HF description of H_2 - restricted HF

Experiment

r_e=0.7417 Å; D_0=104 kcal/mol; ν=4395 cm^{-1}

$E(H_2) = 2h_{11}+J_{11}$

$E(H) = h_1$

HF/STO-3G

R(e) = <u>0.7122 Å</u>

E(H2) = -1.1175059 a.u.

E(H) = -0.4665819 a.u.

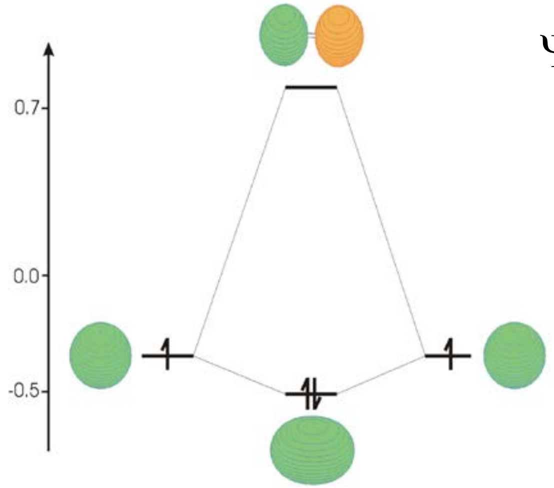
D_e = 0.1843431 a.u. = 115.7 kcal/mol

ZPVE = 7.8 kcal/mol

D_0 = <u>107.9 kcal/mol</u>

STO-3G Basis: →[1s]

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



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

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

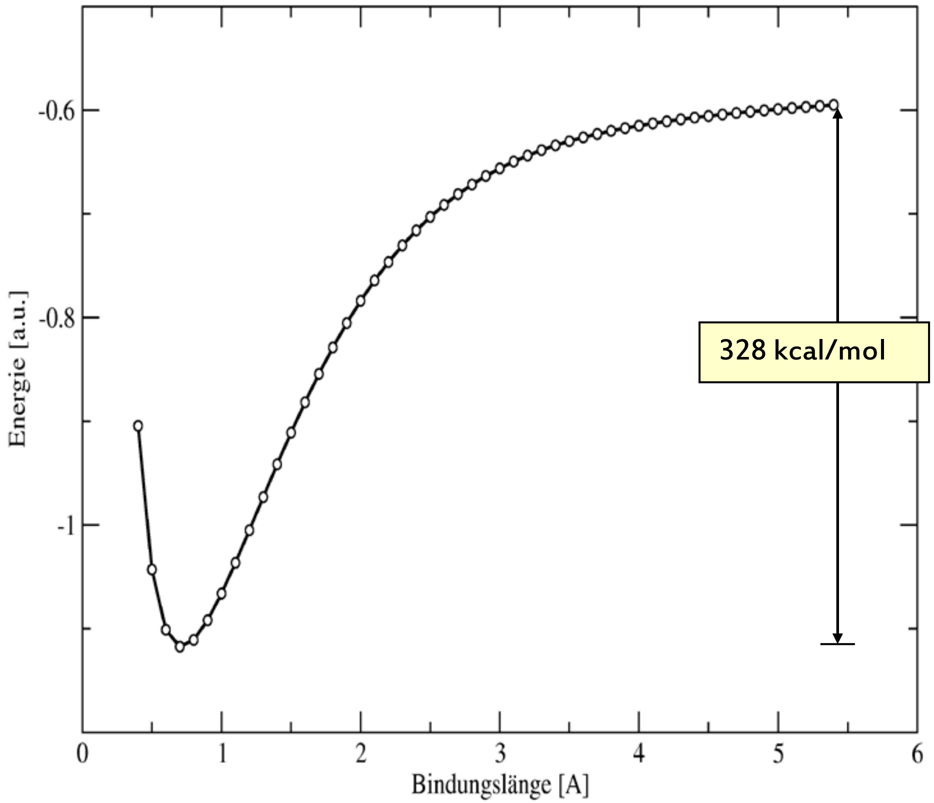
Alpha occ. eigenvalues -- -0.59022
Alpha virt. eigenvalues -- 0.70065

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

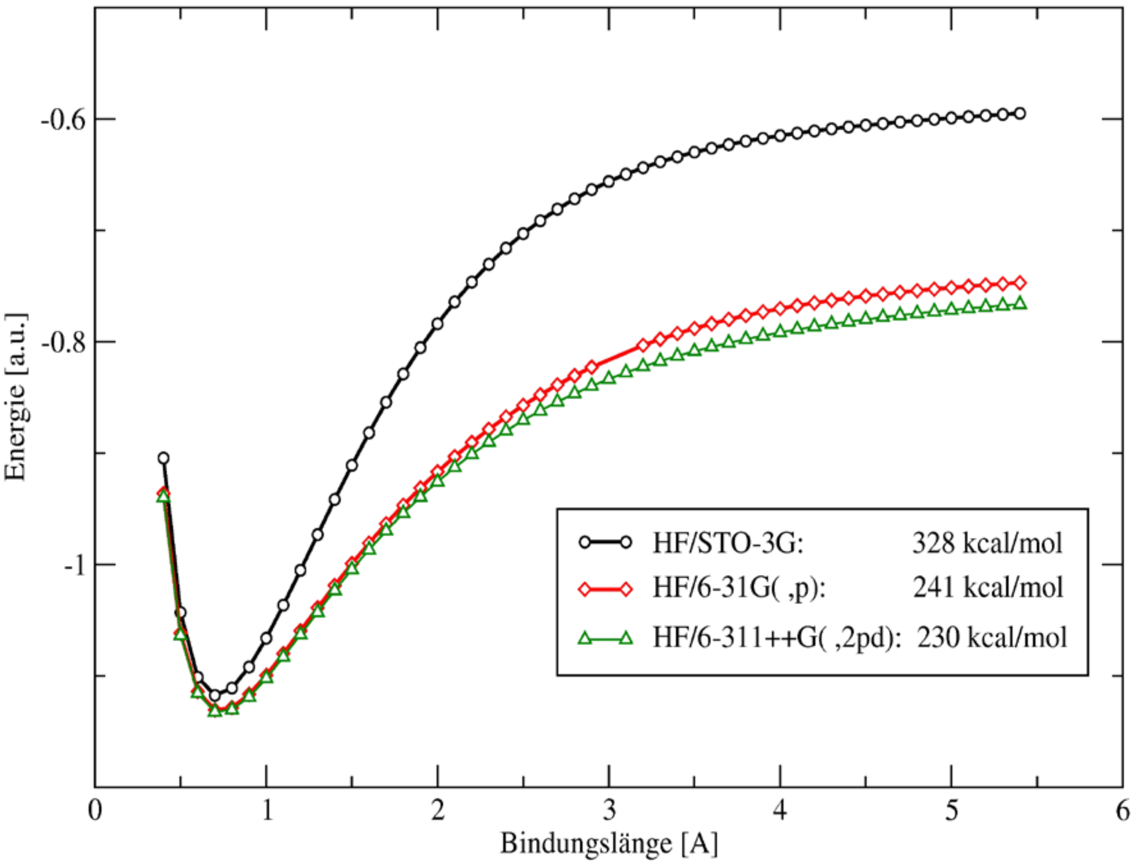
HF description of H_2 - restricted HF

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



HF description of H_2 - restricted HF

Increasing the basis set size:



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

HF description of H_2 - unrestricted HF

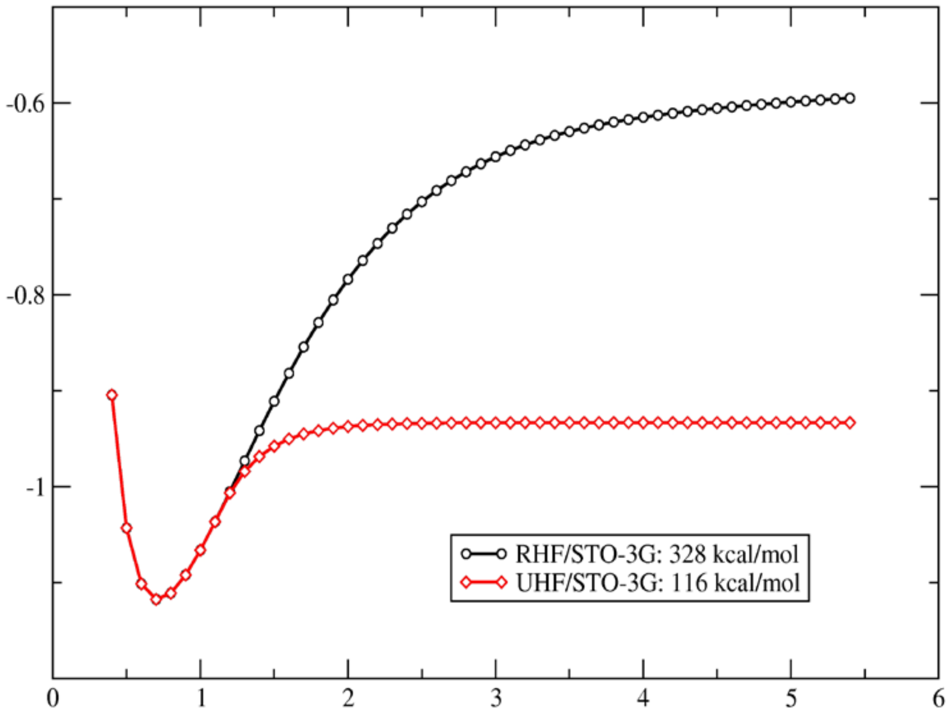
Two solutions may exist for UHF on "closed shell system":

Only one solution around the equilibrium geometry (RHF ~ UHF)

Two solutions for larger $R_{H\text{-}H}$: 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 $\theta = 45^o$

$\Psi_1' \equiv \phi_1$

$\Psi_1'' \equiv \phi_2$ $(S_{12}) = 0$

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

ρ(RHF) - ρ(UHF) (2 Å separation)