

Introduction to Quantum Chemistry

Operators
Postulates of quantum mechanics
Schrodinger equation
Approximations leading to Hartree-Fock method
Slater determinant
Hartree-Fock method
MO LCAO (Hartree-Fock-Roothaan)
Restricted vs. unrestricted description of open-shell systems

Literature:

I. Levin: *Quantum Chemistry*, Prentice Hall, New Jersey 1991.
A. Szabo a N. S. Ostlund: *Modern Quantum Chemistry*, McGraw-Hill, New York 1982.
Ch. J. Cramer: *Essentials of Computational Chemistry*, Wiley.

Operator algebra

OPERATOR - a rule that transform a given function into another function

$$\hat{O} f(x, y) = g(x, y)$$

Linear operator:

$$\hat{O}(f_1 + f_2) = \hat{O} f_1 + \hat{O} f_2$$

$$\hat{O} c f_1 = c \hat{O} f_1$$

$$[\hat{P}, \hat{Q}] = \hat{P}\hat{Q} - \hat{Q}\hat{P}$$

Commutator:

Eigenfunctions and eigenvalues:

$$\hat{O} f_k = o_k f_k$$

Eigenvalue

Eigenfunction

Dirac's notation:
 ("bracket")

$$\int \Phi^*(x)\Phi(x)dx = \langle \Phi(x) | \Phi(x) \rangle = \langle \Phi | \Phi \rangle$$

$$\int \Phi^*(x)\hat{H}\Phi(x)dx = \langle \Phi(x) | \hat{H} | \Phi(x) \rangle = \langle \Phi | \hat{H} | \Phi \rangle$$

“bra”-vector

“ket”-vector

Orthonormal functions

$$\int \varphi_i^*(x)\varphi_j(x)dx = \langle \varphi_i | \varphi_j \rangle = \langle i | j \rangle = 0 \dots i \neq j$$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

Kronecker's delta

Hermitian operators:

$$\int f_1^*(x)\hat{O}f_2(x)dx = \int f_2(x)\hat{O}^*f_1^*(x)dx$$

Eigenvalues are real number !

Eigenfunctions forms COMPLETE ORTHONORMAL SET

$$\Phi = \sum_k c_k f_k$$

$$c_k = \langle f_k | \Phi \rangle$$

THE POSTULATES OF QUANTUM MECHANICS

Postulate 1.

The state of the system is described by the $\Psi(X,t)$ - wave function - contains all the information about the system

Single valued, continuous, and quadratically integrable

Probabilistic character - $\Psi^*(x_1, \dots, x_n, t) \cdot \Psi(x_1, \dots, x_n, t)$

Postulate 2.

To every physical observable there corresponds a linear Hermitian operator.

This operator can be found from classical-mechanical expression for the observable in terms of Cartesian coordinates and linear-momentum components.

$x, t \dots$ no change

$$P_x \longrightarrow -i\hbar \frac{\partial}{\partial x}$$

THE POSTULATES OF QUANTUM MECHANICS

Postulate 3.

The only possible values that can result from measurements of the physically observable property A are the eigenevalues a_k :

$$\hat{A}\gamma_k = a_k\gamma_k$$

Postulate 4.

Assuming $\Psi(x,t)$ is the normalized state function of a system at time t , then the average value of a physical observable A at time t is

$$\bar{a} = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Postulate 5.

Time development of the state of an system is given by the Schrödinger equation:

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

THE POSTULATES OF QUANTUM MECHANICS

Postulate 6.

The wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons.

Pauli principle

Postulate 7.

Electron possesses an internal momentum - spin.

Time dependent vs. stationary Schrödinger equation

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

For systems where $V(x)$ does not depend on time

$$\Rightarrow \Phi(x, t) = \phi(x) f(t)$$

$$\left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial x^2} + V(x) \right]$$

Separation of variable (product form of the wave function)

$$\hat{H} \phi(x) = E \phi(x)$$

$$f(t) = A \cdot \exp(-iEt / \hbar)$$

$$\Phi(x, t) = \exp(-iEt / \hbar) \cdot \phi(x)$$

Stationary states:

$$|\Phi(x, t)|^2 = \Phi(x, t)^* \cdot \Phi(x, t) =$$

$$\exp(iEt / \hbar) \cdot \exp(-iEt / \hbar) \cdot \phi^*(x) \cdot \phi(x) = |\phi(x)|^2$$

Time independent Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

Wave function describing the system

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}$$

Derived from classical Hamilton's function

Example - harmonic oscillator

$$\text{Molecular Hamiltonian} \quad \hat{H} = \hat{T}_J + \hat{T}_e + \hat{V}_{JJ} + \hat{V}_{Je} + \hat{V}_{ee}$$

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=1}^n \frac{\Delta_i}{m_i}$$

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^n \sum_{j=1}^n \frac{z_i z_j}{|r_i - r_j|}$$

Example - water molecule Hamiltonian

Stationary Schrödinger eq. - easy to set up, problem to solve

One-electron atoms:

- exact (analytical) solution
- hydrogen-like atoms --> atomic orbitals



Manyelectron systems:

- Problematic components: depends on the coordinates of more than one particle
- We cannot separate variables and solve the equation

Quest for approximative solution: finding approximations which can be controlled

1. Born-Oppenheimer approximation
2. Model of independent electrons
3. MO LCAO

Born-Oppenheimer approximation

Positions of nuclei are fixed $E_{kin}^J = 0$

$$\hat{H} = \cancel{\hat{T}_J} + \hat{T}_e + \hat{V}_{JJ} + \hat{V}_{Je} + \hat{V}_{ee}$$

$= 0$ $= \text{konst.}$

$$\hat{H} = \hat{T}_e + \hat{V}_{Je} + \hat{V}_{ee} + \text{konst.}$$

One-electron part Two-electron part

Electrons move in the potential of nuclei at fixed positions R:

$$\hat{H} \Psi_i(r, R) = E_i(R) \Psi_i(r, R)$$

POTENTIAL ENERGY SURFACE (PES)

Complete separation of nuclear and electronic motion
Dynamics of atomic nuclei is investigated on PES - quantum or classical dynamics

Water molecule Hamiltonian

Kinetic energy of nuclei

Kinetic energy of electrons

Coulombic attraction nuclei-electron

$$\hat{H} = -\cancel{\frac{\hbar^2}{2}} \sum_{I=1}^3 \frac{\Delta_I}{m_I} - \frac{\hbar^2}{2m_e} \sum_{i=1}^{10} \Delta_i - \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{i=1}^{10} \frac{Z_I}{|R_I - r_i|} +$$

$$\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{1}{|r_i - r_j|} + \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{J>I}^3 \frac{\cancel{Z_I Z_J}}{|R_I - R_J|}$$

Coulombic repulsion electron-electron

Coulombic repulsion nucleus-nucleus

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{10} \Delta_i - \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{i=1}^{10} \frac{Z_I}{|R_I - r_i|} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{1}{|r_i - r_j|} + konst.$$

PROBLEM !!

Model of independent electrons

Hamiltonian can be expressed as a sum of one- and two-electronic contributions:

$$\hat{H} = \sum_i \hat{h}_i(1) + \sum_i \sum_{j>i} \hat{v}_{ij}(1,2)$$



$T_i + V_{ij}$

V_{ee}



Hinders the separation of variables

$$\sum_{i=1}^n \sum_{j>i}^n \hat{v}_{ij}(1,2) \approx \sum_{i=1}^n \hat{V}_i(1)$$



Effective potential - electron moves in an averaged field of all other electrons of the system

$$\hat{H} \approx \sum_{i=1}^n [\hat{h}(i) + \hat{V}(i)] = \sum_{i=1}^n \hat{H}'(i)$$



Each member of this Hamiltonian operates only on a single electron



Separation of variables: Overall wave-function can be expressed as product of one-electron functions

$$\sum_{i=1}^n \hat{H}(i) \Psi(1,2,\dots,n) = E \Psi(1,2,\dots,n)$$


$$\Psi(1,2,\dots,n) = \prod_{i=1}^n \varphi_i(i)$$

Original Schrödinger eq. is splitted to **n** one-electron equations

It is not enough to take just a product function.

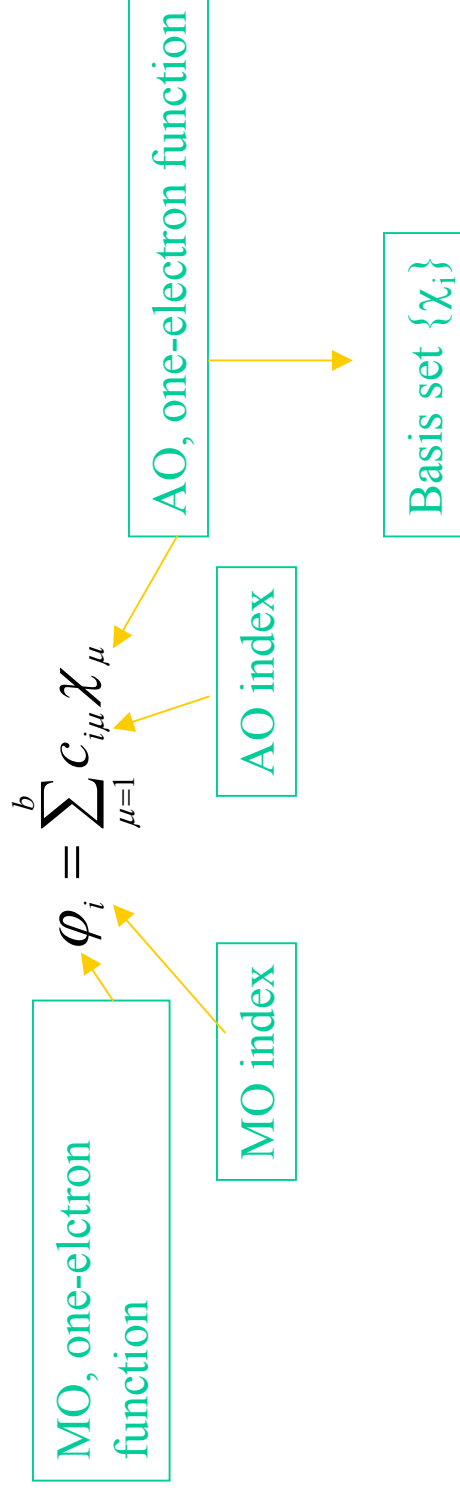
To satisfy the antisymmetrization postulate we express a wave function in the form of SLATER DETERMINANT

$$\Psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \det(\varphi_i) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_2(n) & \dots & \varphi_n(n) \end{vmatrix}$$

Overall wave function describing the system is in the form of the product of one electron functions φ_i (MO)

One-electron functions φ_i -
- MOLECULAR ORBITALS - in the form of linear combination of atomic orbitals

MO LCAO



- we get just n MO when we use n AO
- increasing the basis set size - convergence control
- energy is minimized as a function of $c_{i\mu}$

Variation theorem

$$W = \langle \Phi | \hat{H} | \Phi \rangle \geq E_0$$

Přesná energie

↑ Trial function

Trial function gives energy that is always higher than true energy

Linear variation function

$$\Phi = \sum_k c_k f_k$$

$$\frac{\partial W}{\partial c_i} = 0$$

The best function (giving the lowest energy) must satisfy:

\Rightarrow it leads to secular equations :

$$\sum_{k=1}^b [H_{ik} - WS_{ik}] c_k = 0$$

$$H_{ik} = \langle f_i | \hat{H} | f_k \rangle \quad S_{ik} = \langle f_i | f_k \rangle$$

System of N linear homogeneous equations - non-trivial solution only for $\det=0$

Hartree-Fock method

$$\hat{H} = \sum_i \hat{h}_i(1) + \sum_{i,j>i} \hat{v}_{ij}(1,2)$$

$$\Psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \det(\varphi_i) = \frac{1}{\sqrt{n!}}$$

$\varphi_1(1)$	$\varphi_2(1)$...	$\varphi_n(1)$
$\varphi_1(2)$	$\varphi_2(2)$...	$\varphi_n(2)$
...
$\varphi_1(n)$	$\varphi_2(n)$...	$\varphi_n(n)$

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$\delta E[\Psi] = 0$$

HF methods offers technical solution of the problem:

- one electron equations are solved one by one
- electrons move in the averaged field of all other electrons

Closed-shell system:

$$\{\Phi_B\} \rightarrow \{\varphi_{B/2}^\alpha, \varphi_{B/2}^\beta\}$$

$$\Phi_{2i} \equiv \varphi_i^\beta = \varphi_i \cdot \beta$$

$$\Phi_{2i-1} \equiv \varphi_i^\alpha = \varphi_i \cdot \alpha$$

Spin-orbital $\sim x, y, z, s$

Orbital $\sim x, y, z$

Spin-function $\sim s$

Two-electron system:

$$\sigma(s) = \alpha \text{ oder } \beta$$

$$\langle \alpha | \alpha \rangle = \int \alpha \alpha ds = \langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = \int \alpha \beta ds = \langle \beta | \alpha \rangle = 0$$

$$\begin{aligned} \Psi(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) \\ \varphi_1(2) & \varphi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) \end{vmatrix} = \\ &= \frac{1}{\sqrt{2}} [\varphi_1(1)\alpha(1) \cdot \varphi_1(2)\beta(2) - \varphi_1(1)\beta(1) \cdot \varphi_1(2)\alpha(2)] \end{aligned}$$

$$\begin{aligned} \langle \psi(1,2) | \hat{v}_{12} | \psi(1,2) \rangle &= \langle [\varphi_1(1)\alpha(1) \cdot \varphi_1(2)\beta(2) - \varphi_1(1)\beta(1) \cdot \varphi_1(2)\alpha(2)] | \frac{1}{r_{12}} | [\varphi_1(1)\alpha(1) \cdot \varphi_1(2)\beta(2) - \varphi_1(1)\beta(1) \cdot \varphi_1(2)\alpha(2)] \rangle = \\ &= \frac{1}{2} \{ \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_1(2) \rangle \langle \alpha(1) | \alpha(1) \rangle \langle \beta(2) | \beta(2) \rangle - \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_1(2) \rangle \langle \alpha(1) | \beta(1) \rangle \langle \alpha(2) | \beta(2) \rangle - \\ &\langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_1(2) \rangle \langle \beta(1) | \alpha(1) \rangle \langle \beta(2) | \alpha(2) \rangle + \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_1(2) \rangle \langle \alpha(1) | \alpha(1) \rangle \langle \beta(2) | \beta(2) \rangle \} = J_{11} \end{aligned}$$

OPEN SHELL

CLOSED SHELL

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^n h_{ii} + \frac{1}{2} \sum_{i,j}^n (J_{ij} - K_{ij})$$



$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = 2 \sum_{i=1}^{n/2} h_{ii} + \sum_{i,j}^{n/2} (2J_{ij} - K_{ij})$$

$$E \neq 2 \sum_i^{n/2} \epsilon_i$$

Example: atom Li

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^n h_{ii} + \frac{1}{2} \sum_i^n \sum_j^n (J_{ij} - K_{ij})$$

One-electron integral $h_{ii} = \langle \varphi_i(1) | \hat{h}_1 | \varphi_i(1) \rangle$

Coulombic integral $J_{ij} = \langle \varphi_i(1)\varphi_j(2) | \hat{v}_{ij}(1,2) | \varphi_i(1)\varphi_j(2) \rangle$

Exchange integral $K_{ij} = \langle \varphi_i(1)\varphi_j(2) | \hat{v}_{ij}(1,2) | \varphi_j(1)\varphi_i(2) \rangle$

$\delta E[\Psi]=0 \Rightarrow$ **Fock's equations**

$$\hat{F} \varphi_i' = \varepsilon_i \varphi_i'$$

$$\hat{F}(1) = \hat{h}(1) + \sum_{j=1}^n \langle \varphi_j(2) | \hat{v}'(1,2) | \varphi_j(2) \rangle$$

Fock's equations are solved iteratively - SCF procedure

$$\hat{H}\Psi = E\Psi$$

Configuration Interaction (CI)
Coupled Clusters (CC)
Perturbation Theory (PT, MP)

Electron
correlation

Born-Oppenheimer approximation
Model of independent electrons
Product wave function
(Slater determinant)
MO LCAO

Hartre-Fock method (HF)

Additional approximation

Semiempirical methods
(NDO, AM1, PM3)

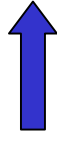
Non-interacting electrons

Extended Hückel Theory
Hückel MO

Hartree-Fock-Roothaan

MO LCAO

$$\varphi_i = \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



FOCK EQUATIONS

$$\hat{\mathbf{F}}(i) \sum_{\mu=1}^L c_{\mu i} \chi_{\mu} = \varepsilon_i \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



$$\sum_{\mu=1}^L \langle \chi_{\nu} | \hat{\mathbf{f}}(i) | \chi_{\mu} \rangle c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L \langle \chi_{\nu} | \chi_{\mu} \rangle c_{\mu i}$$

SECULAR EQUATIONS

$$\sum_{\mu=1}^L F_{\mu\nu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L S_{\mu\nu} c_{\mu i} \Rightarrow \sum_{\mu=1}^L c_{\mu i} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0$$

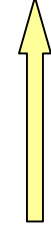
$$F_{\mu\nu} = \langle \chi_{\mu} | \hat{\mathbf{f}}(i) | \chi_{\nu} \rangle = h_{\mu\nu}^{core} + \sum_{\kappa=1}^B \sum_{\lambda=1}^B P_{\kappa\lambda} \left[(\mu\nu | \kappa\lambda) - \frac{1}{2} (\mu\lambda | \kappa\nu) \right]$$

SCF procedure:

- 1) Starting MO \sim set of $c_{\mu i}$
- 2) Calculate integrals $(\mu\nu|\kappa\lambda)$, $S_{\mu\nu}$, $h_{\mu\nu}$
- 3) Constructing $P_{\kappa\lambda}$
- 4) Constructing $F_{\mu\nu}$
- 5) Solving Fock equations \Rightarrow new set of $c_{\mu i}$
- 6) Check the convergence

[back to 3]

$$P_{\kappa\lambda} = 2 \sum_{j=1}^{n/2} c_{\kappa j}^* c_{\lambda j}$$



Let computer to do it !

BASIS SET

1. Hydrogen atom orbitals:

$$\phi = Nr^l e^{-Zr/na_0} \sum_{j=0}^{n-l-1} b_j r^j Y_{l,m}(\vartheta, \varphi)$$

2. Slater-type orbitals:

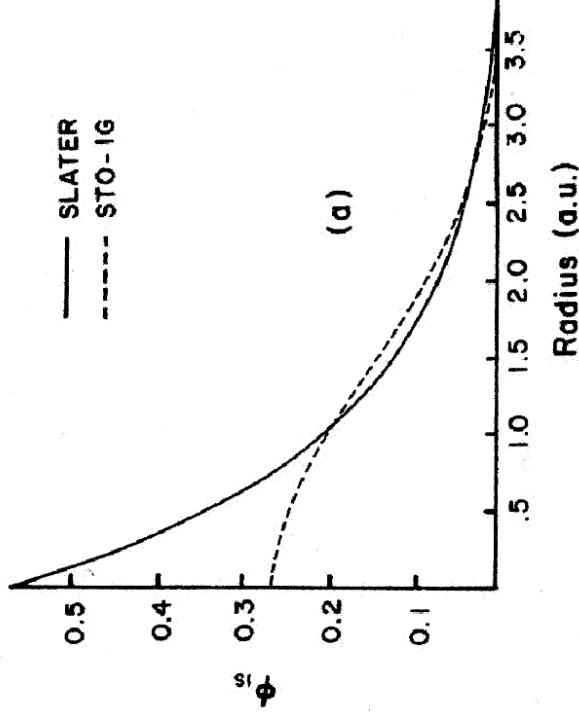
$$\phi_{STO} = \frac{[2\zeta/a_0]^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_{l,m}(\vartheta, \varphi)$$

3. Gaussian orbitals:

$$\phi_{GTO} = Nx^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2}$$

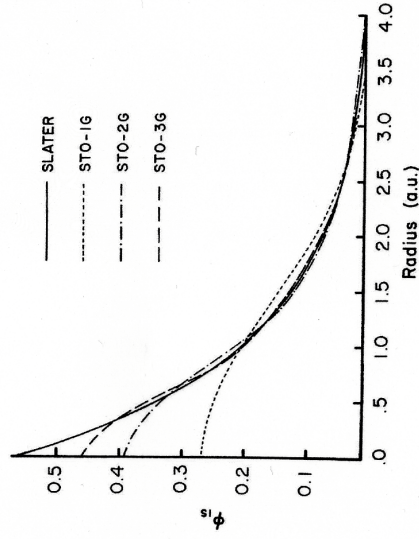
- $l_x = l_y = l_z = 0 \dots$ s
- $l_x + l_y + l_z = 1 \dots$ p
- $l_x + l_y + l_z = 2 \dots$ d (! 6 d-components)

[Boys (Proc. R. Soc. A, 200 (1950) 542)]



Significant differences between GTO and STO description of electrons close to the nucleus

Contracted GTO orbitals:



$$\begin{aligned} \phi_{STO}^{1s} (\zeta = 1.24) &\simeq 0.44\phi_{GTO}^{1s} (\alpha = 0.17) \\ &+ 0.54\phi_{GTO}^{1s} (\alpha = 0.62) \\ &+ 0.15\phi_{GTO}^{1s} (\alpha = 3.43) \end{aligned}$$

Example: STO-3G for C atom

```

S 3 1.00
0.7161683735D+02 0.1543289673D+00
0.1304509632D+02 0.5353281423D+00
0.3530512160D+01 0.4446345422D+00
SP 3 1.00
0.2941249355D+01 -0.9996722919D-01 0.1559162750D+00
0.6834830964D+00 0.3995128261D+00 0.6076837186D+00
0.222289159D+00 0.7001154689D+00 0.3919573931D+00

```

α exponent

Contr. coef.
for **s**

Contr. coef.
for **p**

Basis set classification:

- minimal basis set
- double- ζ bs
- valence double - ζ bs
- triple- ζ bs
- polarization function
- diffuse function

Basis Set	Applies to	Polarization Functions	Diffuse Functions
STO-3G	H-Xe	*	
3-21G	H-Xe	* <i>or</i> **	+
6-31G	H-Kr	(3df,3pd)	++
6-311G	H-Kr	(3df,3pd)	++
D95	H-Cl <i>except Na and Mg</i>	(3df,3pd)	++
D95V	H-Ne	(d) <i>or</i> (d,p)	++
LanL2MB	H-Ba, La-Bi		
LanL2DZ	H, Li-Ba, La-Bi		
SDD, SDDAll	<i>all but Fr and Ra</i>		
cc-pV(DTQ5)Z	H-He, B-Ne, Al-Ar, Ga-Kr	<i>included in definition</i>	<i>added via AUG- prefix</i>
cc-pV6Z	H, B-Ne	<i>included in definition</i>	<i>added via AUG- prefix</i>
SV and SVP	H-Kr	<i>included in definition</i>	
TZV and TZVP	H-Kr	<i>included in definition</i>	
EPR-II, EPR-III	H, B, C, N, O, F	<i>included in definition</i>	

Example: 6-31G(d) basis set for carbon atom:

```
Standard basis: 6-31G(d) (5D, 7F)
Basis set in the form of general basis input:
1 0
S   6 1.00
   0.3047524880D+04  0.1834737130D-02
   0.4573695180D+03  0.1403732280D-01
   0.1039486850D+03  0.6884262220D-01
   0.2921015530D+02  0.2321844430D+00
   0.9286662960D+01  0.4679413480D+00
   0.3163926960D+01  0.3623119850D+00
SP  3 1.00
   0.7868272350D+01 -0.1193324200D+00  0.6899906660D-01
   0.1881288540D+01 -0.1608541520D+00  0.3164239610D+00
   0.5442492580D+00  0.1143456440D+01  0.7443082910D+00
SP  1 1.00
   0.1687144782D+00  0.1000000000D+01  0.1000000000D+01
D   1 1.00
```

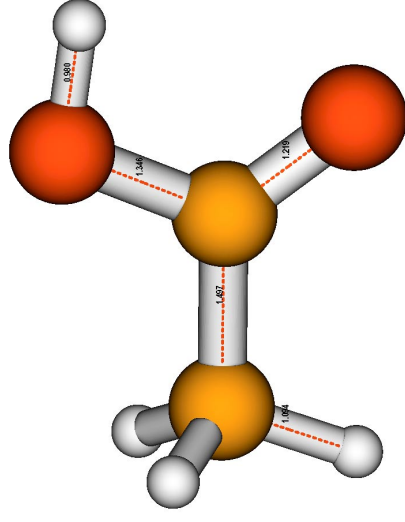
α exponent

Contr. coef.
for s

Contr. coef.
for p

CH₃COOH

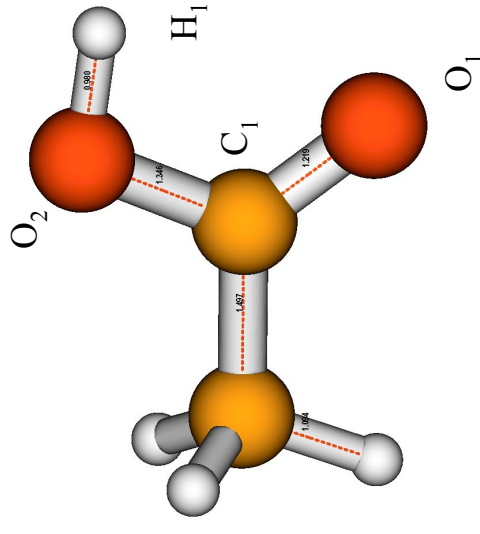
[Geometry: HF/6-31G(d)]



Basis set	No. of bf	E(HF) (a.u.)	E(homo) (a.u.)	Dipole Moment (Debey)	CPU (s)
sto-3g	24	-224.801626	-0.34416	0.8712	6
3-21G	44	-226.532063	-0.44189	1.5629	6
6-31G	44	-227.698149	-0.45659	1.7389	6
6-311G	64	-227.759343	-0.45900	1.7689	7
6-31G(d)	64	-227.809095	-0.44890	1.7908	8
6-31G(d,p)	76	-227.821273	-0.44824	1.8164	10
D95	48	-227.741903	-0.46203	1.8180	7
D95V	44	-227.741397	-0.46190	1.8184	7
LanI2DZ	44	-227.741398	-0.46207	1.8192	7
cc-pvdz	76	-227.834149	-0.44646	1.8149	12
cc-pvtz	176	-227.904686	-0.45319	1.9120	191
cc-pvqz	340	-227.922078	-0.45486	1.9486	2075

Exp = 1.74 D

CH₃COOH



Mulliken charge distribution

	STO-3G	3-21G	6-31G	6-311G	6-31G* 6-31G**	cc- pVDZ	cc- pVTZ	cc- pVQZ	
C ₁	0.343	0.830	0.688	0.667	0.771	0.752	0.290	0.397	0.572
O ₁	-0.287	-0.601	-0.528	-0.487	-0.561	-0.564	-0.358	-0.385	-0.464
O ₂	-0.321	-0.709	-0.693	-0.661	-0.731	-0.615	-0.282	-0.325	-0.411
H ₁	0.225	0.408	0.431	0.422	0.476	0.363	0.174	0.241	0.262
C	-0.214	-0.680	-0.513	-0.582	-0.587	-0.412	-0.017	-0.278	-0.272
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.085	0.249	0.204	0.214	0.215	0.162	0.062	0.125	0.124

HF description of H₂ - restricted HF

$$E(\text{H}_2) = 2h_{11} + J_{11}$$

$$E(\text{H}) = h_1$$

HF/STO-3G

$$R(e) = \underline{0.7122 \text{ \AA}}$$

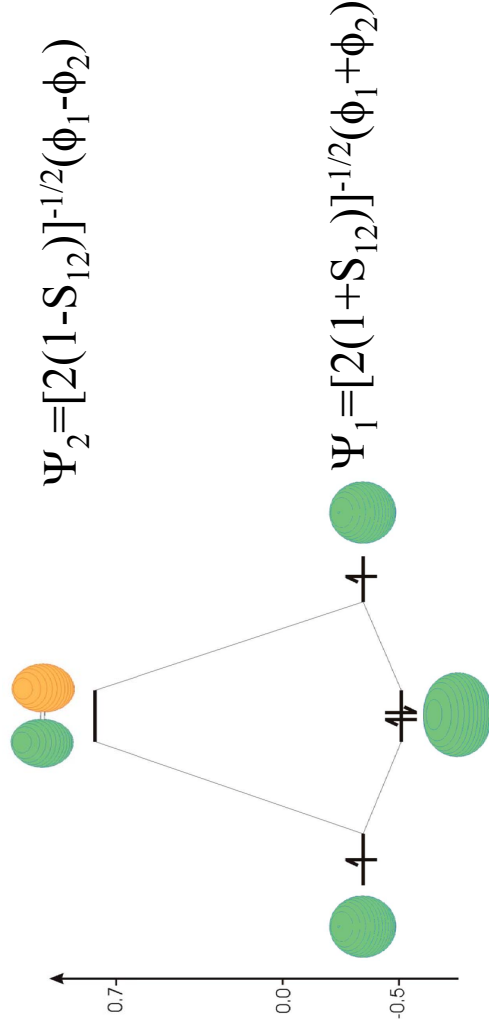
$$E(\text{H}_2) = -1.1175059 \text{ a.u.}$$

$$E(\text{H}) = -0.4665819 \text{ a.u.}$$

$$D_e = 0.1843431 \text{ a.u.} = 115.7 \text{ kcal/mol}$$

$$\text{ZPVE} = 7.8 \text{ kcal/mol}$$

$$D_0 = \underline{107.9 \text{ kcal/mol}}$$



Experiment

$$r_e = 0.7417 \text{ \AA}; D_0 = 104 \text{ kcal/mol}; v = 4395 \text{ cm}^{-1}$$

STO-3G Basis: $\rightarrow [1s]$

Exponent	Coefficient
0.3425250914D+01	0.1543289673D+00
0.6239137298D+00	0.5353281423D+00
0.1688554040D+00	0.4446345422D+00

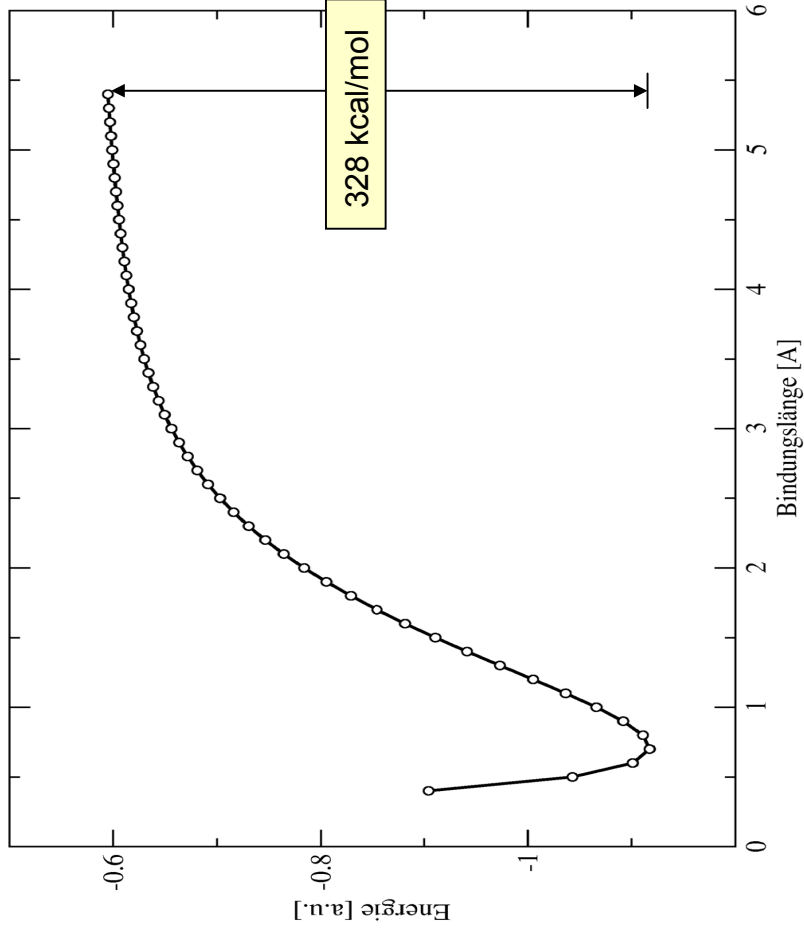
Alpha occ. eigenvalues -- -0.59022
Alpha virt. eigenvalues -- 0.70065

Molecular Orbital Coefficients

	1	2
(SGG)--O (SGU)--V		
EIGENVALUES --	-0.59022	0.70065
1 1 H 1S	0.54586	1.24624
2 2 H 1S	0.54586	-1.24624

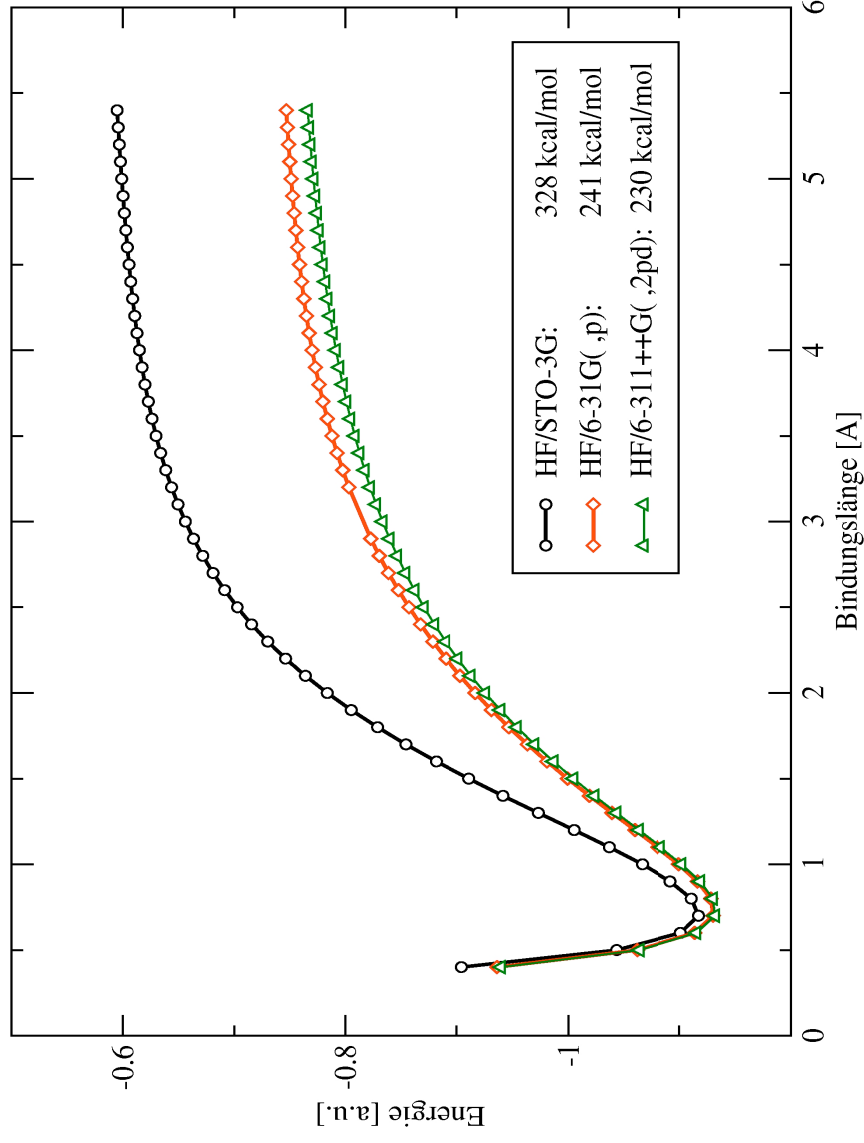
HF description of H_2 - restricted HF

$$E(H...H, R) = 2h_{11} + J_{11}$$



HF description of H_2 - restricted HF

Increasing the basis set size:



Problem: two electrons are forced to be in the same MO $\Rightarrow J_{11} \neq 0$!

HF description of H_2 - unrestricted HF

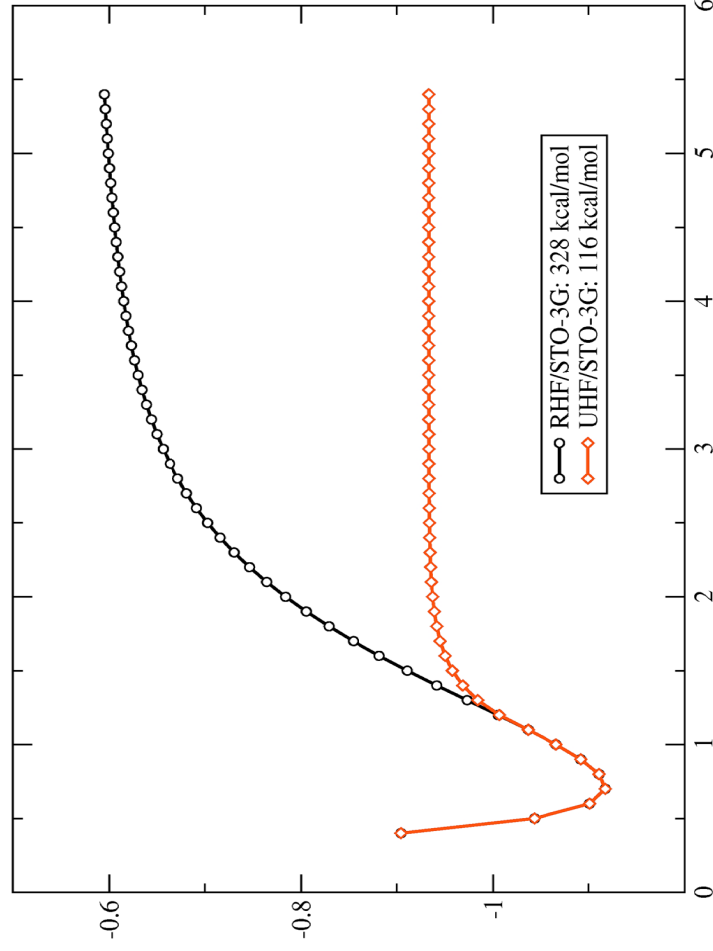
Two solutions may exist for UHF on “closed shell system”:

Only one solution around the equilibrium geometry (RHF \sim UHF)

Two solutions for larger R_{H-H} : mixing of Ψ_1 and Ψ_2 molecular orbitals:

$$\Psi_1' = (\cos\theta) \Psi_1 + (\sin\theta) \Psi_2$$

$$\Psi_1'' = (\cos\theta) \Psi_1 - (\sin\theta) \Psi_2$$



$$\Psi_2 = [2(1-S_{12})]^{-1/2}(\phi_1 - \phi_2)$$

$$\Psi_1 = [2(1+S_{12})]^{-1/2}(\phi_1 + \phi_2)$$

for $\theta=45^\circ$

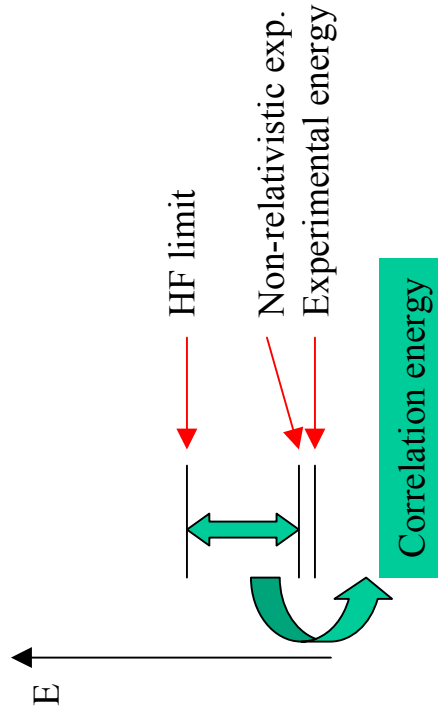
$$\Psi_1' \equiv \phi_1$$

$$\Psi_1'' \equiv \phi_2$$

$$(S_{12})=0$$

**Problem: not a proper spin state
(mixing in a triplet state).**

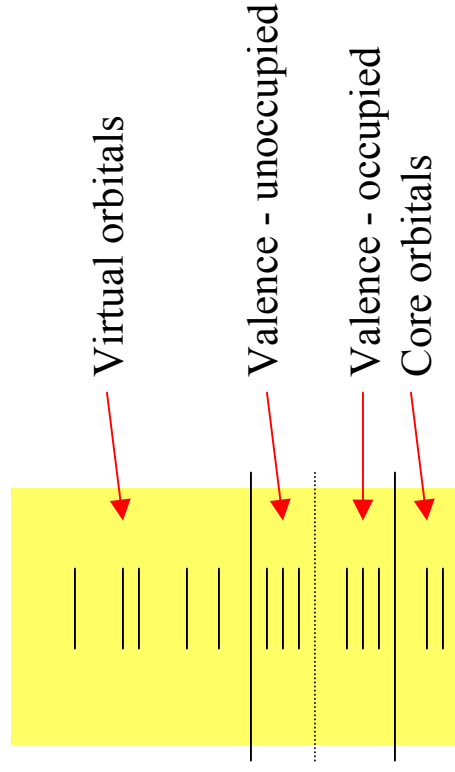
Correlation energy



Importance of electron correlation strongly depend on the nature of studied system/process. It may partially cancel out.

Electron correlation raises from the close proximity of electrons.

To include electron correlation electrons must have a chance to escape away from other electrons. Instead of using single Slater determinant we use combination of more Slater determinants in the wavefunction of the system.



Mono-, di-, tri-, ... excited determinant from “reference” Slater determinant

Example: CH₂, linear CH₂

Dynamic vs. static correlation energy

=> single Slater determinant is replaced by linear combination of many determinants

$$\Phi = \sum_I C_I \Psi_I$$

Various methods differ in the specification of Slater determinants in linear expansion and in the criteria used in search for optimal coefficients C_I

If all Slater determinant that can be created with the given basis set are considered
full CI (configuration interaction)

Number of SD in given basis set:

$$B=100, n=50 \quad N_{\text{full}}^{\text{SD}} \sim 10^{45}$$

$$N_{\text{full}}^{\text{SD}} \sim \frac{B!(B+1)!}{(n/2)!(n/2+1)!(b-n/2)!(b-n/2+1)!}$$

Brillouin's theorem: $\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = 0$

Slater-Condon's rules: *majority of integrals formed by different Slater determinant vanishes*

Monoexcited determinants:

$$\Psi^S = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} c_i^a \Psi_i^a$$

Biexcited determinants:

$$\Psi^D = \sum_i^{\text{occ}} \sum_{\substack{a \\ j \neq i}}^{\text{unocc}} c_{ij}^{ab} \Psi_{ij}^{ab}$$

Tri- and tetra-excitation

$$\Psi_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_1(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_1(n) & \dots & \varphi_n(n) \end{vmatrix} \quad \longrightarrow \quad \Psi_i^a = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_a(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_a(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_a(n) & \dots & \varphi_n(n) \end{vmatrix}$$

Configuration interaction (CI)

Wavefunction in the form:

$$\Phi^{CI} = c_0 \Psi_0 + \Psi^S + \Psi^D + \Psi^T + \Psi^Q + \dots$$

Variation theorem applied

Search only for C coefficients of CI expansion

MO are kept fixed (coefficients c does not change)

Not size consistent !

Various implementations (CID, CISD, CISDTQ,..)

Davidson correction for size consistency: $(1-c_0)^2 \cdot E_{\text{correl}}$

Applications

Modern variant of CI method: AQCC, ACPF

CISD - 2e1 ~ 100% E(corr)
 - 100e1 ~ 60% E(corr)

Example: He...He

Coupled Clusters (CC)

$$|\Psi\rangle = e^{\hat{T}} |\Psi_{HF}\rangle \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots \hat{T}_N \quad e^{\hat{T}} = 1 + \hat{T} + (2!)^{-1}\hat{T}^2 + (3!)^{-1}\hat{T}^3 + \dots = \sum_k \frac{\hat{T}^k}{k!}$$

Wave function

Taylor expansion

$$|\Psi\rangle = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots) |\Psi_{HF}\rangle$$

Eg., double excitation

$$\hat{T}_2 \Psi = \sum_i \sum_{j < i} \sum_a \sum_{b < a} t_{ij}^{ab} \Psi_{ij}^{ab} \quad \hat{T}_2^2 \Psi = \hat{T}_2 \left(\sum_i \sum_{j < i} \sum_a \sum_{b < a} t_{ij}^{ab} \Psi_{ij}^{ab} \right)$$

$$= \sum_i \sum_{j < i} \sum_k \sum_{l < k} \sum_a \sum_{b < a} \sum_c \sum_{d < c} t_{ij}^{ab} t_{kl}^{cd} \Psi_{ijkl}^{abcd}$$

CID $\Phi^{CID} = (1 + \hat{T}_2) \Psi_{HF}$

CCD $\Phi^{CCD} = (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2) \Psi_{HF}$

Makes it size-consistent !

CCSD
CCSD(T), CCSDT

- quite precise
- size consistent
- best routine method for description of dynamic el. correlation

QCISD(T) - neglects some of T_1T_2 cross-terms - only small computer saving,
lost of accuracy

PERTURBATION THEORY

Rayleigh-Schrödinger formulation (non-degenerate systems)

System of interest:

$$\hat{H}\Psi_n = E_n \Psi_n$$

“Reference” (known) system:

$$\hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

Perturbation (small !):

$$\hat{V} \equiv \hat{H}' = \hat{H} - \hat{H}_0$$

Introducing an ordering parameter λ and expand eigenfunctions and eigenvalues in Taylor series:

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

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots$$

$$\Psi_n^{(k)} = \frac{1}{k!} \frac{\partial^k \Psi_n}{\partial \lambda^k} \Big|_{\lambda=0}$$

$$E_n^{(k)} = \frac{1}{k!} \frac{\partial^k E_n}{\partial \lambda^k} \Big|_{\lambda=0}$$

Using “intermediate normalization” + additional manipulation:

$$\begin{aligned} & \hat{H}_0 \Psi_n^{(0)} + \lambda (\hat{H}' \Psi_n^{(0)} + \hat{H}_0 \Psi_n^{(1)}) + \lambda^2 (\hat{H}' \Psi_n^{(1)} + \hat{H}_0 \Psi_n^{(2)}) + \dots = \\ & = E_n^{(0)} \Psi_n^{(0)} + \lambda (E_n^{(1)} \Psi_n^{(0)} + E_n^{(0)} \Psi_n^{(1)}) + \lambda^2 (E_n^{(2)} \Psi_n^{(0)} + E_n^{(1)} \Psi_n^{(1)} + E_n^{(0)} \Psi_n^{(2)}) + \dots \end{aligned}$$

Results cannot depend on λ \longrightarrow independent equations for each λ^k

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$$

$$E_n^{(1)} = \langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle$$

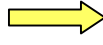
$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \dots$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)}$$

PT for electron correlation - Moller-Plesset formulation

Perturbation $\hat{H}' = \sum_{i < j} r_{ij}^{-1} - \sum_i v^{HF}(i)$



$$E^{MP2} = \underbrace{E^{(0)} + E^{(1)}}_{=E^{HF}} + E^{(2)} = E^{HF} + \sum_a^{occ} \sum_b^{virt} \sum_r \sum_s \frac{|\langle ab | rs \rangle - \langle ab | sr \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Size-consistent, nonvariational
 MP2, MP3, MP4
 MP2 - cheapest post-HF method for electron correlation
 Most popular method

Can be close to 0!

He atom - various approaches

$$\hat{H}^{He} = -\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$e' = \frac{e}{\sqrt{4\pi\epsilon_0}}$$

$$\hat{H}^{He} = \underbrace{-\frac{\hbar^2}{2m_e}\Delta_1 - \frac{Ze^{\prime 2}}{r_1}}_{\hat{h}_1} + \underbrace{-\frac{\hbar^2}{2m_e}\Delta_2 - \frac{Ze^{\prime 2}}{r_2}}_{\hat{h}_2} + \underbrace{\frac{e^{\prime 2}}{r_{12}}}_{\hat{v}_{12}}$$

Exact value: $E^{He^+} + IP(He) = 2.000 + 0,90357 = 2.90357$ a. u.

Exact energy of He^+ :

$$E_{He^+} = -\frac{Z^2}{n^2} \cdot 0.5 a.u.$$

Experiment

1 a.u. = 27.2114 eV = 627.51 kcal/mol

1. Electron repulsion completely neglected

$$\begin{aligned} \Rightarrow \hat{H} &= \hat{h}_1 + \hat{h}_2 \\ \Rightarrow \Psi(1,2) &= \frac{1}{\sqrt{2}} |\psi_1(1)\psi_2(2)| \\ \Rightarrow E &= \varepsilon_1 + \varepsilon_2 \end{aligned}$$

$$E^{\text{He}} = -4.000 \text{ a.u.}$$

$$\text{Error: } +1,09643 \text{ a. u.}$$

$$\begin{aligned} \hat{h}_1 \psi_1(1) &= \left(-\frac{\hbar^2}{2m_e} \Delta_1 - \frac{Ze^2}{r_1} \right) \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr_1/a_0) = \\ &= -\frac{1}{2} Z^2 = -2(a.u.) \end{aligned}$$

2. Electron repulsion treated as perturbation

$$\hat{H}^{\text{He}} = \left[-\frac{\hbar^2}{2m_e} \Delta_1 - \frac{Ze^2}{r_1} - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Ze^2}{r_2} \right] + \left[\frac{e^2}{r_{12}} \right] \hat{H}'$$

$$\begin{aligned} E_n^{(1)} &= \langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle = \frac{Z^6 e^2}{a_0^6 \pi^2} \int_0^\infty \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} r_1^2 r_2^2 \frac{1}{r_{12}} \sin\theta_1 \sin\theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2 = \\ &= \frac{5Ze^2}{8a_0} = \frac{5}{4} a.u. = 1.250 a.u. \end{aligned}$$

$$E^{\text{He}} \sim E^{(0)} + E^{(1)} = -2.750 \text{ a.u.}$$

$$\text{Error: } -0.15357 \text{ a. u.}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = 0.15802 a.u.$$

$$E^{\text{He}} \sim E^{(0)} + E^{(1)} + E^{(2)} = -2.908 \text{ a.u.}$$

$$\text{Error: } +0.00445 \text{ a. u.}$$

Note: convergence of PT with H' with H' ~ electron repulsion is not nearly as good in general.

3. Variation improvement of the wave function

$$\psi_1(1) = \frac{1}{\sqrt{\pi}} \left(\frac{\xi}{a_0} \right)^{3/2} \exp\left(-\frac{\xi}{a_0} r_1 / a_0\right) \quad \Rightarrow E = -\left(Z - \frac{5}{16}\right)^2 \frac{e^2}{a_0}$$

$$E^{\text{He}} \sim -2.848 \text{ a.u.}$$

$$\text{Error: } -0.05591 \text{ a. u.}$$

4. Hartree-Fock description

He atom

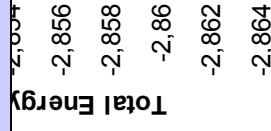
Hartree-Fock description

BASIS SET	No. of bf	No. of prim. G	HF Energy	Orbital En.
sto-3g	1	3	-2.807783	-0.87604
3-21G	2	3	-2.835679	-0.90357
6-31G	2	4	-2.855160	-0.91413
6-311G	3	5	-2.859895	-0.91687
6-31G(d,p)	5	7	-2.855160	-0.91413
tzvp	6	8	-2.859895	-0.91687
cc-pvdz	5	7	-2.855160	-0.91415
cc-pvtz	14	18	-2.861153	-0.91763
cc-pvqz	30	38	-2.861514	-0.91785
cc-pv5z	55	73	-2.861624	-0.91792

NOTE:

- only s-functions play a role

HF limit



basis set size : cc-pVDZ - cc-pV5Z

5. Post-HF description

Method	6-311G	6-311G(d,p)
hf	-2.859895	-2.859895
mp2	-2.872802	-2.884577
mp3	-2.875503	-2.889403
mp4	-2.876169	-2.890341
CID	-2.876289	-2.890484
CISD	-2.876418	-2.890571
CCD	-2.876289	-2.890484
CCSD	-2.876418	-2.890571

Notes:

- CID/CCD and CISD/CCSD gives the same energies
- CID and CISD does not give the same energies

CPU dependence on the size of the system:

Basis set	# BF	E(HF)	full CI
cc-pvdz	5	-2.855160	-2.88759
cc-pvtz	14	-2.861153	-2.90023
cc-pvqz	30	-2.861514	-2.90241
cc-pv5z	55	-2.861624	-2.90315

Method	Formal	Actual
SCF	B^4	$B^{2.7}$
MP2	OB^4	O^2B^3
MP4, QCISD(T)	O^3V^4	O^3V^4
Full CI	$((O+V)!/O!V!)^2$	
B...	total number of basis functions	
O...	number of occupied orbitals	
V...	number of unoccupied orbitals	

Hartree-Fock-Roothaan method for He atom:

Basis set: 2 STO $\xi_1=1.45$ and $\xi_2=2.91$

$$\chi_1 = 2\xi_1^{3/2} e^{-\xi_1 r} Y_0^0 \quad \chi_2 = 2\xi_2^{3/2} e^{-\xi_2 r} Y_0^0$$

Overlap integrals:

$$S_{11} = \langle \chi_1 | \chi_1 \rangle = 1 \quad S_{22} = 1$$

$$S_{12} = S_{21} = \left\langle \chi_1 | \chi_2 \right\rangle = 4\xi_1^{3/2} \xi_2^{3/2} \int_0^\infty e^{-(\xi_1 + \xi_2)r} r^2 dr = \frac{8\xi_1^{3/2} \xi_2^{3/2}}{(\xi_1 + \xi_2)^3} = 0.8366$$

1-el. integrals:

$$H_{11}^{core} = \langle \chi_1 | \hat{H}^{core} | \chi_1 \rangle = -\frac{1}{2}\xi_1^2 + (\xi_1 - 2)\xi_1 = -1.8488$$

$$H_{22}^{core} = \frac{1}{2}\xi_2^2 - 2\xi_2 = -1.5860$$

$$H_{12}^{core} = -1.8826$$

2-el. integrals:

$$(11|11) = \frac{5}{8}\xi_1 = 0.9062$$

$$(22|22) = \frac{5}{8}\xi_2 = 1.8188$$

$$(11|22) = (22|11) = 1.1826$$

$$(12|12) = (21|12) = (12|21) = (21|21) = 0.9536$$

$$(11|12) = (11|21) = (12|11) = (21|11) = 0.9033$$

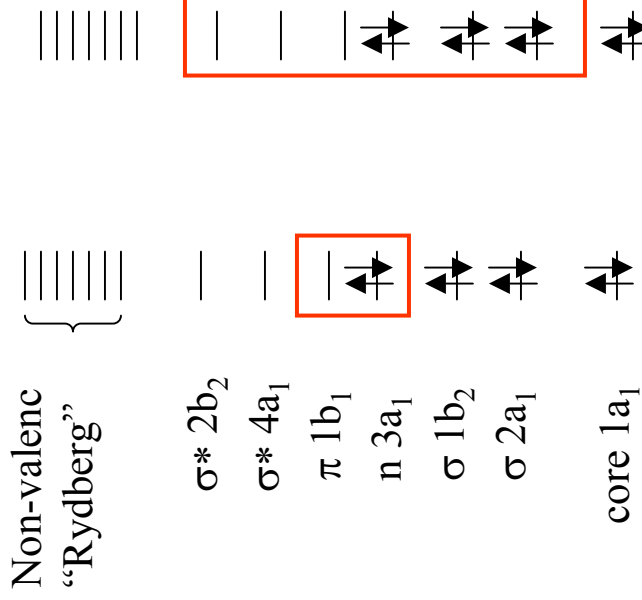
$$(12|22) = (22|12) = (21|22) = (22|21) = 1.2980$$

Multi-reference methods

1. MCSCF - “Multi-configurational self-consistent filed”

- define a set of electronic configurations of interest (Slater determinants) - active space
- define “weights” for electronic states
- find optimal linear combination for these determinants together with optimal MO coefficients both $c_{i\mu}$ and $C_{i\nu}$ varied complicated but it provides balanced description of states

Reference configuration specification: CH₂



Lowest triplet - no problem

Lowest singlet - ???

A) minimum: (2,2) space - 2 el. in 2 orbitals

Either 1A_1

Or 1B_1

B) all-valence: (6,6) - 6 el. in 6 orbitals

Singlet (and triplet) states of any symm.

C) arbitrary specification:

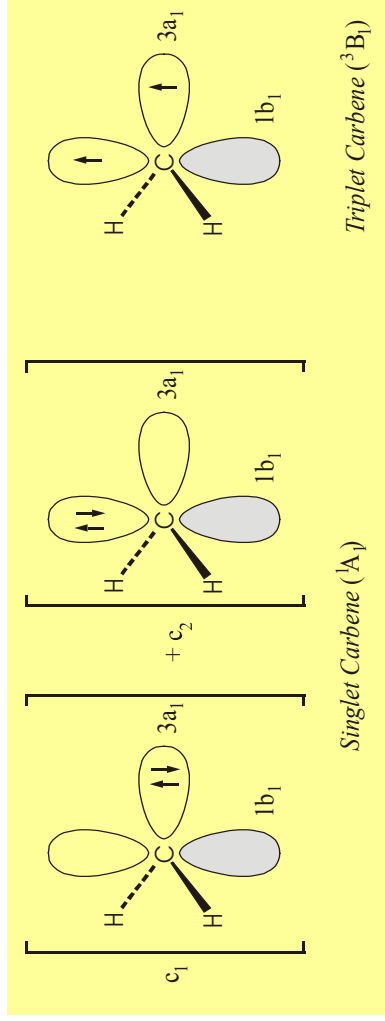
(n,n)

maximum allowed excitation

configuration list

Electron configuration - given by particular orbital occupation - corresponds to particular electronic state.
 The overall symmetry of electronic state is given by the direct product of partially occupied orbitals.
 Electron configurations of the same symmetry and spin can mix - mixing depends on energy difference.

Example: CH₂



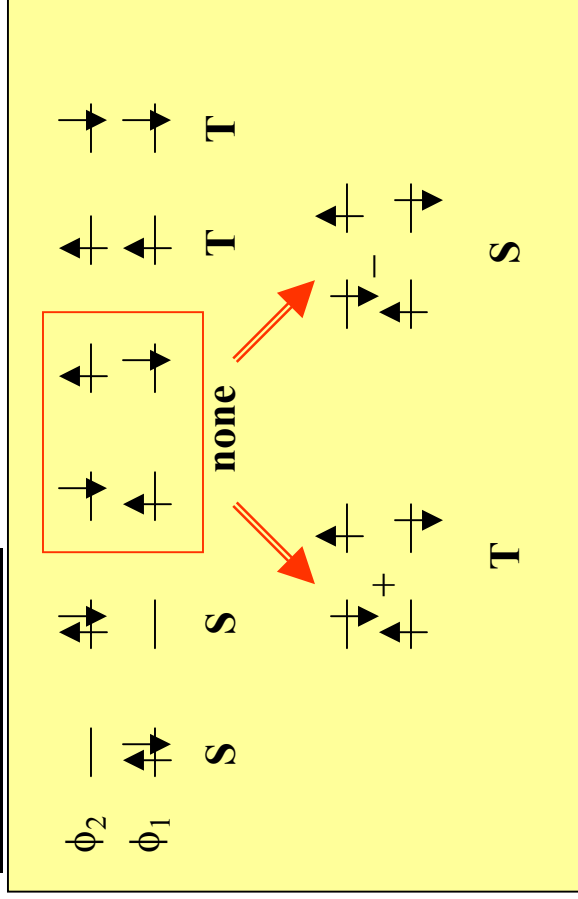
Orbital symmetries
 electron configurations
 Slater determinants

$\sigma^* 2b_2$	—	—	—	—
$\sigma^* 4a_1$	—	—	—	—
$\pi 1b_1$	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$n 3a_1$	$\uparrow\downarrow$	—	—	—
$\sigma 1b_2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\sigma 2a_1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
core $1a_1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

Character table for C_{2v} group of symmetry:

C _{2v}	E	C ₂	σ	σ'
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1

2 el. in 2 orbitals



=> three singlet states and one triplet state
(three-fold degenerate)

Relative energies of states:

- depends on orbital separation
 - triplet below singlet (exchange integral)
- Each electron configuration described with Slater determinant:

(notation: subscript - α el., superscript - β el.)

$$\Psi_1^1 = \det|\phi_1(1)\alpha(1)\phi_1(2)\beta(2)|$$

$$\Psi_2^2 = \det|\phi_2(1)\alpha(1)\phi_2(2)\beta(2)|$$

$$\Psi_1^2 = \det|\phi_1(1)\alpha(1)\phi_2(2)\beta(2)|$$

$$\Psi_2^1 = \det|\phi_1(1)\beta(1)\phi_2(2)\alpha(2)|$$

} “-” combination

Example ethylene, “twisted” ethylene: modeling the orbital separation

two orbitals have different symmetry - first two states can mix together but not with OSS

$$\Phi_{\text{cov}}^S = C_1\Psi_1^1 - C_2\Psi_2^2$$

$$\Phi_{\text{ion}}^S = C_1\Psi_1^1 + C_2\Psi_2^2$$

$$\Phi_{\text{oss}}^S = \frac{1}{\sqrt{2}}(\Psi_1^2 - \Psi_2^1)$$

$$\Phi_{M_s=1}^T = \Psi_{12}^T$$

For large orbital separation C_2 vanishes
in first eq. and C_1 vanishes in second eq.

In ethylene π orbitals are combinations
of “L” and “R” atomic orbitals.

$$\left. \begin{aligned} \phi_2 &\equiv \pi^* = \frac{1}{\sqrt{2}}(L-R) \\ \phi_1 &\equiv \pi = \frac{1}{\sqrt{2}}(L+R) \end{aligned} \right\}$$

Individual states can be characterized with respect to “covalent” and “ionic” configurations.

$$\begin{aligned}
\Phi_{\text{cov}}^S &= C_1 \Psi_1^1 - C_2 \Psi_2^2 = \frac{1}{\sqrt{2}} \left[C_1 |\pi\alpha\pi\beta| - C_2 |\pi^* \alpha \pi^* \beta| \right] \\
&= \frac{1}{2\sqrt{2}} \left[C_1 (|L\alpha L\beta| + |L\alpha R\beta| + |R\alpha L\beta| + |R\alpha R\beta|) - C_2 (|L\alpha L\beta| - |L\alpha R\beta| - |R\alpha L\beta| + |R\alpha R\beta|) \right] = \dots \text{deg} \dots \\
&= \frac{1}{\sqrt{2}} \left[|L\alpha R\beta| + |R\alpha L\beta| \right]
\end{aligned}$$

$$\Phi_{\text{ion}}^S = C_1 \Psi_1^1 + C_2 \Psi_2^2 = \dots = \frac{1}{\sqrt{2}} \left[|L\alpha L\beta| + |R\alpha R\beta| \right]$$

$$\begin{aligned}
\Phi_{\text{oss}}^S &= \frac{1}{\sqrt{2}} (\Psi_1^1 - \Psi_2^2) = \frac{1}{\sqrt{2}} \left[|\pi\alpha\pi^* \beta| - |\pi\beta\pi^* \alpha| \right] \\
&= \frac{1}{2\sqrt{2}} \left[|L\alpha L\beta| - |R\alpha R\beta| + |R\alpha L\beta| - |L\alpha R\beta| - |L\beta L\alpha| + |R\beta R\alpha| - |R\beta L\alpha| + |L\beta R\alpha| \right] = \dots \text{deg} \dots \\
&= \frac{1}{\sqrt{2}} \left[|L\alpha L\beta| - |R\beta R\alpha| \right]
\end{aligned}$$

$$\Phi_{M_S=1}^T = \Psi_{12} = |\pi\alpha\pi^* \alpha| = \frac{1}{2} \left[|L\alpha L\alpha| - |R\alpha R\alpha| + |R\alpha L\alpha| - |L\alpha R\alpha| \right] = |R\alpha L\alpha|$$

Electronic excitation

Contrary to calculations of ground state properties the description of electronic excitation is not routine.

Theoretical model for excited states:

- applicable to a system of interest (larger molecules)
- size-consistent
- variational
- unbiased description of all states of interest
- wavefunctions of electronic states must be orthogonal (complications for the states of the same symmetry and multiplicity)

Two types of methods currently available:

1. Emphasis on the description of electronic transition - **Random Phase Approximation (RPA)** non-variational cannot describe PES for excited state
2. Emphasis on the description of the wavefunction of an excited state
Multi-reference (MR) or multi-configurational (MC) methods.
(Some states can be described with single Slater determinant, e.g., lowest state of given multiplicity.)

Traditional post-HF methods - expansion of molecular wavefunction in terms of many Slater det.

Searching for expansion coefficients

Lowest energy state and a set of expansion coefficients \Rightarrow ground state

In principle, higher energy solution can be found \Rightarrow excited states

Problem: unbalanced description of states - “reference” wavefunction is a good approximation for the ground state but it is far from any excited states (\Rightarrow overestimation of excitation energies).
 \Rightarrow “Multi-reference” methods: the reference wave-function must equally approximate the states of interest