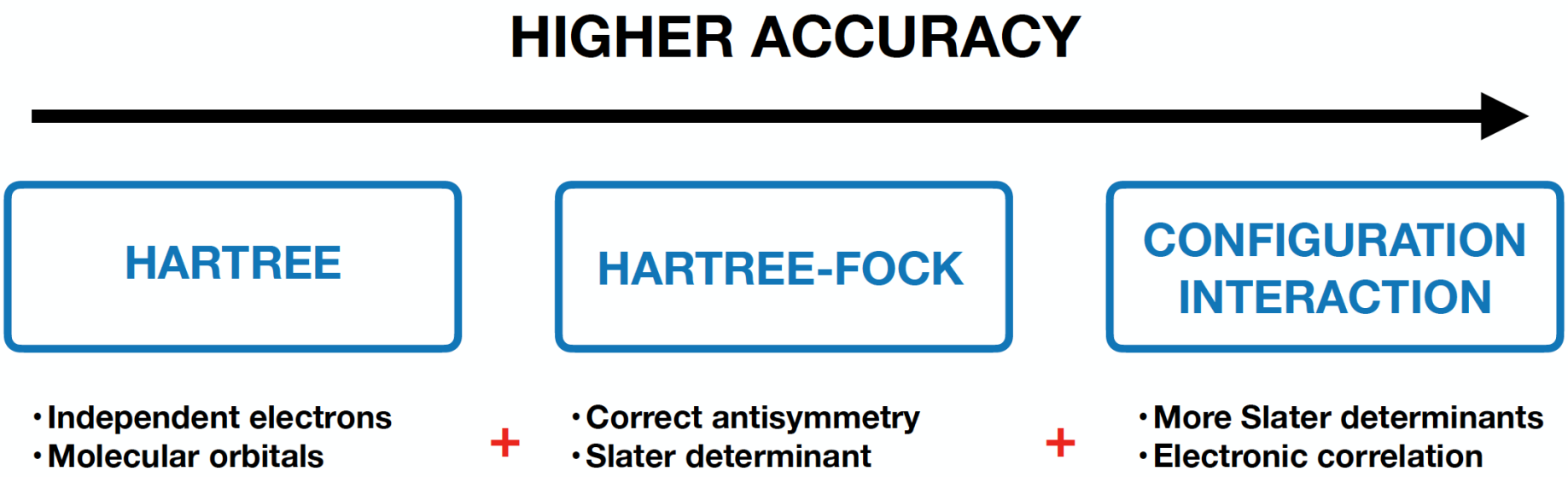


Hartree-Fock method

Solving the Schrödinger equation



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Hartree product

- Independent-particle model

$$\hat{H}_{\mathrm{IP}} = \sum_{i}^{N} \hat{h}_i$$

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{k}^{K} \frac{Z_k}{r_{ik}}$$

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- Eigenfunctions of $\hat{h}_i$ (one-electron molecular orbitals)

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- Eigenfunctions of $\hat{H}_{\mathrm{IP}}$ (product of ϕ_i)

$$\Psi_{\mathrm{HP}} = \phi_1 \phi_2 \cdots \phi_N$$

$$\hat{H}_{\mathrm{IP}} \Psi_{\mathrm{HP}} = \left(\sum_{i}^{N} \epsilon_i \right) \Psi_{\mathrm{HP}}$$

Hartree Hamiltonian

- Including interelectronic repulsion is challenging
- Ψ_{HP} good to estimate the energy from the "true" Hamiltonian $\hat{H}$?
- Orbitals ϕ_i minimizing $\langle \Psi_{HP} | \hat{H} | \Psi_{HP} \rangle$ are eigenfunctions of

$$\begin{aligned} \hat{\tilde{h}}_i &= -\frac{1}{2}\nabla_i^2 - \sum_k^K \frac{Z_k}{r_{ik}} + V_i\{j\} \\ &= \hat{h}_i + V_i\{j\} \end{aligned}$$

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V_i\{j\} &= \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} d\mathbf{r} \\
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\end{aligned}$$

- $V_i\{j\}$ describes the repulsion between electron in ϕ_i and the others in all ϕ_j

Hartree Hamiltonian

- Solving

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  implies knowledge of ϕ_j

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  3. Update $\hat{\tilde{h}}_i$, and solve again Eq. (1)
  4. Repeat points 2 and 3 until convergence
- Convergence criterion: $(E_{\text{step a+i}} - E_{\text{step a}}) < E_{\text{thr}}$ or each $(\tilde{\epsilon}_{i,\text{step a+1}} - \tilde{\epsilon}_{i,\text{step a}}) < \tilde{\epsilon}_{\text{thr}}$
- Tight convergence: more SCF cycles needed

Hartree Hamiltonian

- Ψ_{HP} is eigenfunction of

$$\hat{\tilde{H}}_{IP} = \sum_{i}^{N} \hat{\tilde{h}}_i$$

$$\tilde{E}_{IP} = \sum_{i}^{N} \tilde{\epsilon}_i$$

- Near independent-particle model: each electron sees an average repulsion from the other electrons
- Overcounting in $\tilde{E}_{IP}$

$$E = \tilde{E}_{IP} - \frac{1}{2} \sum_{i \neq j} \int \int \frac{|\phi_i|^2 |\phi_j|^2}{r_{ij}} d\mathbf{r}_i d\mathbf{r}_j$$

$$= \tilde{E}_{IP} - \frac{1}{2} \sum_{i \neq j} J_{ij}$$

Antisymmetry

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- One α and one β electron in a given molecular orbital
- Electronic Ψ is antisymmetric: Ψ changes sign when the coordinates of two electrons are interchanged

$$\begin{aligned} \hat{P}_{ij} \quad \Psi \quad & (\mathbf{q}_1, \cdots, \mathbf{q}_i, \cdots, \mathbf{q}_j, \cdots, \mathbf{q}_N) \\ = \quad & \Psi(\mathbf{q}_1, \cdots, \mathbf{q}_j, \cdots, \mathbf{q}_i, \cdots, \mathbf{q}_N) \\ = \quad & -\Psi(\mathbf{q}_1, \cdots, \mathbf{q}_i, \cdots, \mathbf{q}_j, \cdots, \mathbf{q}_N) \end{aligned}$$

- $\mathbf{q}_i$: spatial + spin coordinates for electron i
- $\hat{P}_{ij}$: operator exchanging coordinates of electrons i and j

Antisymmetry

$$^3\Psi_{HP} = \phi_a(1)\alpha(1)\phi_b(2)\alpha(2)$$

Antisymmetry

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\begin{aligned}
{}^3\Psi_{\mathrm{HP}} &= \phi_a(1)\alpha(1)\phi_b(2)\alpha(2) \\
\hat{P}_{12}[\phi_a(1)\alpha(1)\phi_b(2)\alpha(2)] &= \phi_b(1)\alpha(1)\phi_a(2)\alpha(2) \\
&\neq -\phi_a(1)\alpha(1)\phi_b(2)\alpha(2) = -{}^3\Psi_{\mathrm{HP}}
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While

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{}^3\Psi_{\mathrm{SD}} = \frac{1}{\sqrt{2}}[\phi_a(1)\alpha(1)\phi_b(2)\alpha(2) - \phi_a(2)\alpha(2)\phi_b(1)\alpha(1)]
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&= -{}^3\Psi_{\mathrm{SD}}
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Slater Determinant

- Slater determinant (SD)

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1)\alpha(1) & \phi_b(1)\alpha(1) \\ \phi_a(2)\alpha(2) & \phi_b(2)\alpha(2) \end{vmatrix}$$

- $\hat{P}_{12}$ interchanges the two rows: property of a determinant (Math overview)

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- In general

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix}$$

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- ψ_i is a spin-orbital

Slater determinant

- Electron repulsion energy with ${}^3\Psi_{SD}$

$$\langle {}^3\Psi_{SD}| \quad \frac{1}{r_{12}} \quad |{}^3\Psi_{SD}\rangle = \int {}^3\Psi_{SD} \frac{1}{r_{12}} {}^3\Psi_{SD} \, d\mathbf{r}_1 \, d\omega_1 \, d\mathbf{r}_2 \, d\omega_2$$

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$$= \frac{1}{2} \int |\phi_a(1)|^2 |\alpha(1)|^2 \frac{1}{r_{12}} |\phi_b(2)|^2 |\alpha(2)|^2 \, d\mathbf{r}_1 \, d\omega_1 \, d\mathbf{r}_2 \, d\omega_2$$

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&= \frac{1}{2} \int |\phi_a(1)|^2 |\alpha(1)|^2 \frac{1}{r_{12}} |\phi_b(2)|^2 |\alpha(2)|^2 \, d\mathbf{r}_1 \, d\omega_1 \, d\mathbf{r}_2 \, d\omega_2 \\
&- \int \phi_a(1)\phi_b(1) |\alpha(1)|^2 \frac{1}{r_{12}} \phi_b(2)\phi_a(2) |\alpha(2)|^2 \, d\mathbf{r}_1 \, d\omega_1 \, d\mathbf{r}_2 \, d\omega_2
\end{aligned}$$

Slater determinant

- Electron repulsion energy with ${}^3\Psi_{SD}$

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&+ \frac{1}{2} \int |\phi_a(2)|^2 |\alpha(2)|^2 \frac{1}{r_{12}} |\phi_b(1)|^2 |\alpha(1)|^2 \, d\mathbf{r}_1 \, d\omega_1 \, d\mathbf{r}_2 \, d\omega_2
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&- \int \phi_a(1)\phi_b(1) \frac{1}{r_{12}} \phi_b(2)\phi_a(2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (K_{ab}) \\
&+ \frac{1}{2} \int |\phi_a(2)|^2 \frac{1}{r_{12}} |\phi_b(1)|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (J_{ab})
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&+ \frac{1}{2} \int |\phi_a(2)|^2 \frac{1}{r_{12}} |\phi_b(1)|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (J_{ab}) \\
&= J_{ab} - K_{ab}
\end{aligned}
$$

Slater determinant

- Exchange integral K_{ab}: Fermi hole around each electron
- Correlation effect with the same spin

Slater determinant

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$$^1\Psi_{SD} = \frac{1}{\sqrt{2}}[\phi_a(1)\alpha(1)\phi_b(2)\beta(2) - \phi_a(2)\alpha(2)\phi_b(1)\beta(1)]$$

- Electron repulsion energy

$$\langle {}^1\Psi_{SD}| \quad \frac{1}{r_{12}} \quad |{}^1\Psi_{SD}\rangle = \int {}^1\Psi_{SD}\frac{1}{r_{12}}{}^1\Psi_{SD}\, d\mathbf{r}_1\, d\omega_1\, d\mathbf{r}_2\, d\omega_2$$

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&- \int \phi_a(1)\phi_b(1)\alpha(1)\beta(1)\frac{1}{r_{12}}\phi_b(2)\phi_a(2)\alpha(2)\beta(2) d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2
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&+ \frac{1}{2}\int |\phi_a(2)|^2|\alpha(2)|^2\frac{1}{r_{12}}|\phi_b(1)|^2|\beta(2)|^2 d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \\
&= \frac{1}{2}J_{ab} + \frac{1}{2}J_{ab} = J_{ab}
\end{aligned}$$

Hartree-Fock method

- SCF extension to Slater determinants
- Orbitals ϕ_i eigenfunctions of the Fock operator

$$
\begin{aligned}
\hat{f}_i &= -\frac{1}{2}\nabla_i^2 - \sum_k^K \frac{Z_k}{r_{ik}} + V_i^{\mathrm{HF}}\{j\} \\
V_i^{\mathrm{HF}}\{j\} &= \sum_{j\neq i}(\hat{J}_j - \hat{K}_j) \\
\hat{J}_j\psi_i(2) &= \left[\int \psi_j(1)\frac{1}{r_{12}}\psi_j(1)d\mathbf{r}_1 d\omega_1\right]\psi_i(2) \\
\hat{K}_j\psi_i(2) &= \left[\int \psi_j(1)\frac{1}{r_{12}}\psi_i(1)d\mathbf{r}_1 d\omega_1\right]\psi_j(2)
\end{aligned}
$$

Hartree-Fock method

- Hartree-Fock energy

$$E_{\mathrm{HF}} = \sum_{i}^{N} \epsilon_i^{\mathrm{HF}} - \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} (J_{ij} - K_{ij})$$

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- Koopmans' theorem
  - Frozen MO approximation
  - Ionization energy equal to $-\epsilon_i^{\mathrm{HF}}$

Restricted and unrestricted Hartree-Fock

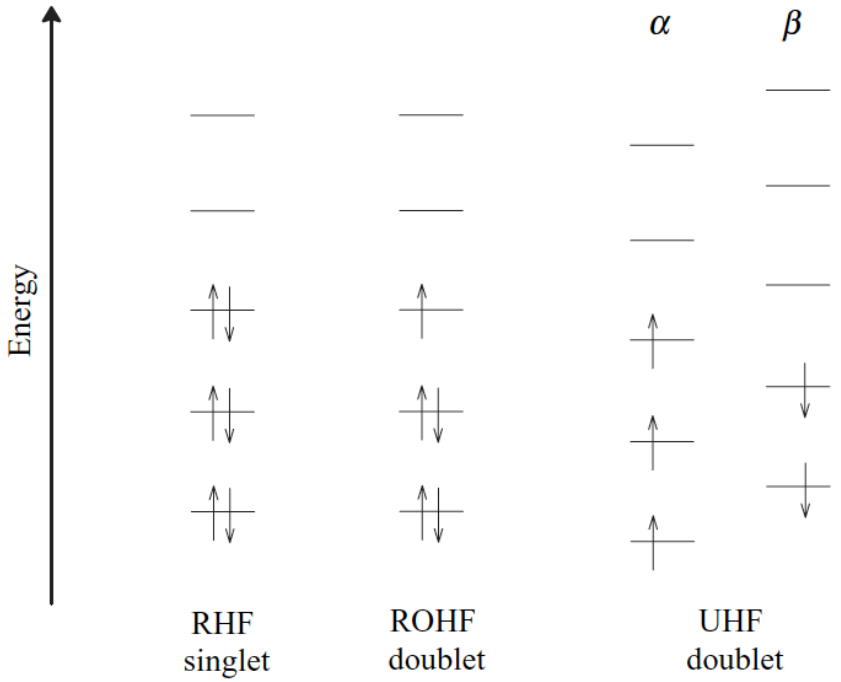
- RHF: Restricted Hartree-Fock
  - Same spatial orbital for α and β
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- ROHF: Restricted Open-shell Hartree-Fock
  - Same spatial part of doubly-occupied orbitals



Restricted and unrestricted Hartree-Fock

- RHF:
  - Ethanol CH_3CH_2OH
  - 26 electrons, closed-shell molecule
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- ROHF:
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  - 9 electrons, open-shell system
  - 4 doubly-occupied MOs, 1 for the ninth electron
- UHF:
  - Same system
  - 5 α MOs, 4 β MOs
  - Spin contamination: UHF wave function is not a pure spin state
  - $\langle \hat{S}^2 \rangle = 0.75$ for a doublet, $= 2$ for a triplet

Linear combination of atomic orbitals (LCAO)

- Molecular orbitals represented by a basis set (see Basis sets)

$$\phi_i = \sum_\mu C_\mu^i \chi_\mu$$

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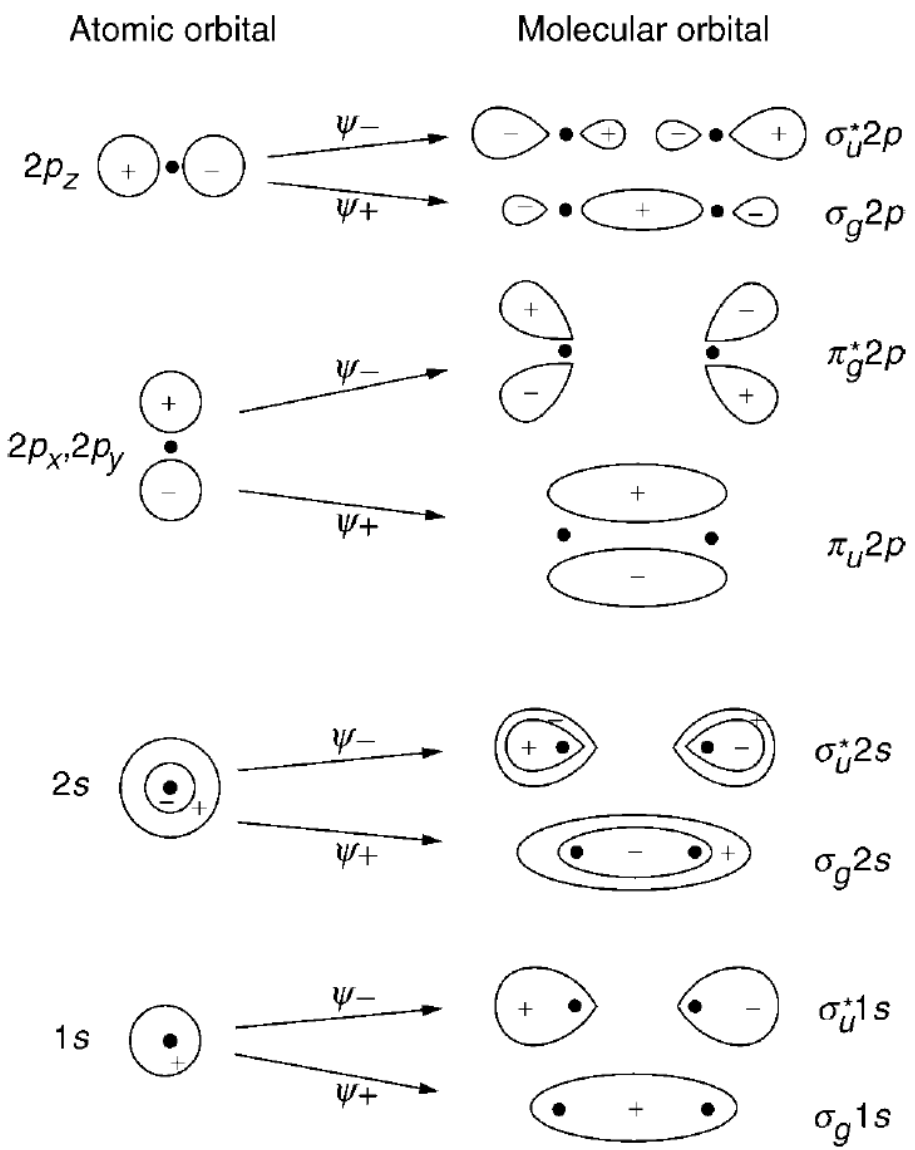
Linear combination of atomic orbitals (LCAO)

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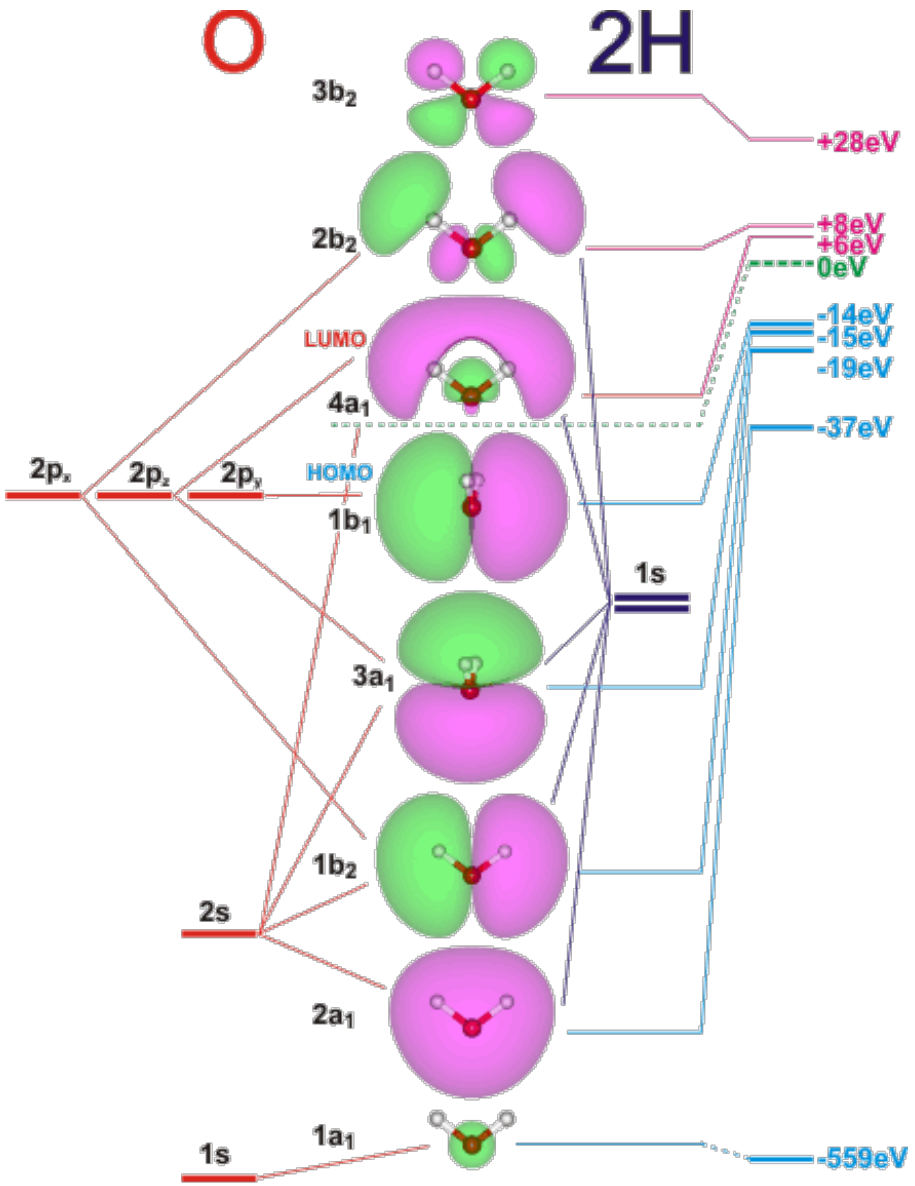
$$\phi_i = \sum_\mu C_\mu^i \chi_\mu$$

- Atomic orbital (AO) on each nucleus
- Effective linear combination:
  - AO energies are comparable
  - AO must overlap
  - Same symmetry properties

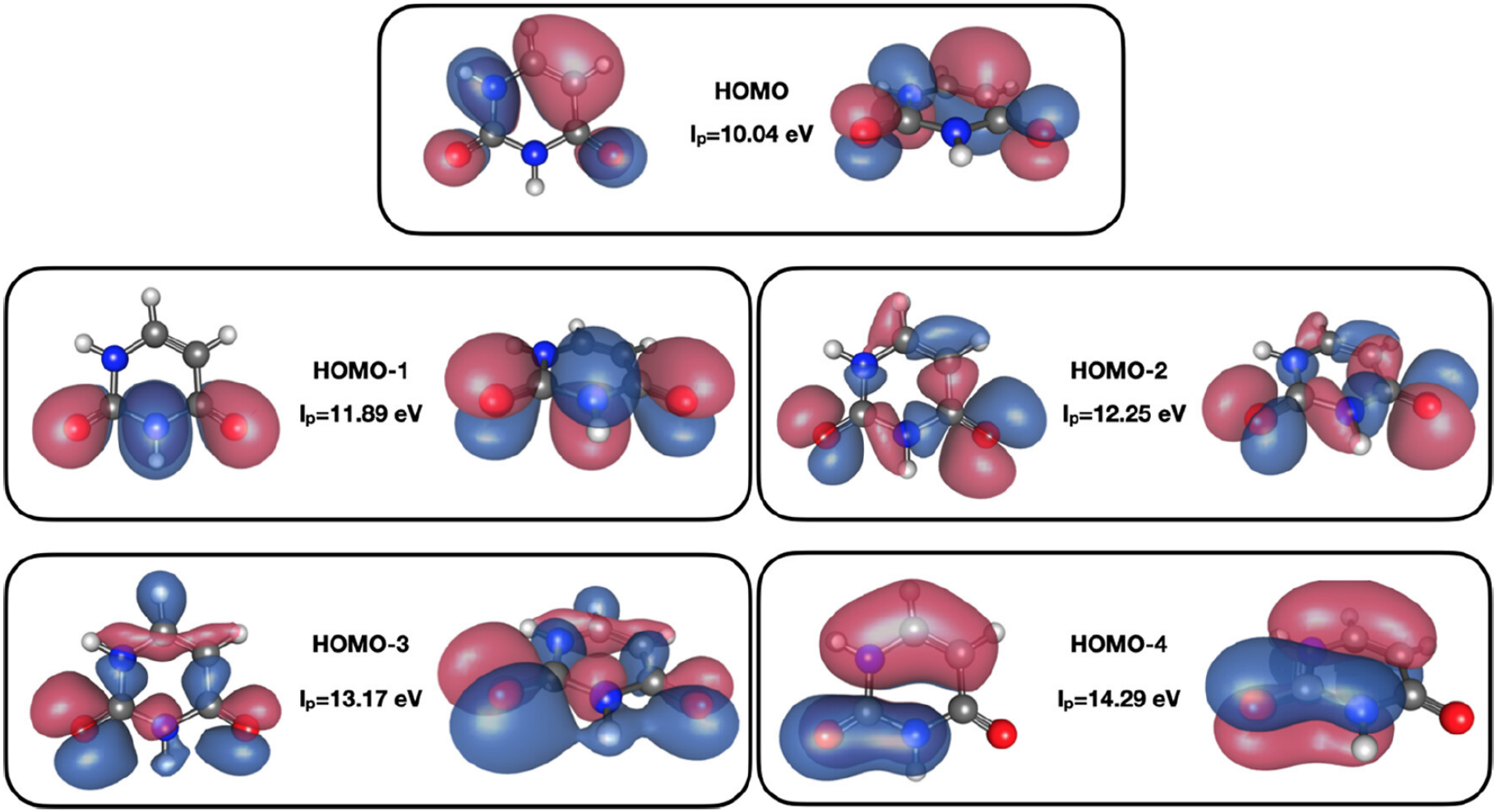
LCAO: diatomic molecule



LCAO: water


O
2H
3b2
2b2
LUMO
4a1
HOMO
1b1
3a1
1b2
2a1
1a1
2px
2pz
2py
2s
1s
1s
+28eV
+8eV
+6eV
0eV
-14eV
-15eV
-19eV
-37eV
-559eV

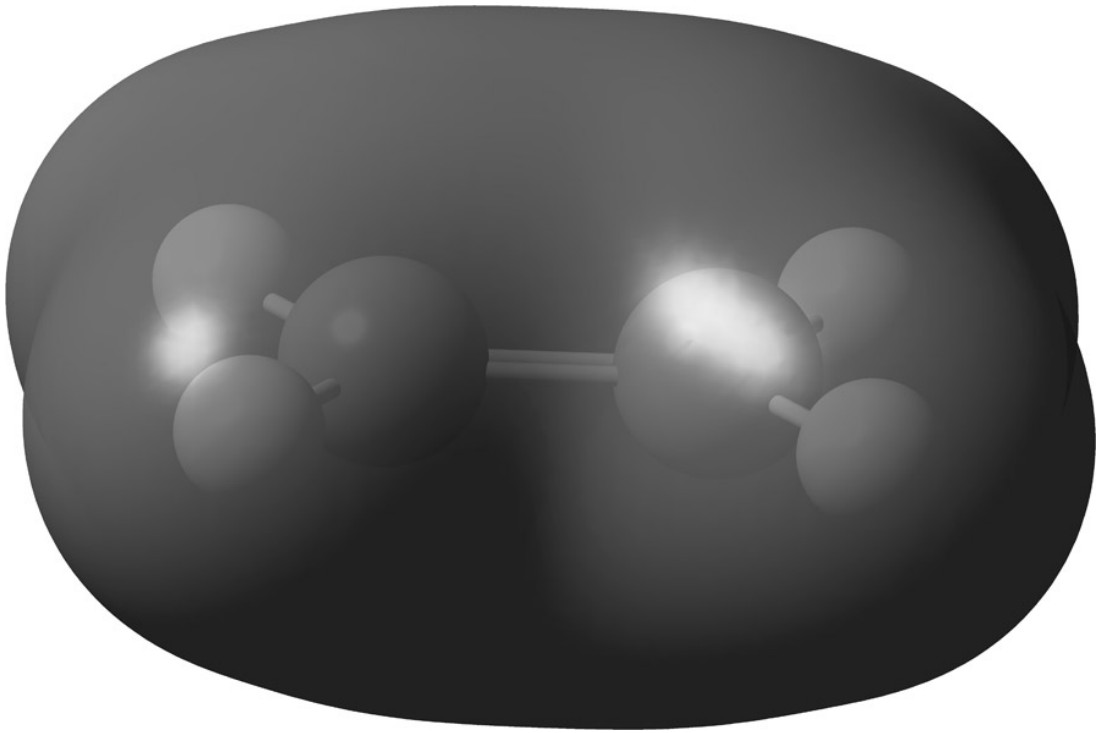
LCAO: uracil


HOMO
I_p=10.04 eV
HOMO-1
I_p=11.89 eV
HOMO-2
I_p=12.25 eV
HOMO-3
I_p=13.17 eV
HOMO-4
I_p=14.29 eV

Electron density: ethylene

$$\rho = \sum_i |\phi_i|^2$$

Isodensity surface



Basis sets

Basis functions

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- Two types of basis functions (atomic orbitals):
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$$\chi_{\zeta,n,l,m}(r,\theta,\phi) = NY_{l,m}(\theta,\phi) r^{n-1} e^{-\zeta r}$$

  - Gaussian-type orbitals (GTO)

$$\chi_{\zeta,n,l,m}(r,\theta,\phi) = NY_{l,m}(\theta,\phi) r^{2n-2-l} e^{-\zeta r^2}$$

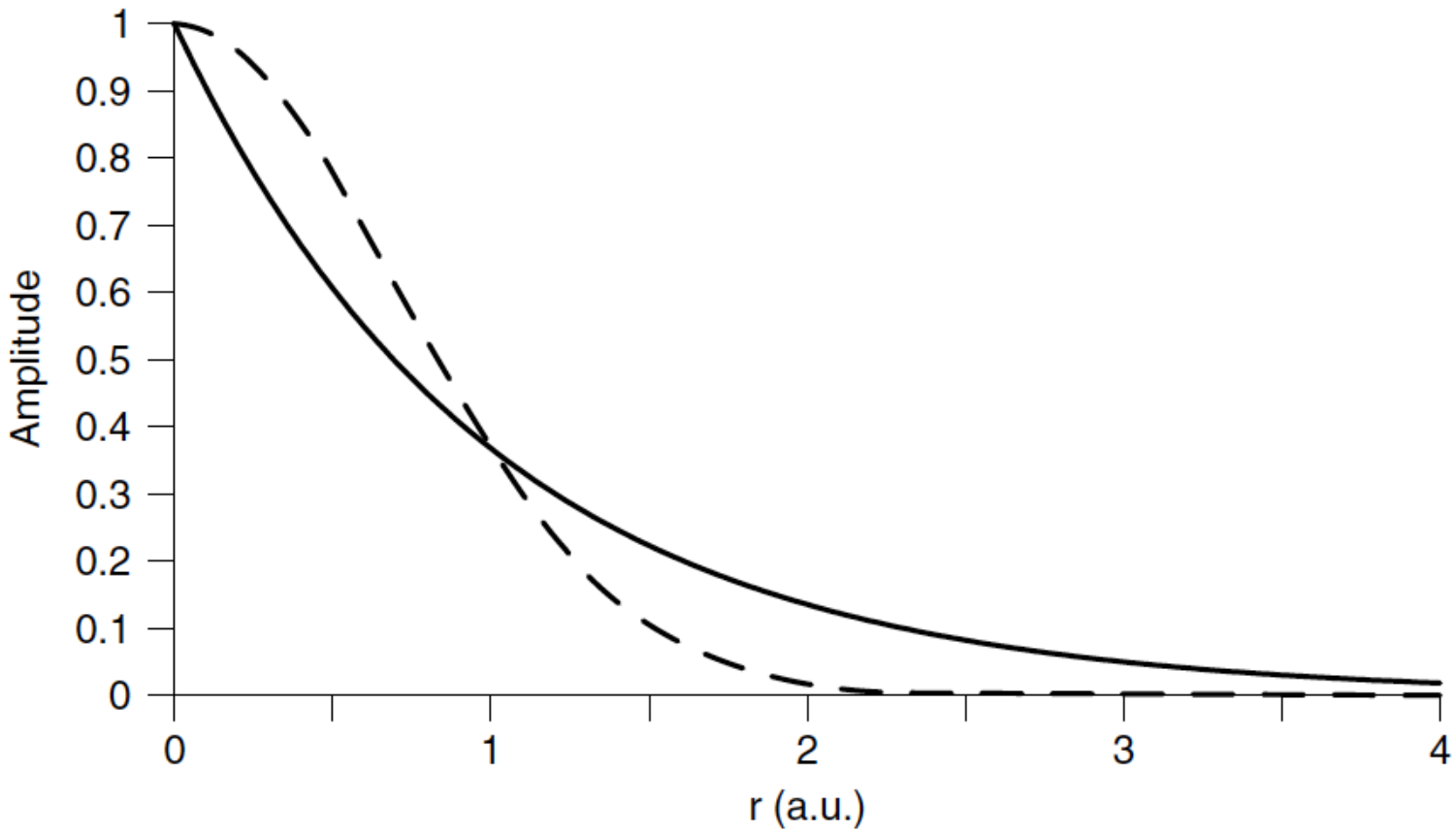
- N normalization constant
- n principal quantum number
- l electron angular momentum
- m projection of l on an axis
- $Y_{l,m}(\theta,\phi)$ spherical harmonics

STO vs GTO

- At the nucleus STO has a cusp, GTO has zero slope
- GTO falls off too rapidly at large distances

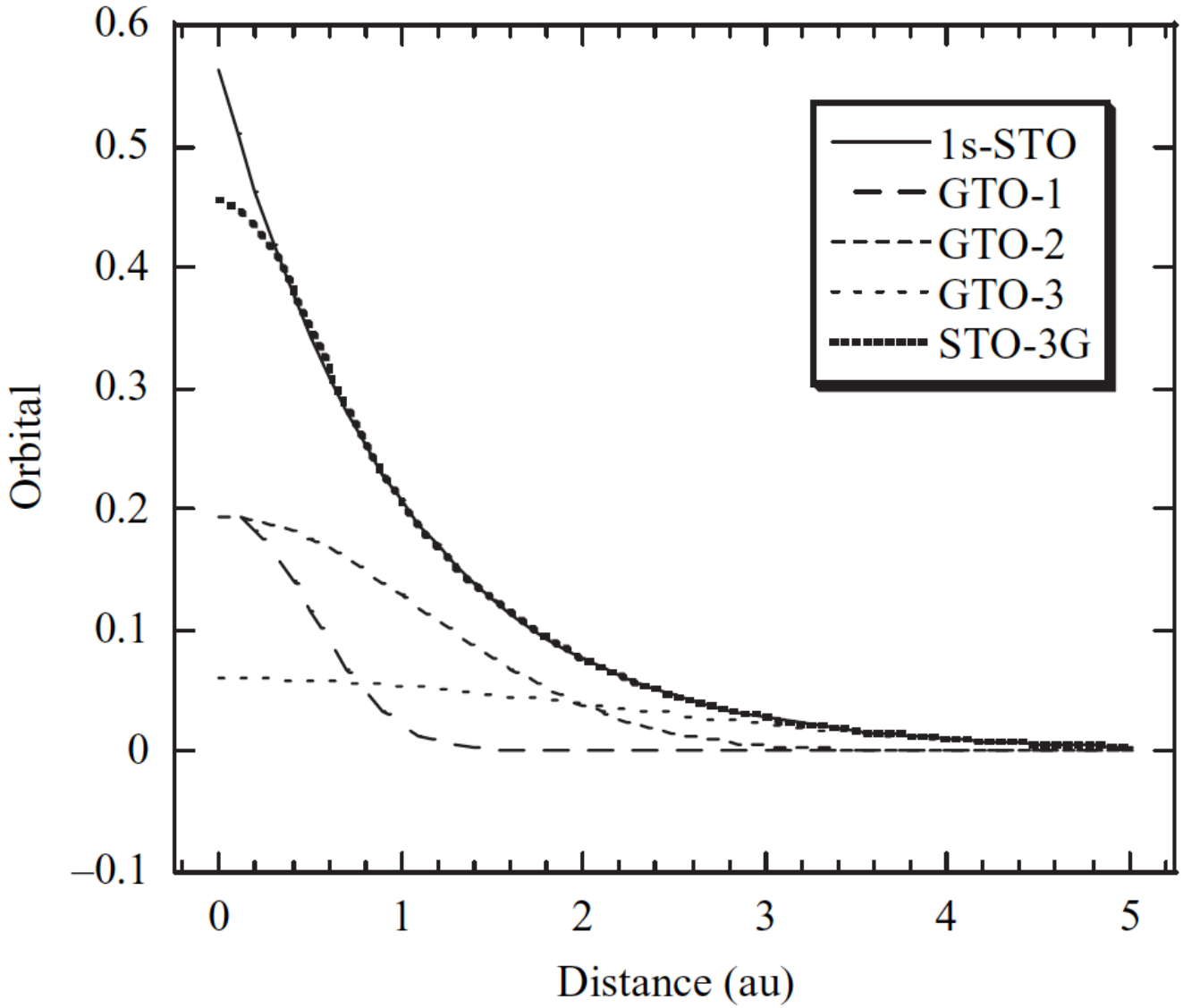
STO vs GTO

- At the nucleus STO has a cusp, GTO has zero slope
- GTO falls off too rapidly at large distances
- But GTOs are computationally more efficient



GTO contraction

STO-3G = a_1GTO-1 + a_2GTO-2 + a_3GTO-3



Classification of a basis set

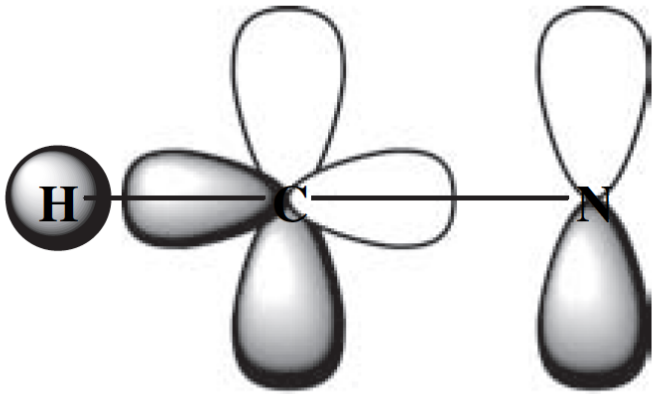
- GTOs centered on nuclei

Classification of a basis set

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- Minimal basis set:
  - Single s function for H and He
  - $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ for first-row atoms
  - Etc.

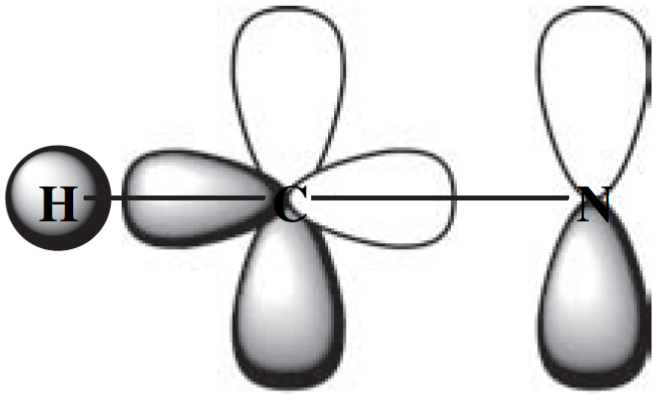
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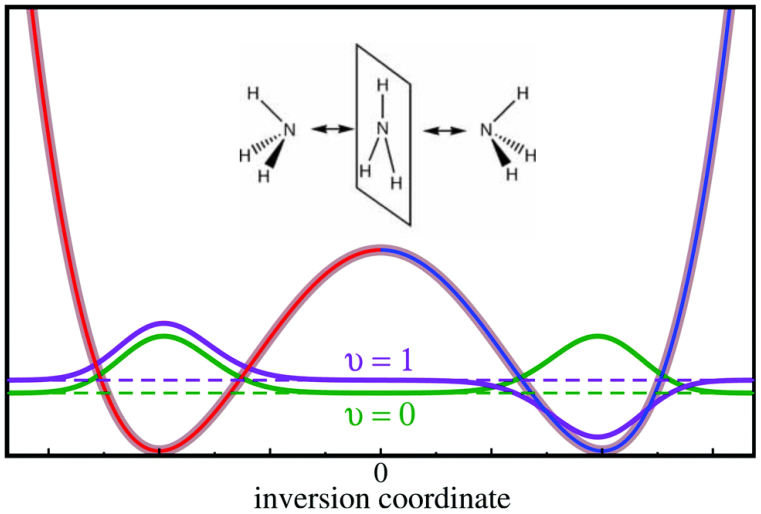
- Triple (TZ), quadruple (QZ), quintuple (5Z) and sextuple (6Z)
- Split-valence type

Polarization functions

- Higher angular momentum functions

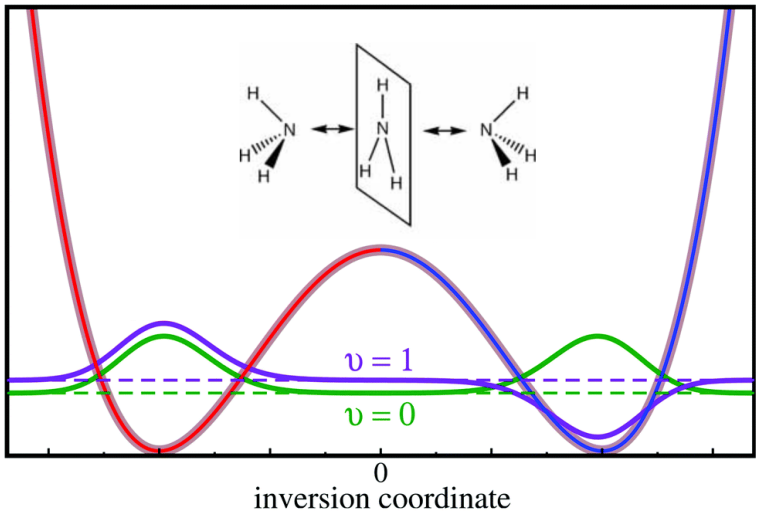
Polarization functions

- Higher angular momentum functions
- Ammonia umbrella inversion (5.8 kcal/mol)
- With only *s* and *p* functions, HF predicts the planar geometry as a minimum structure

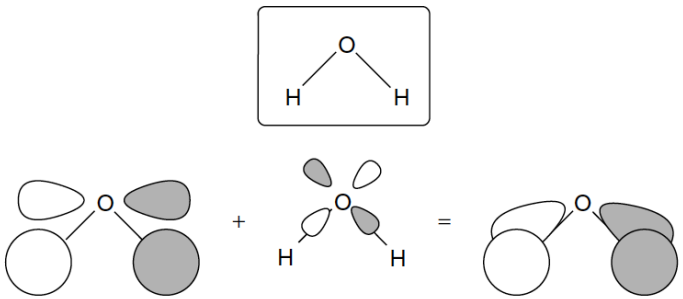


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- *d* functions in H_2O improve hydrogen bond description

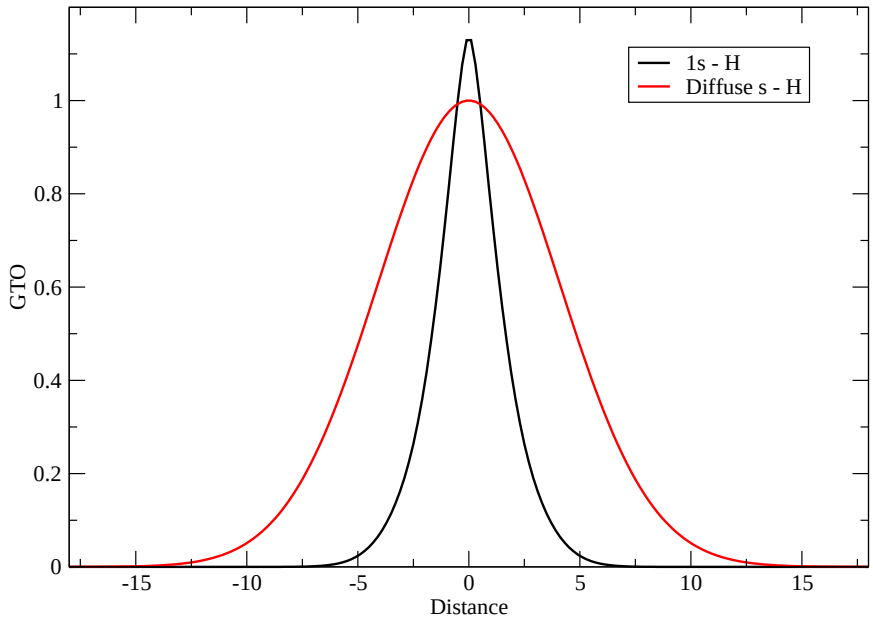


Diffuse functions

- Standard basis sets fail in describing large spatial extension
  - Molecular orbitals of anions
  - Rydberg electronic states
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  - Molecular orbitals of anions
  - Rydberg electronic states
  - Supramolecular complexes
- "Augmentation" with diffuse GTOs
  - Smaller exponent than valence GTOs
  - Same angular momentum as valence GTOs
  - Uncontracted GTOs



Pople-type basis sets

- STO-*n*g:
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  - Split-valence basis: 3 PGTOs for core, inner (outer) valence with 2 (1) PGTOs
- 6-31G:
  - Split-valence basis: 6 PGTOs for core, inner (outer) valence with 3 (1) PGTOs
- 6-311G:
  - Triple split-valence basis: 6 PGTOs for core, valence with 3 functions: 3, 1 and 1 PGTOs

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
STO-3G	1s	3s	2s1p	6s3p	3s2p	9s6p
3-21G	2s	3s	3s2p	6s3p	4s3p	9s6p
6-31G(d,p)	2s1p	4s	3s2p1d	10s4p	4s3p1d	16s10p
6-311G(2df,2pd)	3s2p1d	5s	4s3p2d1f	11s5p	6s4p2d1f[a]	13s9p[a]

Dunning-type basis sets

- Correlation consistent (cc) basis sets
- Functions with similar amount of correlation energy included at the same stage
- *s* and *p* exponents optimized at HF level, polarization exponents at CISD level
- cc-pVXZ: correlation consistent polarized Valence X Zeta (X=D, T, Q, 5, 6)

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
cc-pVDZ	2s1p	4s	3s2p1d	9s4p	4s3p2d	12s8p
cc-pVTZ	3s2p1d	5s	4s3p2d1f	10s5p	5s4p3d1f	15s9p
cc-pVQZ	4s3p2d1f	6s	5s4p3d2f1g	12s6p	6s5p4d2f1g	16s11p
cc-pV5Z	5s4p3d2f1g	8s	6s5p4d3f2g1h	14s8p	7s6p5d3f2g1h	20s12p
cc-pV6Z	6s5p4d3f2g1h	10s	7s6p5d4f3g2h1i	16s10p	8s7p6d4f3g2h1i	21s14p

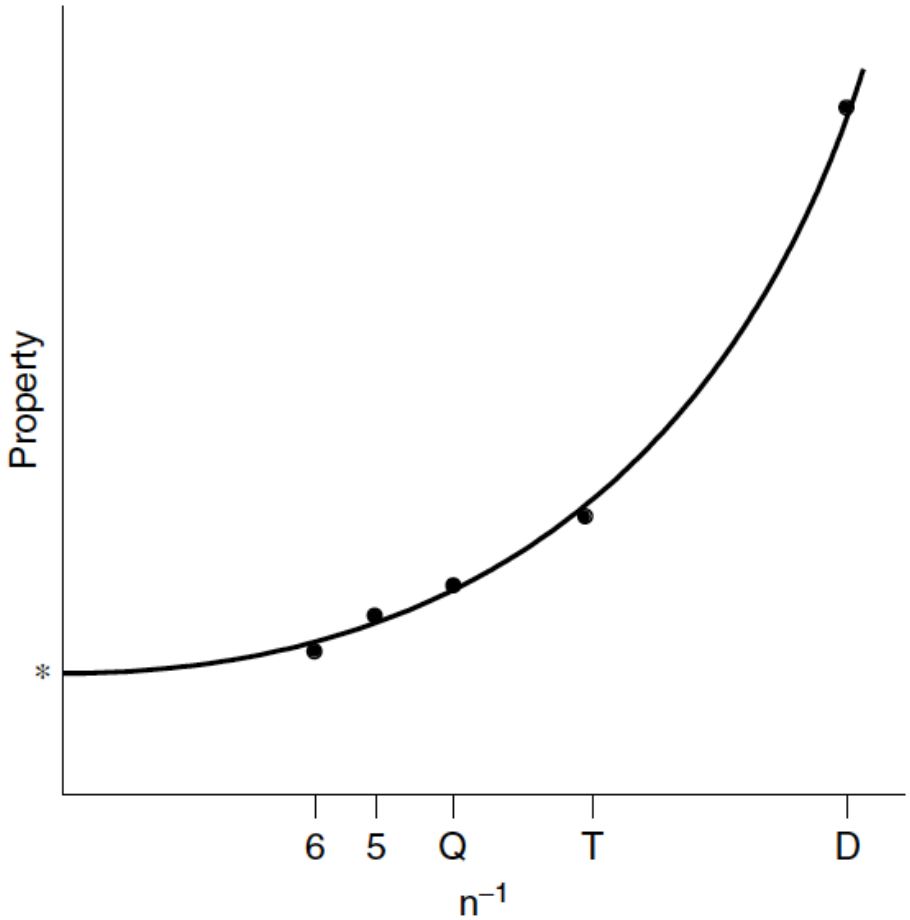
Ahlrichs-type basis sets

- Basis sets of DZ, TZ and QZ quality
- Split Valence Polarized (SVP)
- Triple Zeta Valence (TZV)
- Quadruple Zeta Valence (QZV)

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
SVP	2s1p	4s	3s2p1d	7s4p	4s3p1d	10s7p
TZV	3s2p1d	5s	5s3p2d1f	11s6p	5s4p2d1f	14s9p
QZV	4s3p2d1f	7s	7s4p3d2f1g	15s8p	9s6p4d2f1g	20s14p

HF limit

- HF solution with infinite basis set
- Extrapolation



Effective core potentials

- Heavy elements are challenging for quantum chemistry
- Large number of electrons $\rightarrow$ large number of basis functions

Effective core potentials

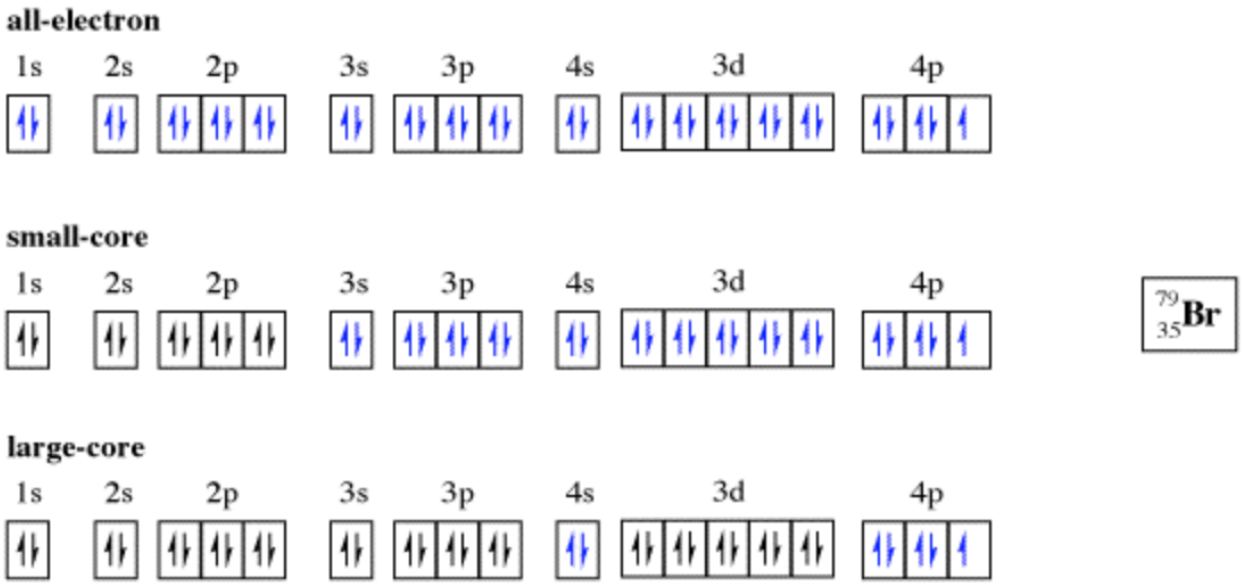
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- ECP describes the nuclear-electronic core to explicit electrons

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- Replace core electrons with analytical functions: effective core potential (ECP)
- ECP describes the nuclear-electronic core to explicit electrons
- Also relativistic effects included



Beyond Hartree-Fock

Correlation energy

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$$E_{\text{corr}} = E_0 - E_{\text{HF}}$$

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- Electronic correlation: dynamical and static

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- Recovered in density functional theory (see Density functional theory) in different flavours
- Explicit electron-electron distance in Ψ (quantum Monte Carlo)

HF Failure for Stretched H_2: Spurious Ionic Contamination

Molecular orbitals from 1s AOs:

$$\sigma_g = \frac{1}{\sqrt{2}}(\chi_A + \chi_B), \quad \sigma_u^* = \frac{1}{\sqrt{2}}(\chi_A - \chi_B)$$

HF ground state:

$$|\Psi_{\text{HF}}\rangle = |\sigma_g \bar{\sigma} g\rangle$$

Expanding in AOs reveals hidden ionic terms:

$$|\Psi_{\text{HF}}\rangle \propto \underbrace{|\chi_A \bar{\chi}_B\rangle + |\chi_B \bar{\chi}_A\rangle}_{\text{covalent } \mathrm{H}\cdot + \cdot\mathrm{H}} + \underbrace{|\chi_A \bar{\chi}_A\rangle + |\chi_B \bar{\chi}_B\rangle}_{\text{ionic } \mathrm{H}^+\mathrm{H}^-}$$

At $R \to \infty$: both terms have equal weight!
HF *cannot* eliminate the ionic component.

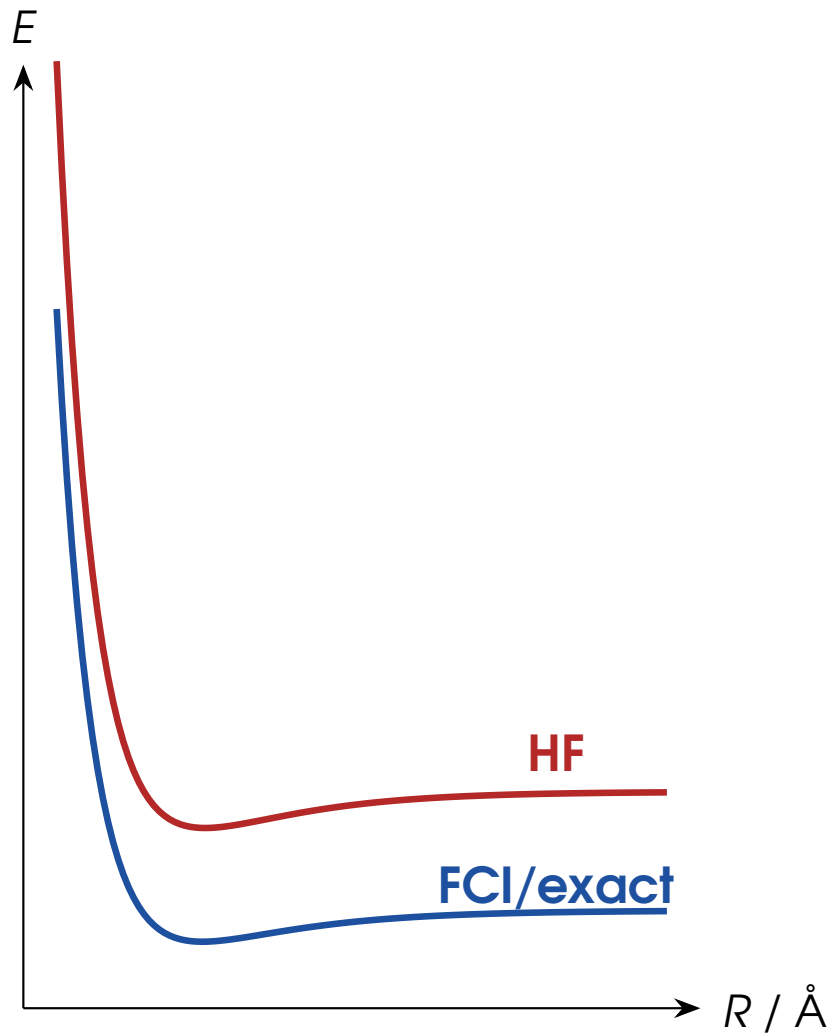
Fix: two-configuration wavefunction

$$|\Psi\rangle = C_1 |\sigma_g \bar{\sigma}_g\rangle - C_2 |\sigma_u^* \bar{\sigma}_u^*\rangle$$

$\sigma_u^* \bar{\sigma}_u^*$ contribution cancels ionic terms:

$$C_1 = C_2 \;\Rightarrow\; |\Psi\rangle \propto |\chi_A \bar{\chi}_B\rangle + |\chi_B \bar{\chi}_A\rangle \;\checkmark$$

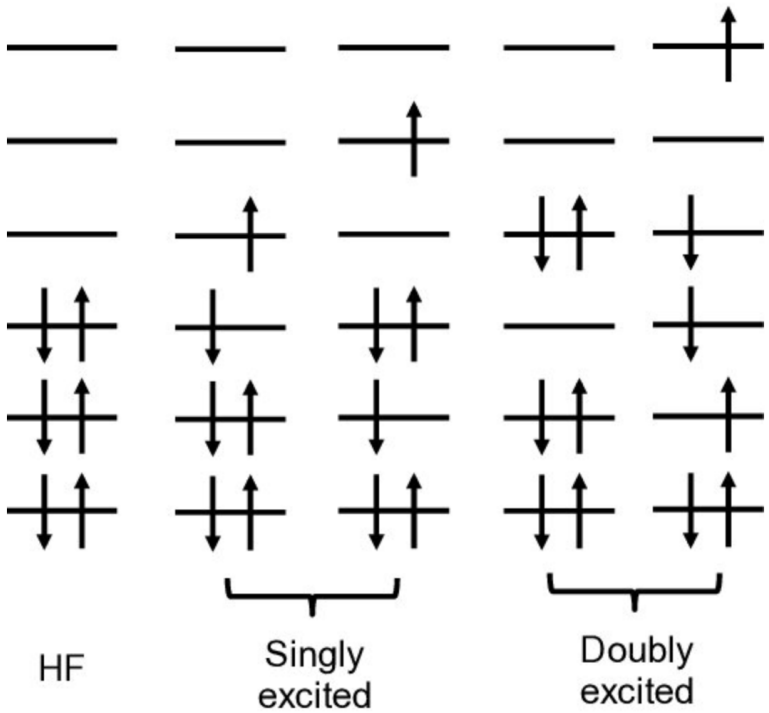
Potential energy curves for H_2



Configuration Interaction

$$\Psi = c_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} c_i^a \Psi_i^a + \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots$$

- Post-HF method
- Ψ_i^a: singly-excited Slater determinant
- Ψ_{ij}^{ab}: doubly-excited Slater determinant
- HF Slater determinant as reference



Configuration Interaction

- Optimization of the CI coefficients c_0, c_i^a, c_{ij}^{ab}...
- MOs are not re-optimized, MOs from HF calculation
- Secular equation in Slater-determinant space

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} - E & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdot & H_{NN} - E \end{vmatrix} = 0$$

- With

$$H_{mn} = \langle \Psi_m | \hat{H} | \Psi_n \rangle$$

- Ψ_m and Ψ_n are Slater determinants
- $\hat{H}$: electronic Hamiltonian

Which excitations to include?

$$\Psi = c_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} c_i^a \Psi_i^a + \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} c_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{i,j,k}^{\mathrm{occ}} \sum_{a,b,c}^{\mathrm{vir}} c_{ijk}^{abc} \Psi_{ijk}^{abc} + \ldots$$

Brillouin's theorem: $\langle \Psi_{\mathrm{HF}} | \hat{H} | \Psi_i^a \rangle = 0$

	Ψ_{HF}	Ψ_i^a	Ψ_{ij}^{ab}	Ψ_{ijk}^{abc}
Ψ_{HF}	E_{HF}	**0**	dense	**0**
Ψ_i^a	**0**	dense	sparse	very sparse
Ψ_{ij}^{ab}	dense	sparse	sparse	extremely sparse
Ψ_{ijk}^{abc}	**0**	very sparse	extremely sparse	extremely sparse

CI with doubles (CID)

- Example: H_2 with a minimal basis set
- Two HF orbitals, σ_g and σ_u^*
- Double excitation: both electrons in σ_u^*

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- Secular equation

$$\begin{vmatrix} H_{11} - E_{\text{CID}} & H_{12} \\ H_{21} & H_{22} - E_{\text{CID}} \end{vmatrix} = 0$$

- With solutions

$$E_{\text{CID},\pm} = \frac{1}{2}\left[H_{11} + H_{22} \pm \sqrt{(H_{22} - H_{11})^2 + 4H_{12}^2}\right]$$

- $E_{\text{CID},-}$ is the CID ground-state energy
- $E_{\text{HF}} \equiv H_{11}$ and $H_{12} > 0$

H_2 energy

- H-H distance of 0.75 Å
- Minimal basis set STO-6G

$$\Psi = c_0 \Psi_{HF} + c_1 \Psi_{11}^{22}$$

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- E_{HF} = -1.12473 Ha
  E_{CI} = -1.14574 Ha ($>$ 50 kJ mol^{-1} lower)

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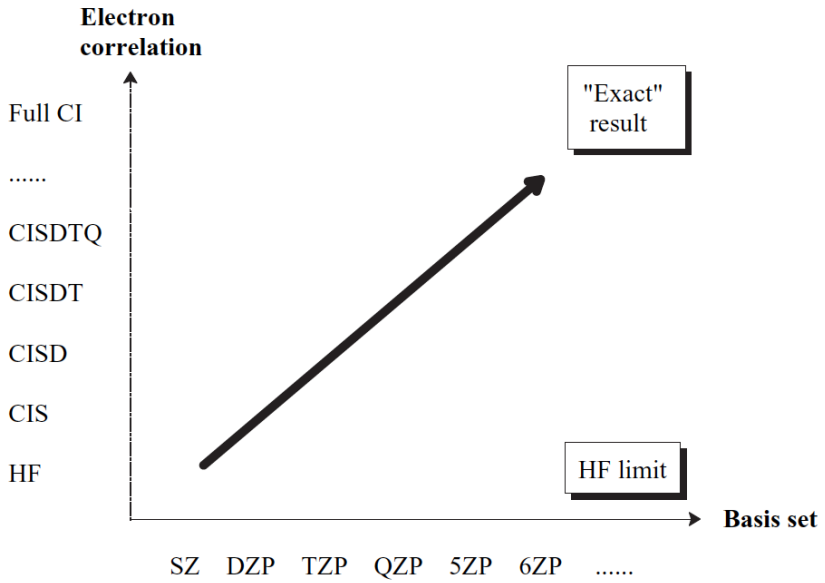
- E_{HF} = -1.12473 Ha
  E_{CI} = -1.14574 Ha ($>$ 50 kJ mol^{-1} lower)
- $|c_0|^2 = 0.986$, $|c_1|^2 = 0.013$

Role of multiple excitations

- H_2O energy with cc-pVDZ basis set
- 90% of E_{corr} recovered with double excitations

Level	E (Hartree)	E_{corr} (Hartree)	E_{corr} (kJ mol^{-1})
HF	-76.02129	0.00000	0.00
CISD	-76.22749	-0.20620	-541.37
CISDT	-76.23066	-0.20937	-549.70
CISDTQ	-76.23970	-0.21841	-573.43
Full CI	-76.24006	-0.21877	-574.38

Size of the CI matrix



- Full CI: all excited determinants are included, provided a finite basis set
- With N electrons and B basis functions ($2B$ spin orbitals), the number S of Slater determinants is

$$S = \binom{2B}{N}$$

- $N = 10, B = 20 \rightarrow S \approx 8.5 \times 10^8$

MCSCF methods

Unlike CI, MCSCF optimizes **two sets** of parameters simultaneously:

1. **CI Coefficients (c_I):** Weights of the Slater determinants in the expansion
2. **Orbital Coefficients (C^i_μ):** The shape of the molecular orbitals

The Variational Energy:

$$E_{MCSCF} = \min_{\{c_I\},\{C^i_\mu\}} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

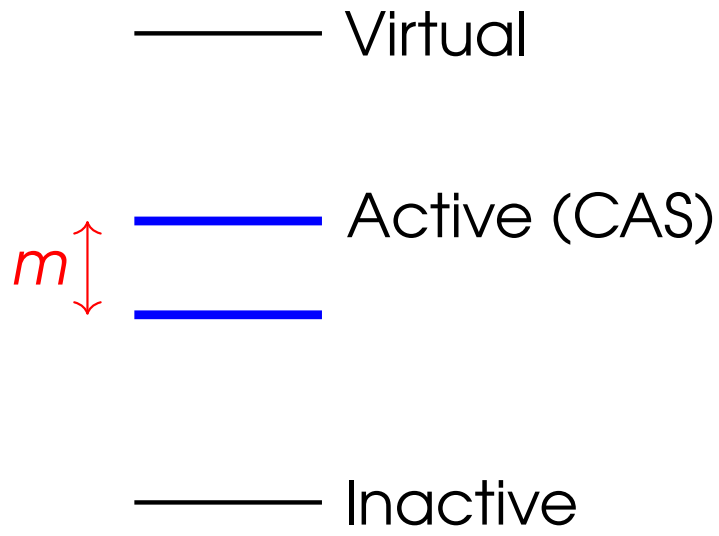
Key Characteristic

The orbitals are "relaxed" specifically for the multi-determinant wave function, providing a *self-consistent field* for the specific multi-reference state

Complete Active Space (CASSCF)

The most common MCSCF variant is **CASSCF**. Orbitals are divided into three spaces:

- **Inactive (Core):** Doubly occupied in all determinants.
- **Active:** Orbitals where electrons are distributed in all possible ways (Full CI in this space).
- **Virtual:** Empty in all determinants.



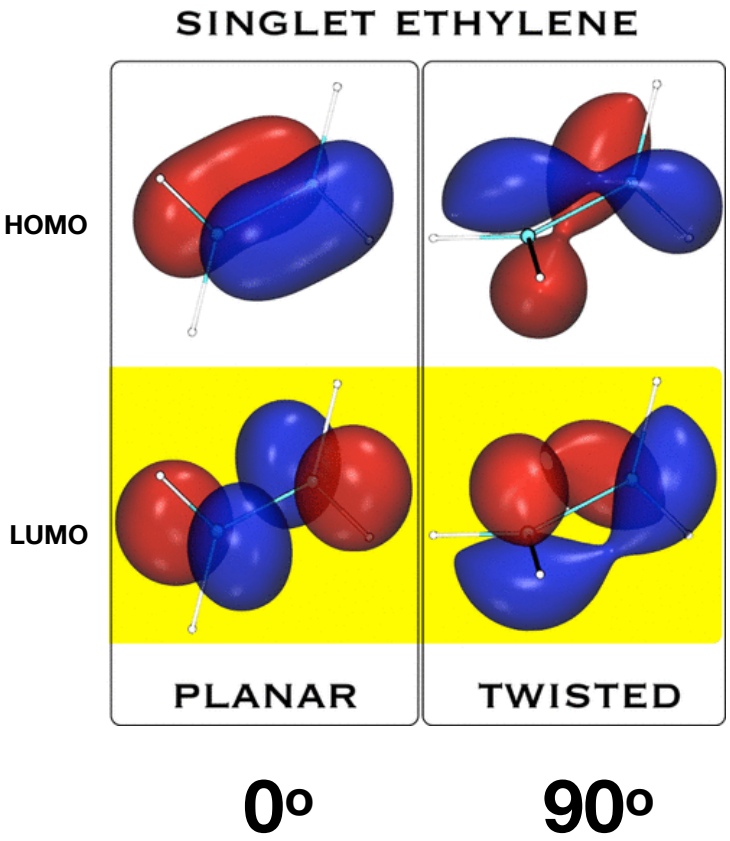
Notation: CAS(n, m)
n electrons in m orbitals.

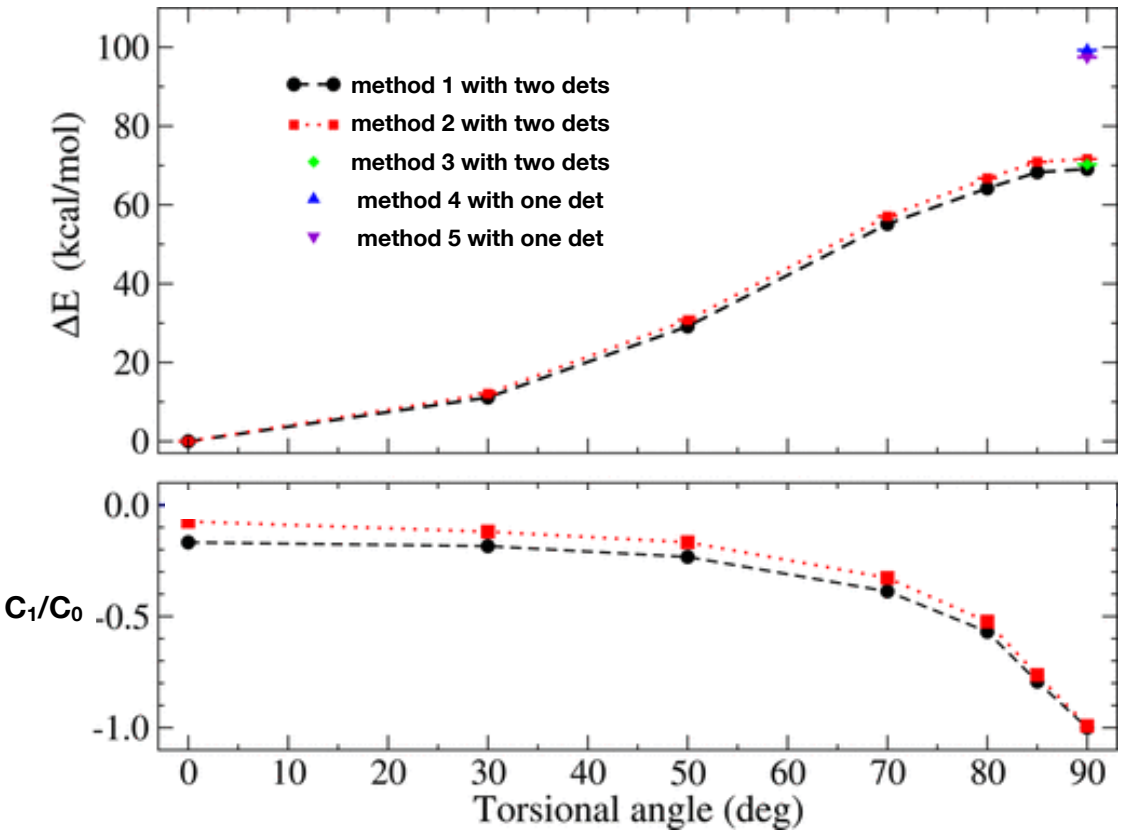
Selection of the active space is the most critical/difficult step for the user.

Static correlation

Ethylene torsional barrier

$$\Psi = c_0\Psi_0 + c_1\Psi_1$$





CAS(2,2) for the twisted C_2H_4

Planar (0°):

- HOMO (π) and LUMO (π^*) are well-separated
- RHF is qualitatively correct
- $\Psi \approx \ldots \pi^2$

Twisted (90°):

- *p*-orbitals non-bonding and degenerate
- Diradical character emerges
- Single reference fails (Static Correlation)

The active space includes 2 electrons in the π and π^* orbitals

$$\Psi_{\text{CASSCF}} = c_1\pi^2 + c_2(\pi^*)^2$$

- At 0°: $c_1 \approx 1, c_2 \approx 0$
- At 90°: $|c_1| \approx |c_2|$

CASSCF provides the correct qualitative description of bond breaking and where single-reference methods break down

Density functional theory

Electronic density

- Ψ is a complicated function of $3N$ and N spin coordinates
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$$N = \int \rho(\mathbf{r}) d\mathbf{r}$$

$$\frac{\partial \bar{\rho}(\mathbf{R}_A)}{\partial \mathbf{R}_A} = -2Z_A \rho(\mathbf{R}_A)$$

- $\mathbf{R}_A$: position of nucleus A
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- $\mathbf{R}_A$: position of nucleus A
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- How to get the energy from ρ? $\rightarrow$ Density functional theory (DFT)

Rigorous foundation of DFT

- Electrons interact with each other and with an external potential
- External potential: nuclear attraction in atoms and molecules

First Hohenberg-Kohn theorem

- Existence theorem
- The external potential (and hence the total energy) is a unique functional of the electron density
- Reductio per absurdum

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- The external potential (and hence the total energy) is a unique functional of the electron density
- Reductio per absurdum
- Two different external potentials $\hat{v}_a$ and $\hat{v}_b$ define the same nondegenerate ground-state density ρ_0

$$\hat{v}_a \rightarrow \hat{H}_a \rightarrow \Psi_{0,a}, E_{0,a}$$
$$\hat{v}_b \rightarrow \hat{H}_b \rightarrow \Psi_{0,b}, E_{0,b}$$

- According to the variational principle

$$E_{0,a} < \langle \Psi_{0,b} | \hat{H}_a | \Psi_{0,b} \rangle$$

First Hohenberg-Kohn theorem

$$
\begin{aligned}
E_{0,a} &< \langle \Psi_{0,b} | \hat{H}_a | \Psi_{0,b} \rangle \\
E_{0,a} &< \langle \Psi_{0,b} | \hat{H}_a - \hat{H}_b + \hat{H}_b | \Psi_{0,b} \rangle \\
&< \langle \Psi_{0,b} | \hat{H}_a - \hat{H}_b | \Psi_{0,b} \rangle + \langle \Psi_{0,b} | \hat{H}_b | \Psi_{0,b} \rangle \\
&< \langle \Psi_{0,b} | \hat{V}_a - \hat{V}_b | \Psi_{0,b} \rangle + E_{0,b}
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&< \langle \Psi_{0,b} | \hat{V}_a - \hat{V}_b | \Psi_{0,b} \rangle + E_{0,b}
\end{aligned}
$$

- Integral form

$$E_{0,a} < \int (\hat{v}_a(\mathbf{r}) - \hat{v}_b(\mathbf{r}))\rho_0(\mathbf{r})d\mathbf{r} + E_{0,b} \quad (2)$$

$$E_{0,b} < \int (\hat{v}_b(\mathbf{r}) - \hat{v}_a(\mathbf{r}))\rho_0(\mathbf{r})d\mathbf{r} + E_{0,a} \quad (3)$$

- (2) + (3)

First Hohenberg-Kohn theorem

$$
\begin{aligned}
E_{0,a} + E_{0,b} &< \int (\hat{v}_b(\mathbf{r}) - \hat{v}_a(\mathbf{r}))\rho_0(\mathbf{r})d\mathbf{r} + \int (\hat{v}_a(\mathbf{r}) - \hat{v}_b(\mathbf{r}))\rho_0(\mathbf{r})d\mathbf{r} \\
&+ E_{0,b} + E_{0,a} \\
&< \int (\hat{v}_b(\mathbf{r}) - \hat{v}_a(\mathbf{r}) + \hat{v}_a(\mathbf{r}) - \hat{v}_b(\mathbf{r}))\rho_0(\mathbf{r})d\mathbf{r} + E_{0,b} + E_{0,a} \\
&< E_{0,b} + E_{0,a} \quad \text{impossible!}
\end{aligned}
$$

- Initial assumption incorrect
- The nondegenerate ground-state density ρ_0 must determine $\hat{v}$, $\hat{H}$ and Ψ_0

Second Hohenberg-Kohn theorem

- The first theorem only states a ρ_0 exists
- Variational principle applied to the density
- Given an approximate ρ'

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$$E[\rho'] \geq E_0[\rho_0]$$

- Equality holds when ρ' is the exact ground-state density ρ_0

Kohn-Sham approach

- Fictitious system: non-interacting electrons
- Same ground-state $\rho(\mathbf{r})$ as for the real system (electrons do interact!)

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\end{aligned}
$$

$$
V_{ne}[\rho(\mathbf{r})] = -\sum_{k}^{\text{nuclei}} \int \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} \rho(\mathbf{r}) d\mathbf{r}
$$

$$
V_{ee}[\rho(\mathbf{r})] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_i)\rho(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j
$$

- T_{ni}: sum of kinetic energy of the electrons

Kohn-Sham approach

- Using molecular orbitals

$$\rho = \sum_{i}^{N} \langle \phi_i | \phi_i \rangle$$

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$$\rho = \sum_{i}^{N} \langle \phi_i | \phi_i \rangle$$

- the energy becomes

$$\begin{aligned} E[\rho(\mathbf{r})] &= \sum_{i}^{N} \left(\langle \phi_i | -\frac{1}{2}\nabla_i^2 | \phi_i \rangle - \langle \phi_i | \sum_{k}^{\text{nuclei}} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} | \phi_i \rangle \right) \\ &+ \sum_{i}^{N} \langle \phi_i | \frac{1}{2} \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} d\mathbf{r} | \phi_i \rangle + E_{xc}[\rho(\mathbf{r})] \end{aligned}$$

- $E_{xc}[\rho(\mathbf{r})]$: exchange-correlation energy (contains ΔT and ΔV_{ee})

Kohn-Sham approach

- Find the ϕ_i set minimising E

$$
\begin{aligned}
h_i^{KS}\phi_i &= \epsilon_i\phi_i \\
h_i^{KS} &= -\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} d\mathbf{r} + V_{xc} \\
V_{xc} &= \frac{\partial E_{xc}}{\partial \rho}
\end{aligned}
$$

- In principle, one gets exact ground-state energy E
- Exact density ρ provided by orbitals ϕ_i

Kohn-Sham approach

- Separable non-interacting Hamiltonian $\hat{H}_{ni} = \sum_i^N h_i^{KS}$
- Slater determinant of optimized ϕ_i as eigenfunction of $\hat{H}_{ni}$

$$\hat{H}_{ni}|\phi_1\phi_2\cdots\phi_N\rangle = \sum_i^N \epsilon_i|\phi_1\phi_2\cdots\phi_N\rangle$$

- Fictitious system of non-interacting electrons with exact density
- T_{ni} is a large fraction of the actual system

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- LCAO approach to represent molecular orbitals

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Exchange-correlation functionals

- HF theory is approximate, DFT is in principle exact
- No guidance to find E_{xc}
- Practical use of DFT implies approximations in E_{xc}
- DFT can violate the variational principle, because of E_{xc}
  - H atom energy with BPW91 = -0.5042 Hartree
  - Exact H energy is -0.5 Hartree
- In general $E_{xc} = E_x + E_c$

Exchange-correlation functionals

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$$\begin{aligned} E_x^{\mathrm{LDA}}[\rho(\mathbf{r})] &= -C_x \int \rho^{4/3}(\mathbf{r})d\mathbf{r} \\ \epsilon_x^{\mathrm{LDA}} &= -C_x \rho^{1/3} \end{aligned}$$

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- E_c estimated by accurate quantum Monte Carlo calculations

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- In molecules, ρ is not spatially uniform!
- LDA for molecules is a rough approximation

Exchange-correlation functionals

- Correction to LDA: include nonlocal effects, i.e. the gradient of the density
- Generalized gradient approximation (GGA)

$$\epsilon_{xc}^{\mathrm{GGA}} = \epsilon_{xc}^{\mathrm{LDA}} + \Delta\epsilon_{xc}\left[\frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})}\right]$$

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- PBE is likely the most known GGA functional

$$\begin{aligned}
\epsilon_x^{\mathrm{PBE}} &= \epsilon_x^{\mathrm{LDA}} F(x) \\
F(x) &= 1 + a - \frac{a}{1 + bx^2} \\
x &= \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}}
\end{aligned}$$

Exchange-correlation functionals

$$
\begin{aligned}
\epsilon_C^{\mathrm{PBE}} &= \epsilon_C^{\mathrm{LDA}} + B(g) \\
B(g) &= c f_3^3 \ln\left[1 + d g^2 \left(\frac{1 + A g^2}{1 + A g^2 + A^2 g^4}\right)\right] \\
A &= d\left[\exp\left(-\frac{\epsilon_C^{\mathrm{LDA}}}{c f_3^3} - 1\right)\right]^{-1} \\
f_3(\zeta) &= \frac{1}{2}[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}] \\
g &= [2(3\pi^3)^{1/3} f_3]^{-1} x \\
\zeta &= \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}
\end{aligned}
$$

- a, b, c and d are parameters

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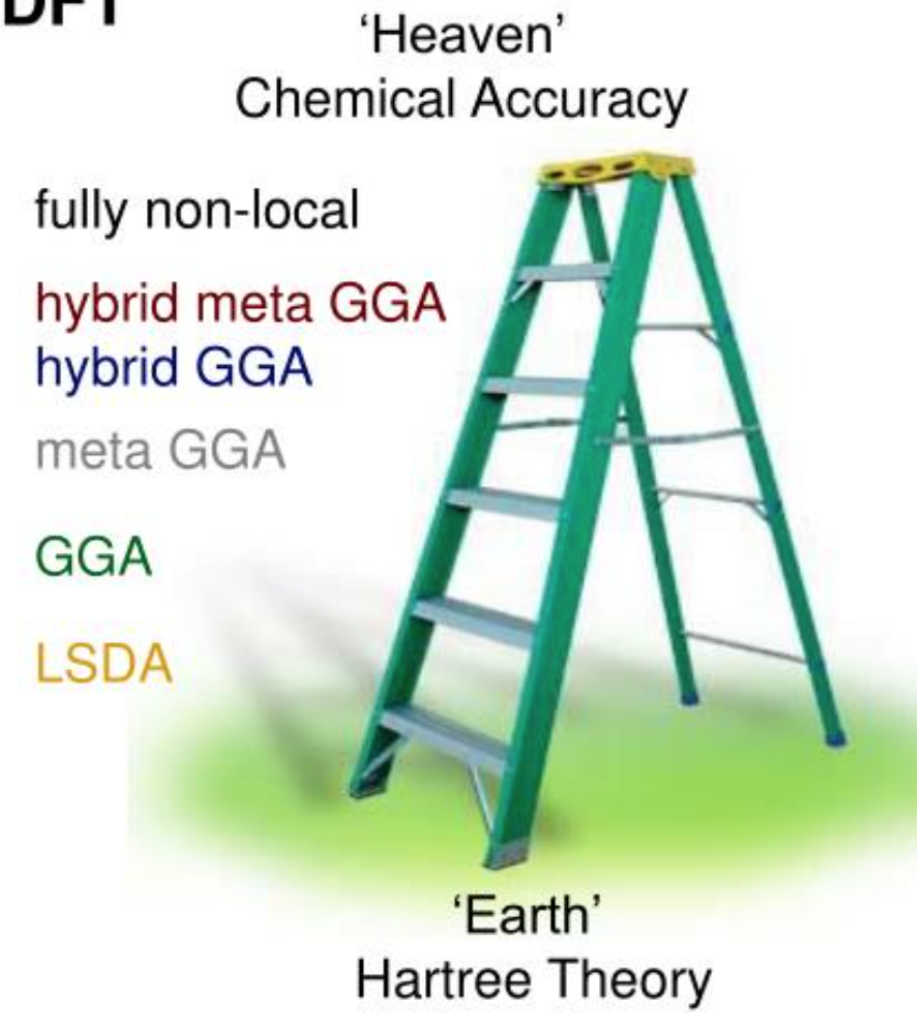
$$E_{xc}^{\mathrm{B3LYP}} = (1-a)E_x^{\mathrm{LDA}} + aE_x^{\mathrm{HF}} + b\Delta E_x^{\mathrm{B}} + (1-c)E_c^{\mathrm{LDA}} + cE_c^{\mathrm{LYP}}$$

- $a = 0.20$, $b = 0.72$ and $c = 0.81$ (fitted parameters)

Exchange-correlation functionals

Jacobs Ladder of DFT

As you go up the rungs of Jacob's Ladder the functional forms get more complex but the energies get more accurate (and more expensive to compute)



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- Parameters in DFT functionals
- DFT election method for large-size applications (catalysis, biomolecules etc.)

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- Inter- and intra-molecular charge transfer is badly described
  - Range-separated functionals mitigate the issue
- Different spin multiplicity
  - Transition metal systems: several low-energy spin states are often possible
  - Such states cannot be described by a single determinant
  - Broken-symmetry DFT

DFT performances

- RMS: root mean square deviation $\sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - x_i)^2}$
- MAD: mean absolute deviation $\frac{1}{n}\sum_{i=1}^{n}|y_i - x_i|$
- Over a large set of molecules (atomization energies, ionization potentials, electron and proton affinities)
- Against experimental data
- Residual gradient $\rightarrow$ accuracy of optimized geometries

Functional	RMS (gradient)	RMS (kJ/mol)	MAD (kJ/mol)
HF	35	649	885
LSDA	16	439	510
PW91	15	80	99
PBE	16	87	93
PKBZ	21	75	29
BLYP	19	41	40
PBE0	11	50	28
OLYP	14	40	25
B3LYP	11	40	21
VSXC	11	39	14
HTCT	11	33	30
τ-HCTH	11	31	
τ-HCTH-hybrid	10	26	
TPSS			24
TPSSh			16