Chemical Materials Department

Accounting of electron correlation effects

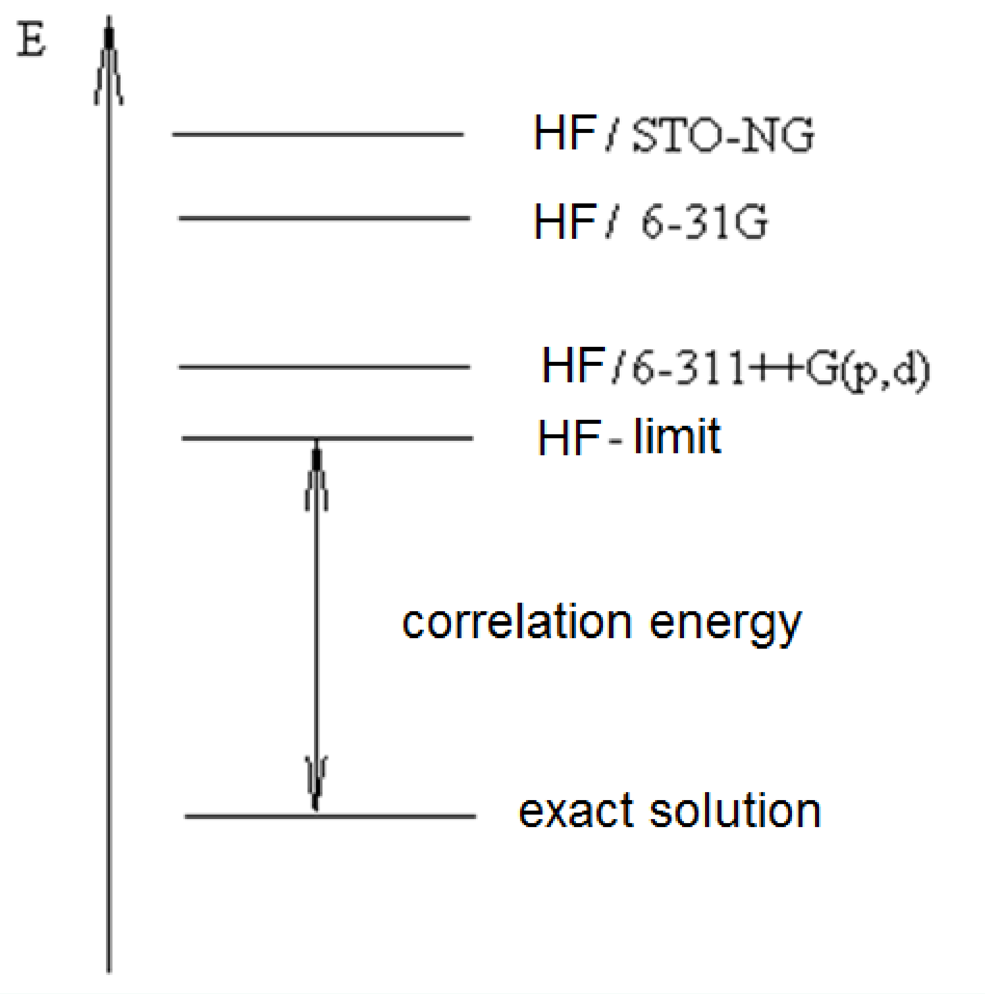
I. Many configurational Self Consistent Field Method

V. Ivanov

Gaussian, GAMESS, DALTON, COLUMBUS, SAPT

Kharkiv 2024

Correlation Energy



$$E_{corr} = E_{exact} - E_{HF}$$

Methods for accounting of electron correlations

1. Configuration Interaction methods:

CIS, CISD, CISDT, CISDTQ, …

2. Manyparticle perturbation theory:

MP2, MP3, MP4(SDQ), MP4, …

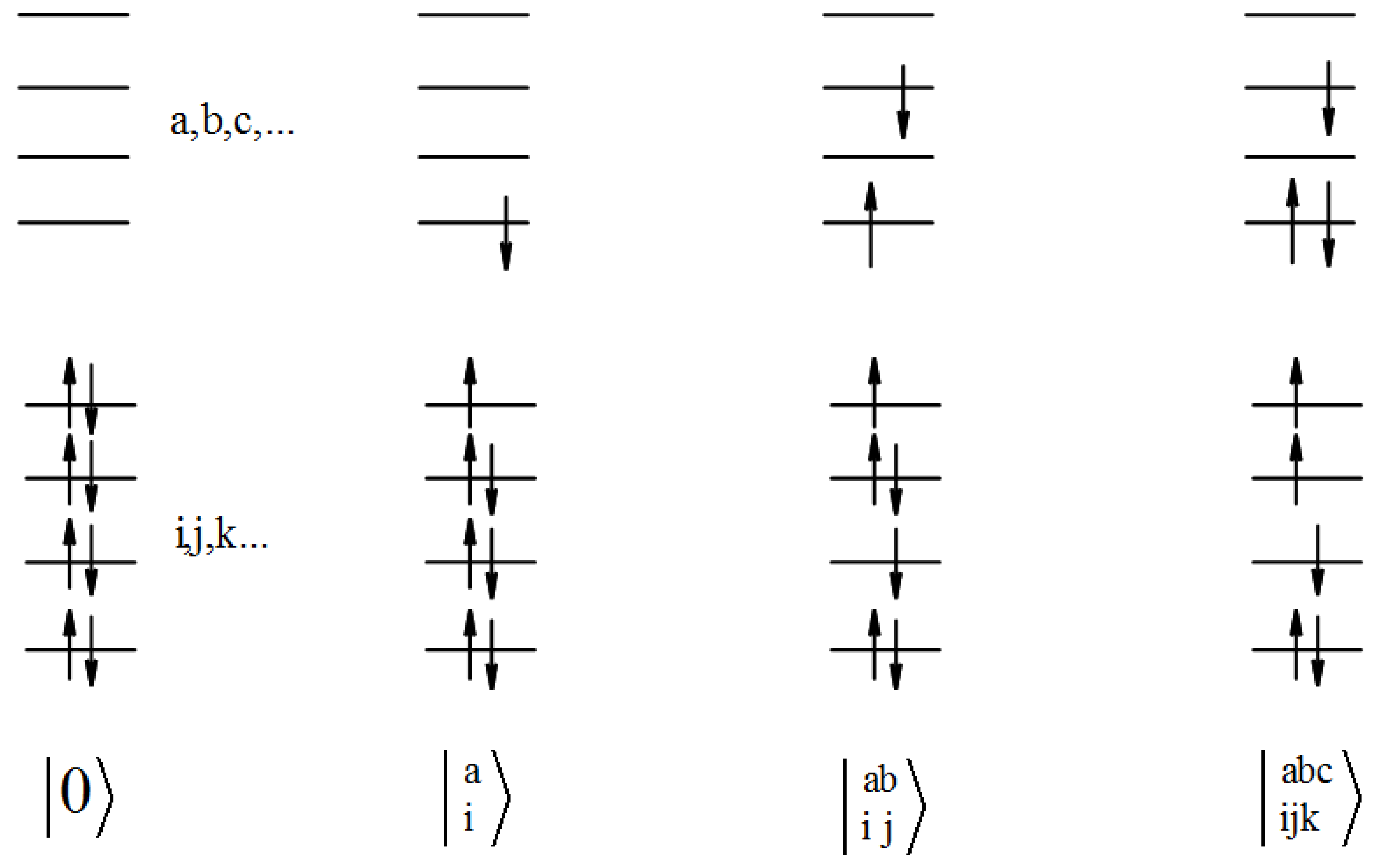
3. Coupled Cluster Theory:

CCD, CCSD, CCSD(T), ...

4. Density Functional Theory:

B3LYP, CAM-B3LYP, PBE, M062X, …

Configuration Interaction methods



Exact Wave Function (Full Configuration Interaction, FCI)

$$\left|\Psi_{FCI}\right\rangle = \left|0\right\rangle + \sum_{i,a} C_i^a \left|{}_i^a\right\rangle + \sum_{\substack{i>j\\a>b}} C_{ij}^{ab} \left|{}_{ij}^{ab}\right\rangle + \sum_{\substack{i>j>k\\a>b>c}} C_{ijk}^{abc} \left|{}_{ijk}^{abc}\right\rangle + \ldots$$

$$E_{FCI} = E_{FCI}\left(C_i^a, C_{ij}^{ab}, C_{ijk}^{abc}, C_{ijkl}^{abcd}, \ldots\right)$$

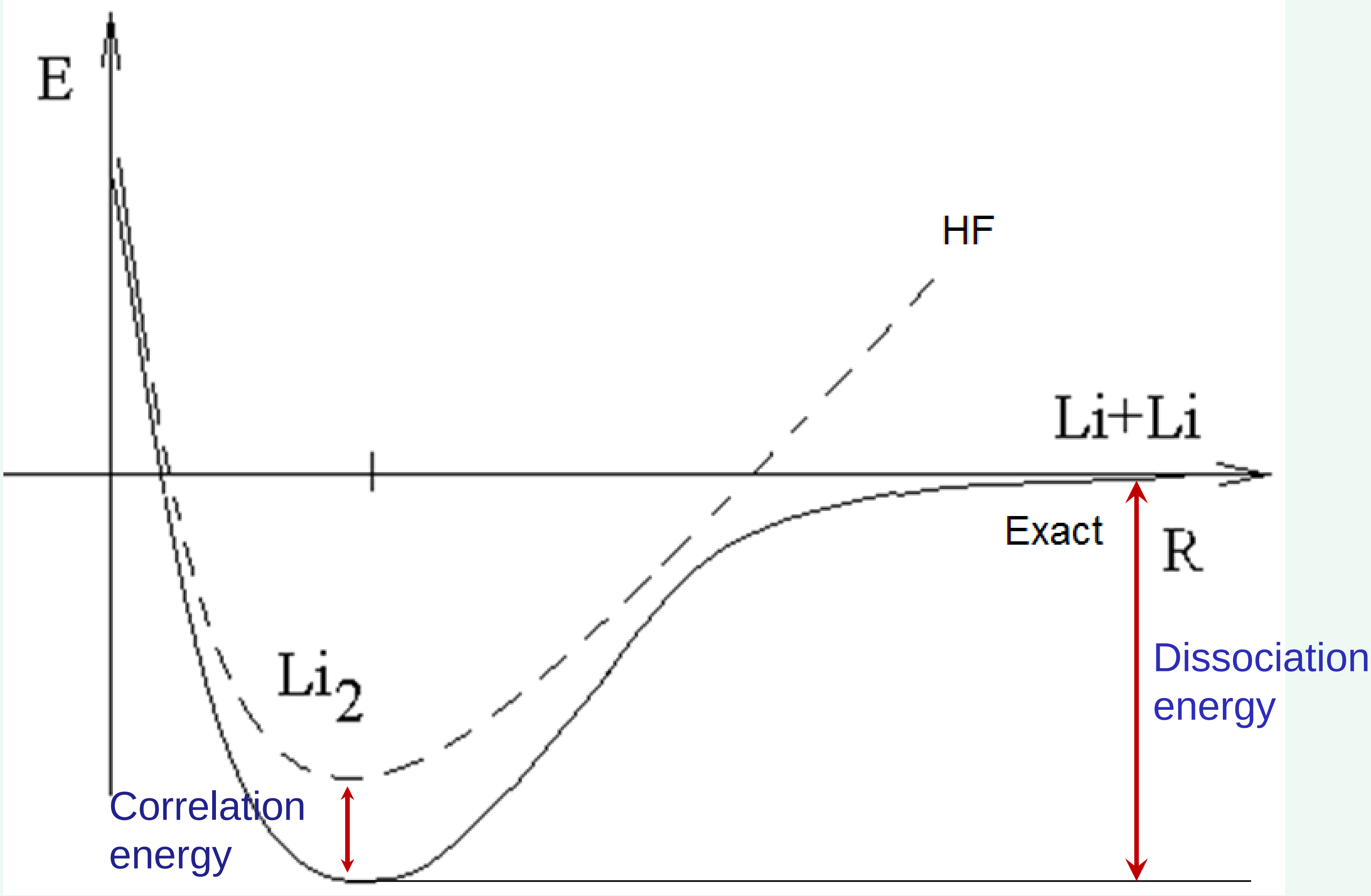
$$\upsilon(M,N,s) = \frac{2s+1}{N/2+s+1}\binom{M+1}{N/2-s}\binom{M}{N/2+s}$$

N – number of electrons
M – number of basis functions (AO)
s – spin of system

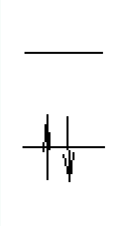
Water, N=10	M	$\upsilon(M,N,s)$
STO-6G	7	196
6-31G	13	428,429
6-311G	19	30,046,752
6-311++G(3p,3d,1f)	71	30,361,438,274,192

Many Configurational Self Consistent Field (MCSCF)

Li_2 Dissociation



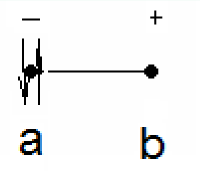
Ionic-covalent composition of the wave function

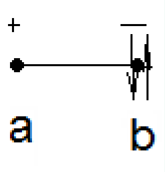


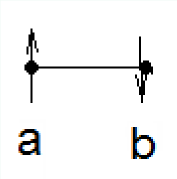
$$\varphi = \frac{1}{\sqrt{2}}\left(\chi_\mathrm{a} + \chi_\mathrm{b}\right)$$

$$\Psi_0 = \varphi(1)\varphi(2) = \tfrac{1}{2}\left(\chi_a(1) + \chi_b(1)\right)\left(\chi_a(2) + \chi_b(2)\right)$$

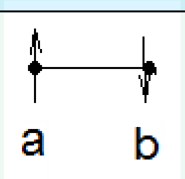
$$\Psi_0 = \frac{1}{2}\left(\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) + \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)\right)$$



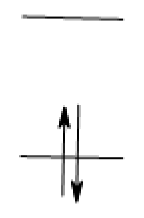




$$R \rightarrow \infty: \quad \Psi_{\text{exact}} \sim \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)$$

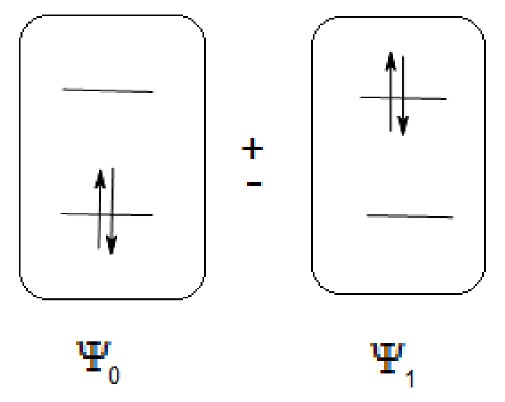


Method CI



$$\phi = \frac{1}{\sqrt{2}}\left(\chi_a - \chi_b\right)$$

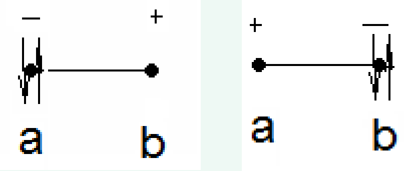
$$\varphi = \frac{1}{\sqrt{2}}\left(\chi_a + \chi_b\right)$$



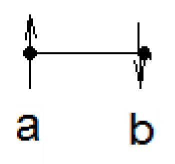
$$\Psi_0 = \frac{1}{2}\left(\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) + \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)\right)$$

$$\Psi_1 = \frac{1}{2}\left(\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) - \chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)\right)$$

$$\Psi^{+}_{exact} = \Psi_0 + \Psi_1 = \chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2)$$

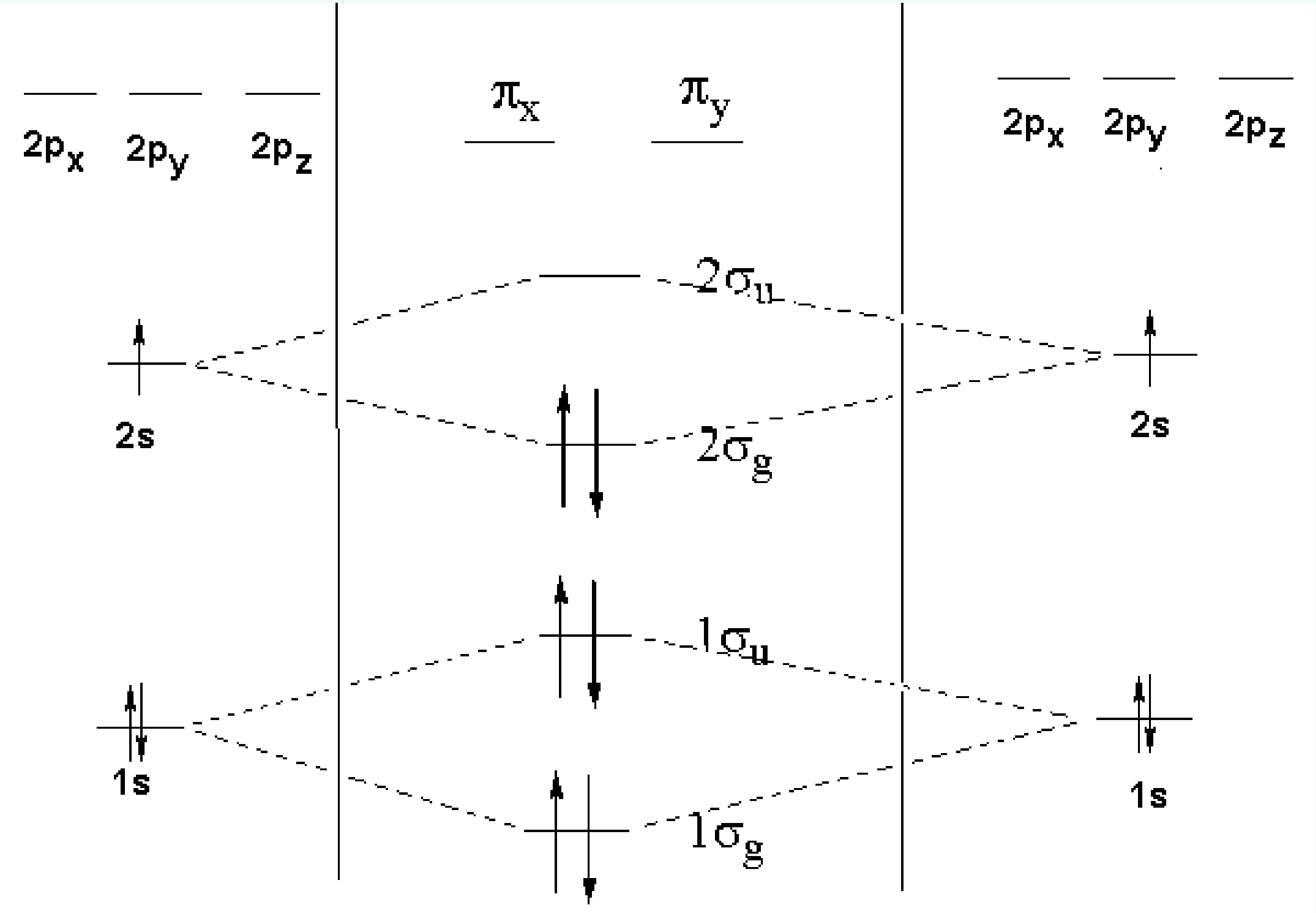


$$\Psi^{-}_{exact} = \Psi_0 - \Psi_1 = \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)$$

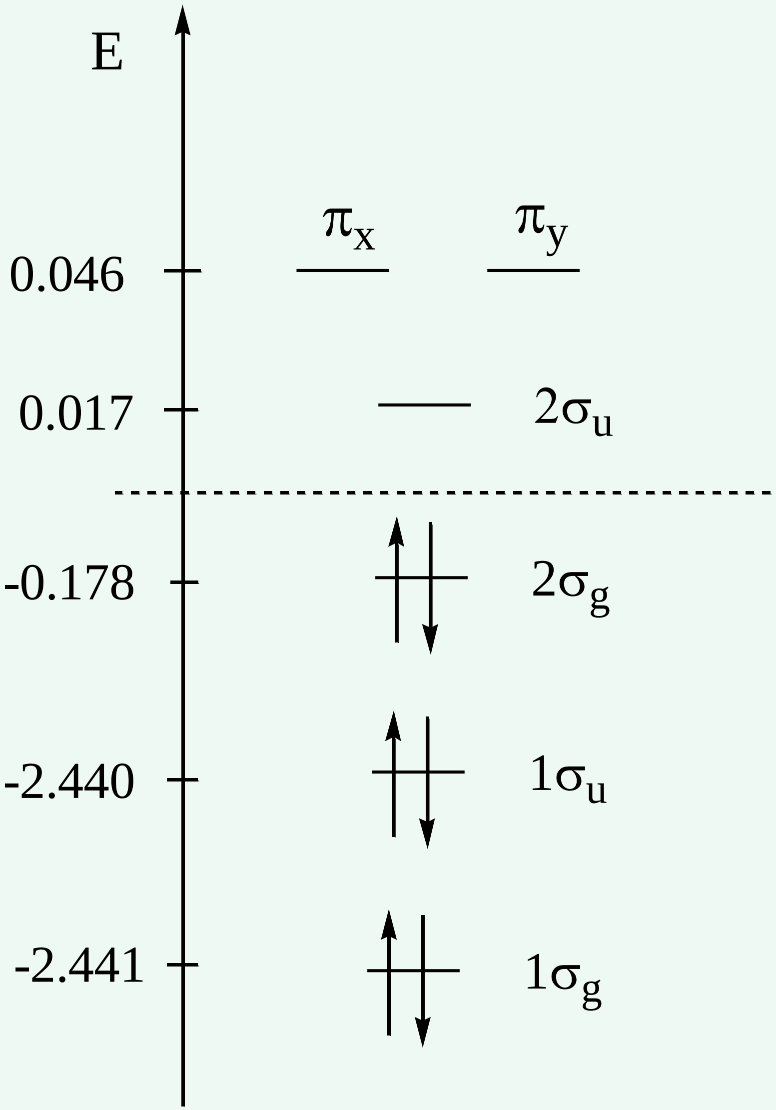


$$\boxed{\Psi^{-}_{exact} = \Psi_0 - c\,\Psi_1}$$

Li_2 Correlation Diagram



Li_2 Molecular Orbitals

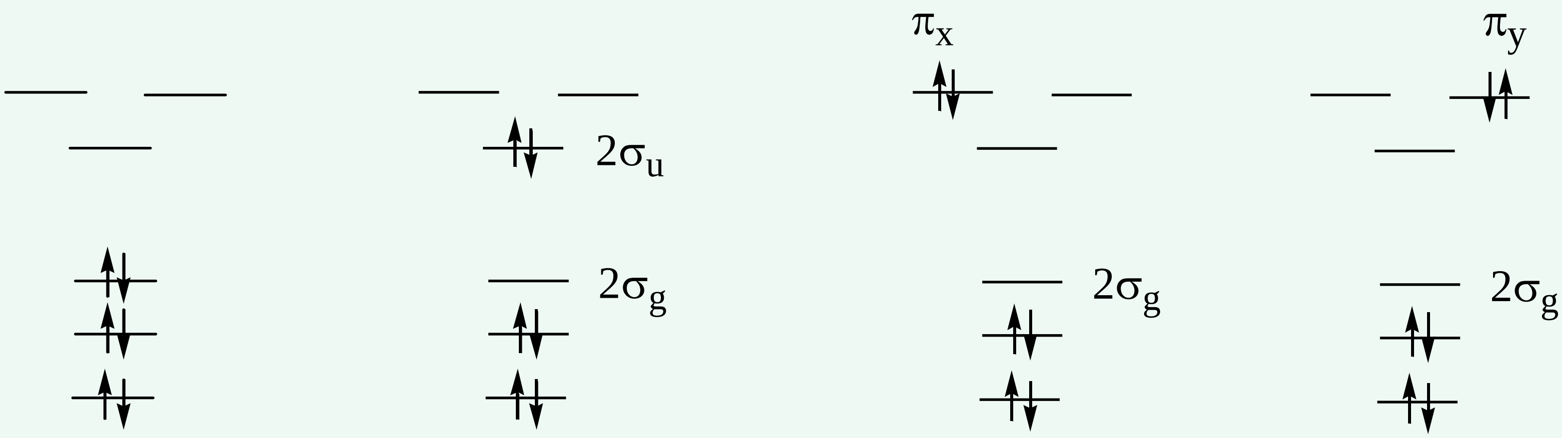


RHF/6-31G

R=5.05 a.u.

The structure of exact wave function of Li_2 $(R = R_e)$

$$\left|\Psi_{\mathrm{FCI}}\right\rangle = 0.959\left|0\right\rangle - 0.102\left|\begin{matrix} 2\sigma_u 2\sigma_u \\ 2\sigma_g 2\sigma_g \end{matrix}\right\rangle - 0.135\left\{\left|\begin{matrix} \pi_x \pi_x \\ 2\sigma_g 2\sigma_g \end{matrix}\right\rangle + \left|\begin{matrix} \pi_y \pi_y \\ 2\sigma_g 2\sigma_g \end{matrix}\right\rangle\right\} + \ldots\ldots$$



The structure of exact wave function of Li_2 (R = $2R_e$)

$$\left|\Psi_{\mathrm{FCI}}\right\rangle = 0.809\left|0\right\rangle - 0.516\left|\begin{matrix}2\sigma_u\,2\sigma_u\\ 2\sigma_g\,2\sigma_g\end{matrix}\right\rangle - 0.044\left\{\left|\begin{matrix}\pi_x\pi_x\\ 2\sigma_g\,2\sigma_g\end{matrix}\right\rangle + \left|\begin{matrix}\pi_y\pi_y\\ 2\sigma_g\,2\sigma_g\end{matrix}\right\rangle\right\} + \ldots\ldots$$

R = ∞

$$\left|\Psi_{\mathrm{FCI}}\right\rangle \approx 0.707\left|0\right\rangle - 0.707\left|\begin{matrix}2\sigma_u\,2\sigma_u\\ 2\sigma_g\,2\sigma_g\end{matrix}\right\rangle$$

Classification of electronic correlations

1. *Dynamic correlations* (formed by excitations, which make small contributions to the exact wave function. (However, there are a lot of them !)
2. *Non-dynamic correlations* (small number of excitations making significant contributions !)
3. *Static correlations* (groups of excitations which provide correct symmetry properties of the wave function)

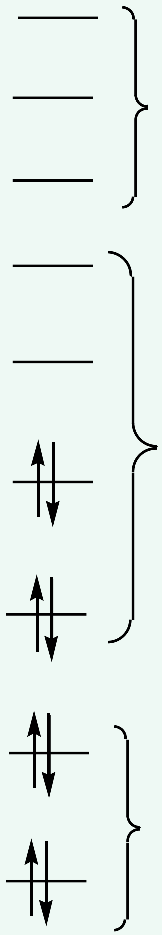
MCSCF

$$\left|\Psi_{\mathrm{MCSCF}}\right\rangle = \sum_{k} A_k \left|\Phi_k\right\rangle$$

$$\left|\Phi_k\right\rangle = \left|\varphi_1 \varphi_2 \ldots\ldots \varphi_N\right| \qquad \varphi_i = \sum_{\mu} C_{\mu i} \chi_{\mu}$$

$E_{\mathrm{MCSCF}}\left(A_k, C_{\mu i}\right)$ Compare it with CI $E_{\mathrm{CI}}\left(A_k\right)$

Active Space



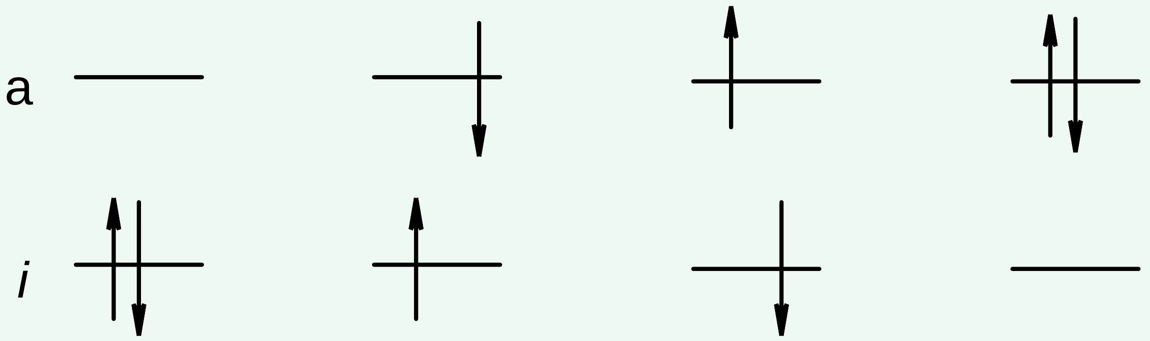
external (inactive)

active orbitals

core (inactive)

Complete Active Space, CAS

Full optimized reaction space (FORS = .TRUE.)



$$|0\rangle \qquad \left|\begin{matrix} a_\beta \\ i_\beta \end{matrix}\right\rangle \qquad \left|\begin{matrix} a_\alpha \\ i_\alpha \end{matrix}\right\rangle \qquad \left|\begin{matrix} a_\alpha a_\beta \\ i_\alpha\, i_\beta \end{matrix}\right\rangle$$

Determinantal basis

$$\left|\Psi_{CASSCF\,(2,2)}\right\rangle = c_0\left|0\right\rangle + c_1\left|\begin{matrix} a_\beta \\ i_\beta \end{matrix}\right\rangle + c_1'\left|\begin{matrix} a_\alpha \\ i_\alpha \end{matrix}\right\rangle + c_2\left|\begin{matrix} a_\alpha a_\beta \\ i_\alpha\, i_\beta \end{matrix}\right\rangle$$

CFS basis

$$\left|\Psi_{CASSCF\,(2,2)}\right\rangle = c_0\left|0\right\rangle + c_1\left|\begin{matrix} a \\ i \end{matrix}\right\rangle + c_2\left|\begin{matrix} aa \\ i\,i \end{matrix}\right\rangle$$

$\mathrm{Li_2}$ CASSCF(2,2)

$R=R_e$

$$\left|\Psi_{\mathrm{CASSCF(2,2)}}\right\rangle = 0.976\left|0\right\rangle - 0.224\left|\begin{matrix}2\sigma_u\, 2\sigma_u\\ 2\sigma_g\, 2\sigma_g\end{matrix}\right\rangle$$

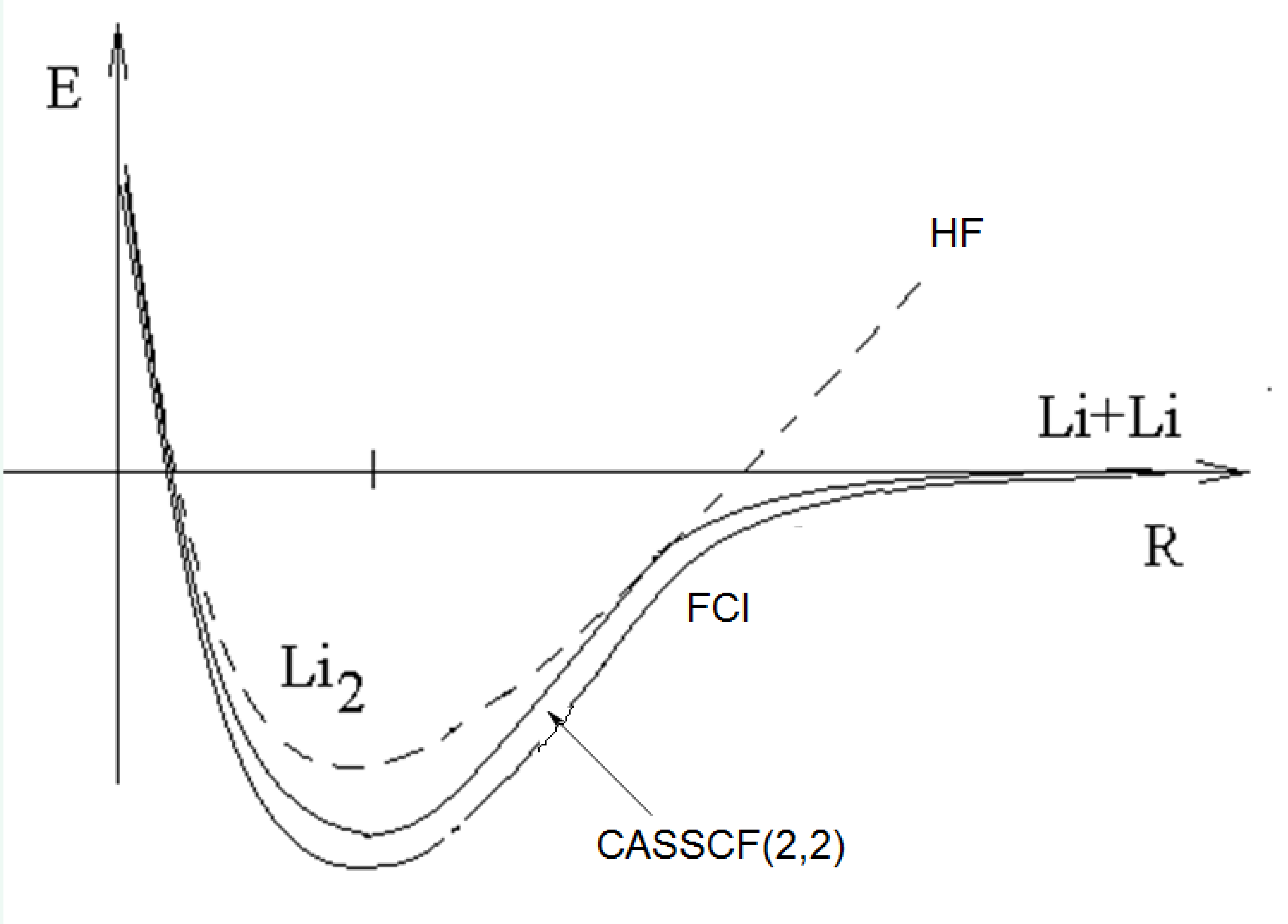
$R=2R_e$

$$\left|\Psi_{\mathrm{CASSCF(2,2)}}\right\rangle = 0.806\left|0\right\rangle - 0.591\left|\begin{matrix}2\sigma_u\, 2\sigma_u\\ 2\sigma_g\, 2\sigma_g\end{matrix}\right\rangle$$

$R>>R_e$

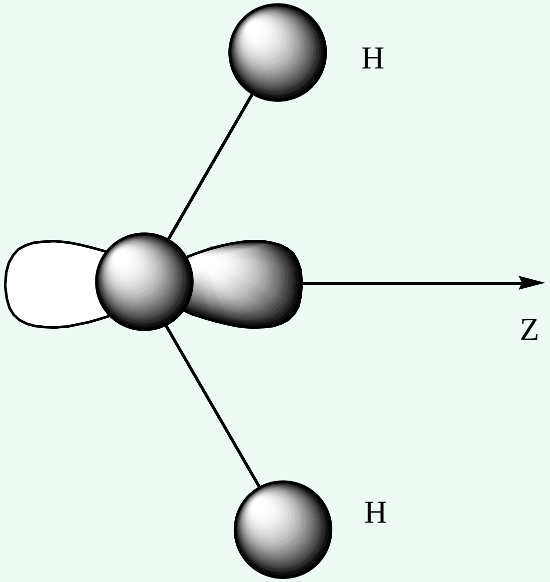
$$\left|\Psi_{\mathrm{CASSCF(2,2)}}\right\rangle = 0.707\left|0\right\rangle - 0.707\left|\begin{matrix}2\sigma_u\, 2\sigma_u\\ 2\sigma_g\, 2\sigma_g\end{matrix}\right\rangle$$

CASSCF curve for Li_2 molecule

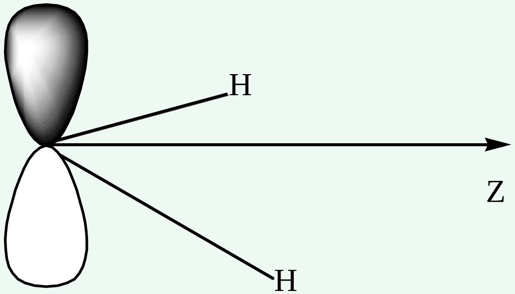


Methylene biradical (CH_2)

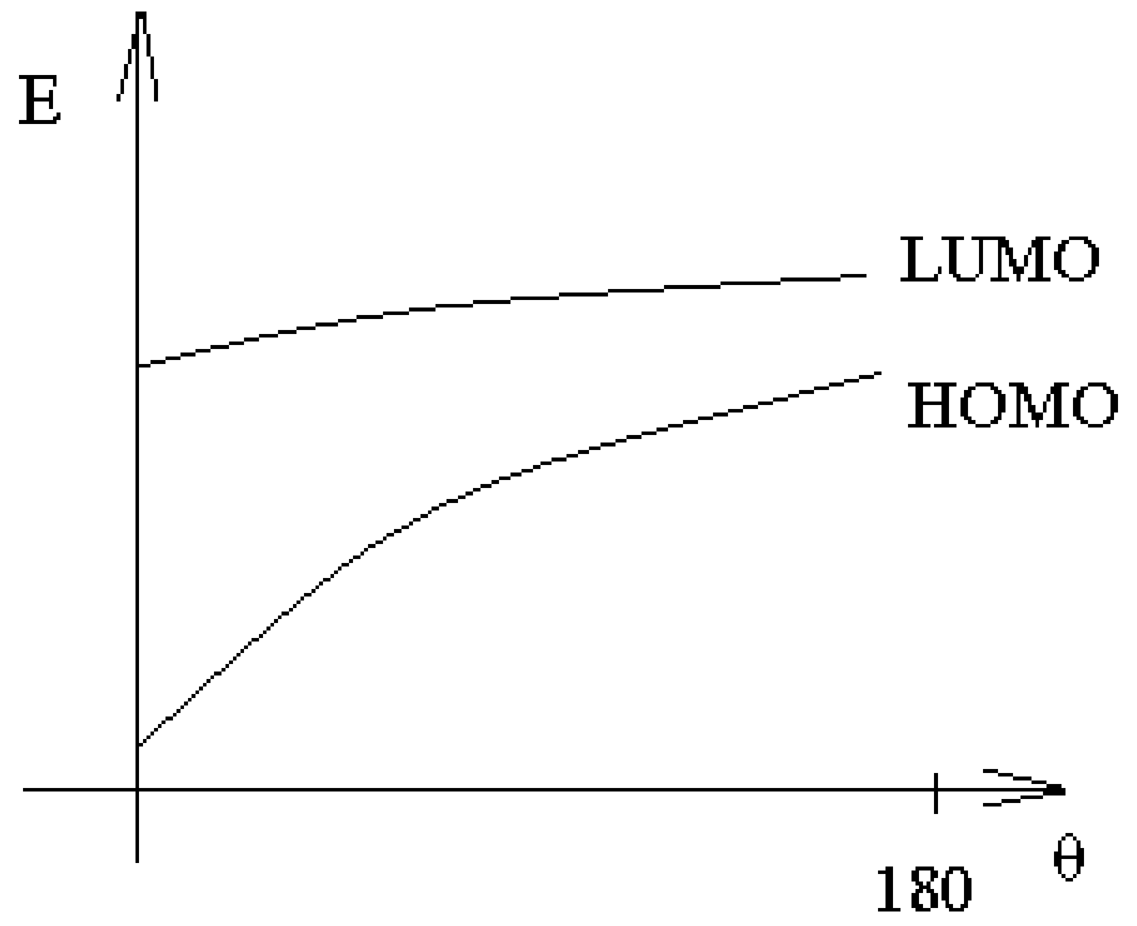
HOMO



LUMO

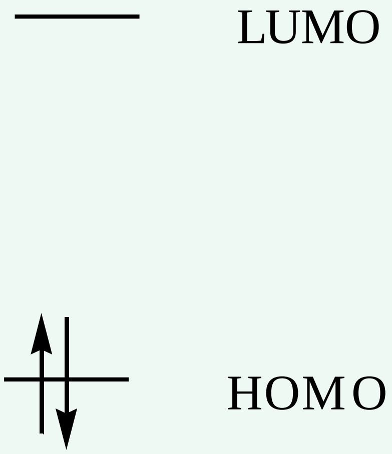


Energy of MO *vs* angle HCH

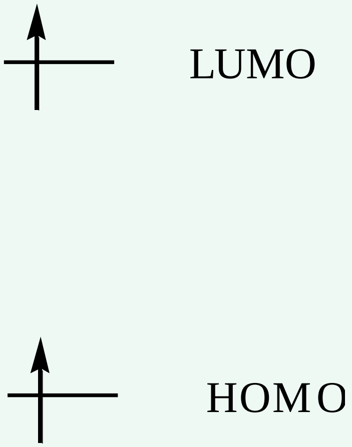


The wave function of CH_2

$$\left|\Psi^{s=0}_{X\Phi}\right\rangle = [\mathrm{core}]\varphi_{\mathrm{HOMO}}(\alpha)\varphi_{\mathrm{HOMO}}(\beta)$$



$$\left|\Psi^{s=1}_{X\Phi}\right\rangle = [\mathrm{core}]\varphi_{\mathrm{HOMO}}(\alpha)\varphi_{\mathrm{LUMO}}(\alpha)$$



CASSCF(2,2) wave function

$$\left|\Psi^{s=0}_{\mathrm{CASSCF(2,2)}}\right\rangle = 0.985\left|0\right\rangle - 0.175\left|\begin{matrix}\mathrm{LL}\\ \mathrm{HH}\end{matrix}\right\rangle \qquad E = 38.8688\ \mathrm{a.u.}$$

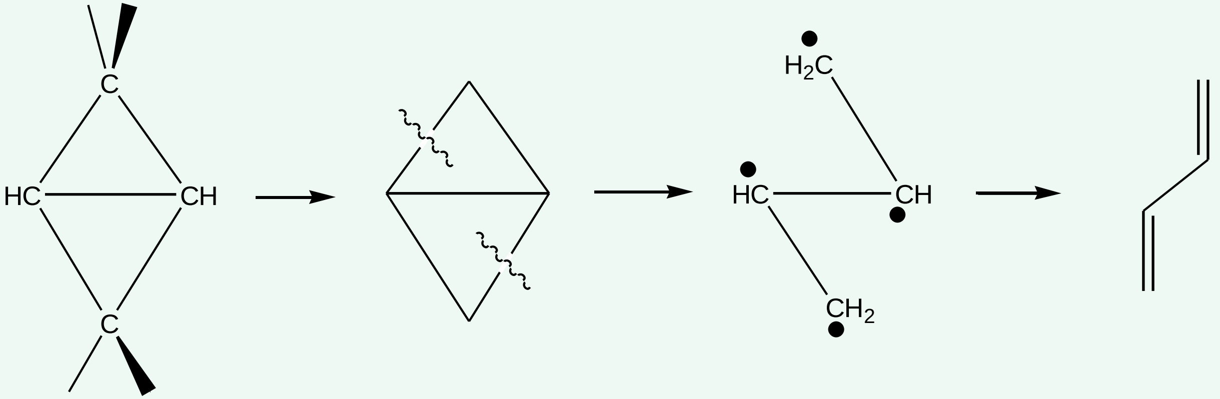
$$R_{\mathrm{CH}} = 1.10\ \overset{0}{\mathrm{A}} \qquad \angle\mathrm{HCH} = 104^{0}$$

$$\left|\Psi^{s=1}_{\mathrm{CASSCF(2,2)}}\right\rangle = \left|\begin{matrix}\mathrm{L}\\ \mathrm{H}\end{matrix}\right\rangle \qquad E = -38.9073\ \mathrm{a.u.}$$

$$R_{\mathrm{CH}} = 1.07\ \overset{0}{\mathrm{A}} \qquad \angle\mathrm{HCH} = 129^{0}$$

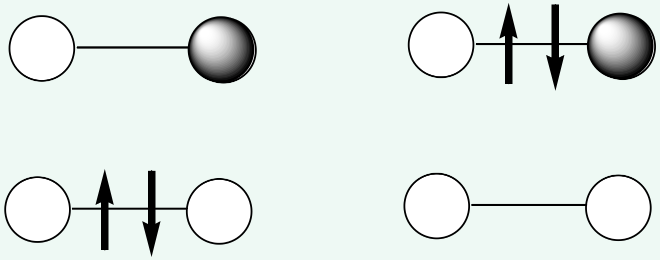
Many electron processes

CASSCF(4,4)

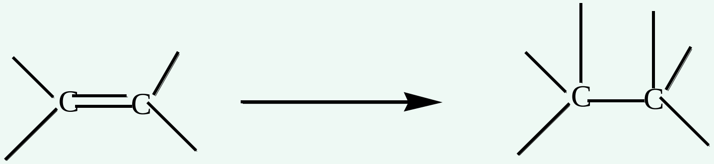


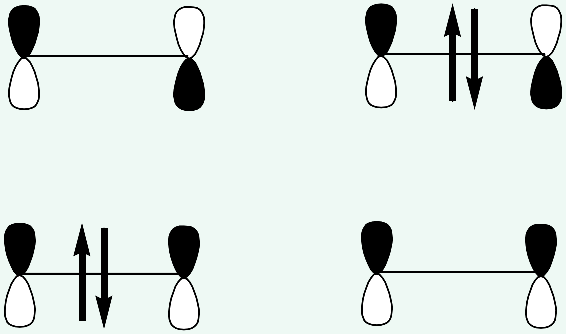
Active orbitals (Examples)

σ-bond breaking: LiH, Li_2, BH, FH….

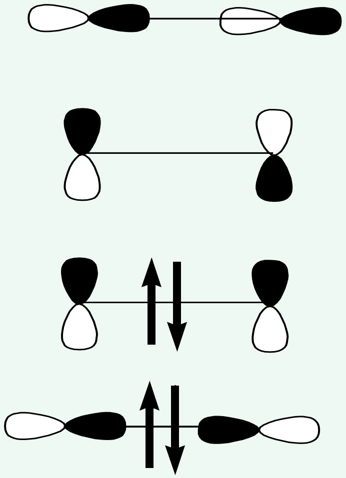


π-bond breaking .

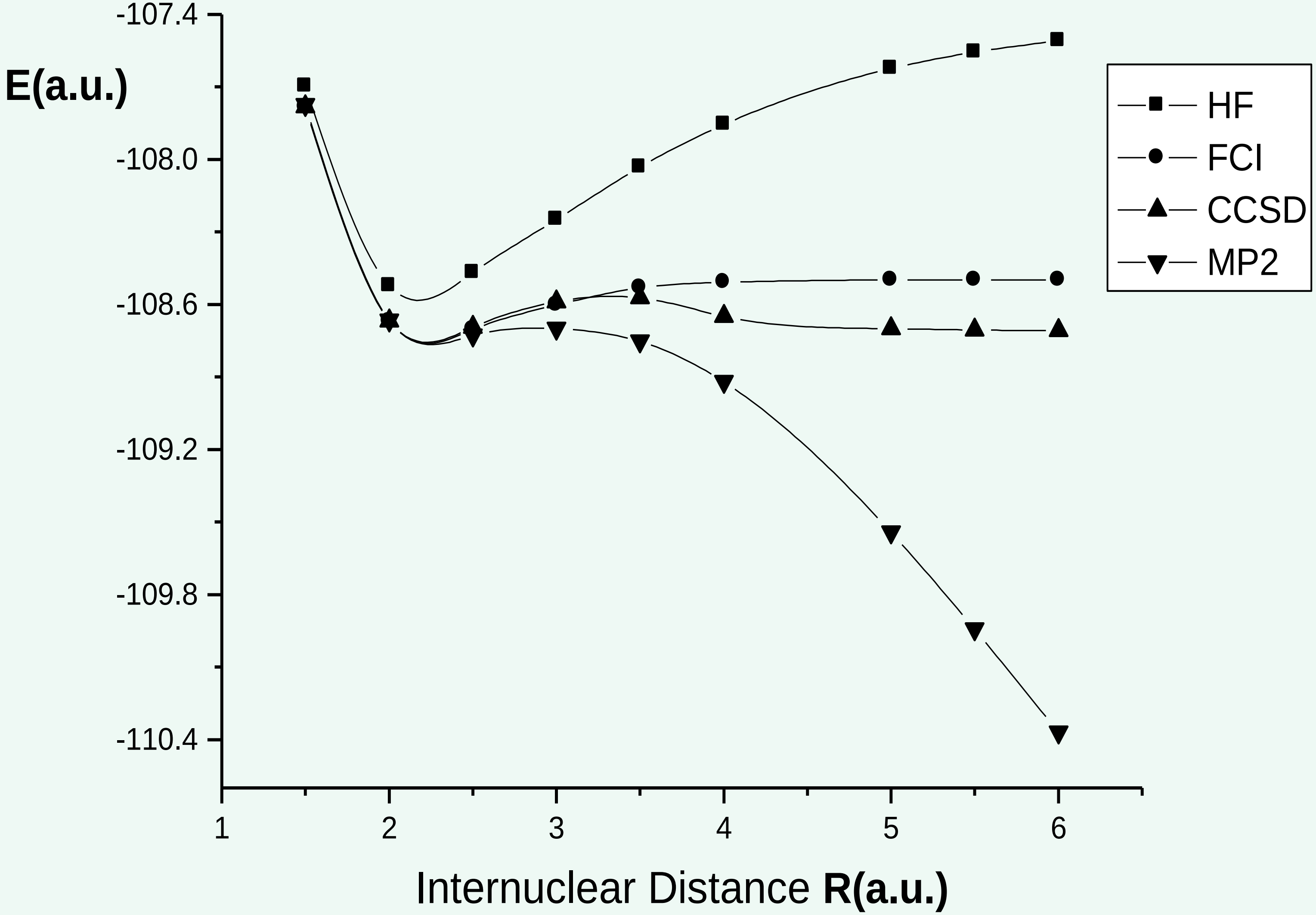




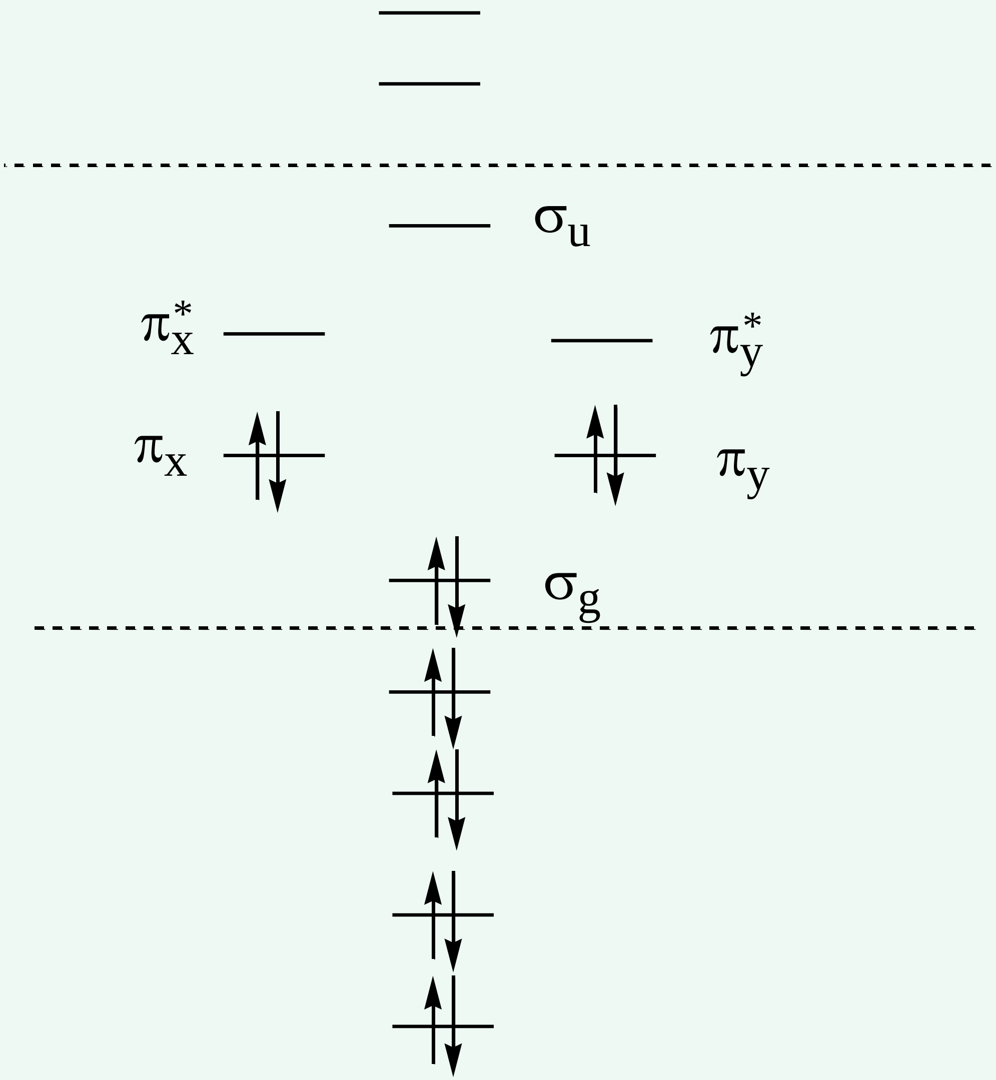
σ- and π- bonds simultaneously breaking



Nitrogen molecule dissociation



Molecular orbitals of nitrogen molecule



CASSCF(6,6) для N_2

$R_e \approx 1.1\overset{0}{A}$ $\mathrm{TZP}:\ (16s,6p,2d,1f) \rightarrow [4s,3p,2d,1f]$

$$\left|\Psi_{\mathrm{CASSCF(6,6)}}(R = 3R_e)\right\rangle = 0.285\left|0\right\rangle - 0.273\left\{\left|\begin{matrix}\pi_x^*\pi_x^* \\ \pi_x\pi_x\end{matrix}\right\rangle + \left|\begin{matrix}\pi_y^*\pi_y^* \\ \pi_y\pi_y\end{matrix}\right\rangle\right\}$$

$$+0.262\left|\begin{matrix}\pi_x^*\pi_x^*\pi_y^*\pi_y^* \\ \pi_x\pi_x\pi_y\pi_y\end{matrix}\right\rangle - 0.230\left|\begin{matrix}\sigma_u\sigma_u \\ \sigma_g\sigma_g\end{matrix}\right\rangle + \ldots.$$

Totally 175 configurations

Occupation numbers of MO

σ_g	π_x	π_y	π_x^*	π_y^*	σ_u
1.12	1.03	1.03	0.97	0.97	0.88

Multireference perturbation theory

$$\left|\Psi_{\mathrm{PT}}\right\rangle = \left|\Psi_{\mathrm{CASSCF}}\right\rangle + \left|\Psi^{(1)}\right\rangle + \left|\Psi^{(2)}\right\rangle + \ldots.$$

$$\mathrm{H} = \mathrm{H}^{(0)} + \mathrm{V}$$

$$\mathrm{E}_{\mathrm{PT}} = \mathrm{E}_{\mathrm{CASSCF}} + \mathrm{E}^{(2)} + \mathrm{E}^{(3)} + \ldots.$$

CASPT2, MCQDPT

First order interaction space

CH_2 6-311++G(2d,2p)

	$E_{S=0}$ a. u.	$E_{S=1}$ a. u.	**ΔE (kcal/mol)**
CASSCF(2,2)	-38.9141	-38.9315	10.9
MCQDPT	-39.0257	-39.0511	15.9

CASSCF не задовольняє критерію Дж. Попла для «**model chemistry**»

Згідно Дж. Поплу квантовохімічний метод, повинен бути універсальним і має бути використаним «стандартним способом». При цьому його ефективність (точність) має бути оцінена на широкому наборі систем шляхом стандартних розрахунків.

Huzinaga-Dunning basis sets

double zeta: DZ, triple zeta: TZ.

Valence double zeta: VDZ, Valence triple zeta: VTZ.

Correlation consists X-zeta basis sets: cc-pVXZ, X=D,T,Q,5,6

aug-cc-pVXZ–augmented basis set

cc-pCVXZ – for best description of core orbitals

Basis	**Primitive**	**Contract**	**Polariz**	**aug**	**cc-pCVXZ**
cc-pVDZ	(9s4p)	[3s2p]	[1d]	[1s1p1d]	[1s1p]
cc-pVTZ	(10s5p)	[4s3p]	[2d1f]	[1s1p1d1f]	[2s2p1d]
cc-pVQZ	(12s6p)	[5s4p]	[2d2f1g]	[1s1p1d1f1g]	[3s3p2d1f]

To be continued

Many-particle perturbation theory