

Ab initio calculations for potential energy surfaces

D. Talbi GRAAL- Montpellier

A theoretical study of a reaction is a two step process

I-Electronic calculations : techniques of quantum chemistry

- potential energy surfaces or energy profiles
 - structures (minima ,transition states)
 - energy balances (heights of barriers, thermodynamics etc)
 - zero point energies and frequencies

II-Calculation of the dynamics using the potential energy surfaces

Molecular Electronic calculations

Schrödinger equation

$$H\Psi = E\Psi$$

Approximations

- Born Oppenheimer

motions of nuclei and electrons decoupled

→ He $\Psi_e = E_e \Psi_e$ (for each R)

- Independent electrons : Hartree-Fock equations

electrons are non interacting particles : an electron moves in the average field of the others and described by a one-electron function : spin-orbital ϕ_i

⇒ SCF (RHF,UHF,ROHF) method ϕ : **molecular orbital**

↳ Total wave function Slater determinant $\Phi = | \phi_1 \phi_2 \phi_3 \dots \phi_n |$

- L.C.A.O : $\phi_i = \sum_{(p)} C_{pi} X_p$ X_p atomic orbital

functions describing isolated atoms are good representation of the atoms in the molecule

- SCF method : not always valid for bond breaking



- MSCF method

$\Phi_0 = | \phi_1 \phi_2 \phi_3 \dots \phi_n |$ SCF determinant ground state

$\Phi_i = | \phi_1 \phi_2 \dots \phi_n \phi_{n+1} |$ excited Slater determinant

mixing ground state configuration with appropriate excited state configuration

$$\Psi_{MC} = \sum_{(i)} a_i \Phi_i$$

*Concept of **valence space** = space where **chemistry takes place**
 = molecular space describing the **bonding, antibonding** and electron pairs levels =space spanned by the union of the atomic orbitals that are occupied in the atomic ground states of the atoms*

Core

Valence space

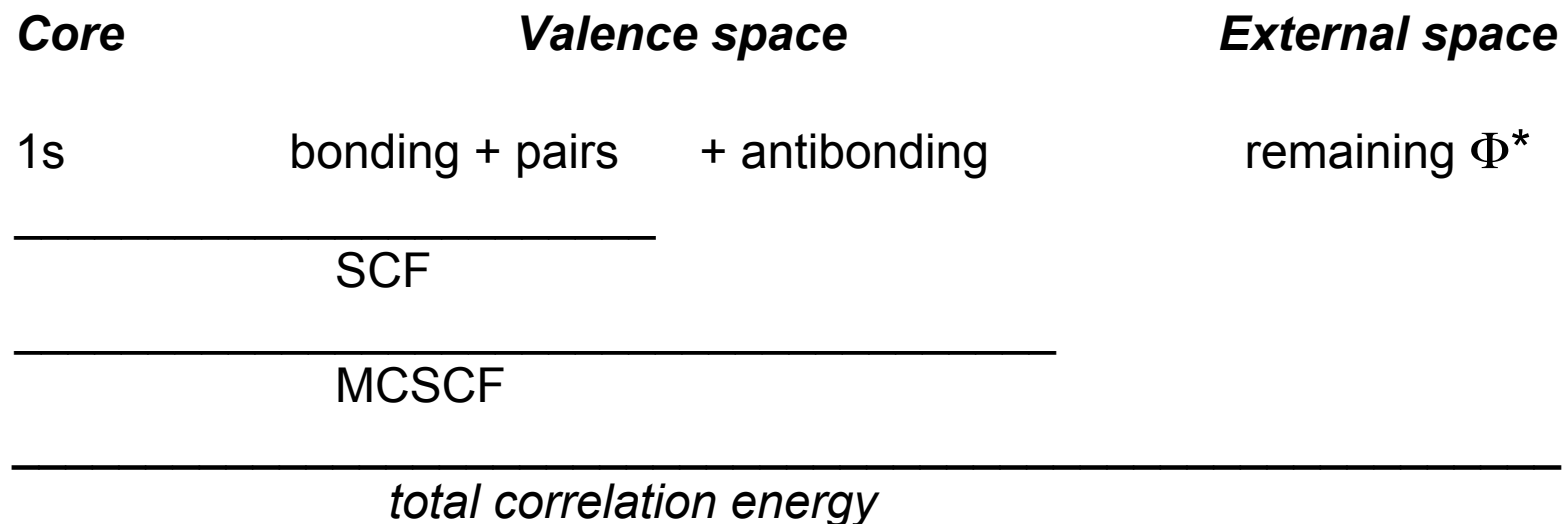
$1S_A \ 1S_B$

$\sigma_{A-B} \ \sigma_{AH} \ \sigma_{BH} \ \mathbf{lp}_A \ \Pi_{A-B} \ \sigma^*_{A-B} \ \sigma^*_{AH} \ \sigma^*_{BH} \ \mathbf{lp}^*_A \ \Pi^*_{A-B}$

• **SCF method** : missing correlation energy : $E_c = E_{\text{exact}} - E_{\text{scf}}$

*the motion of the electron not only depend upon average electrostatic field in the molecule **but also upon the instantaneous position of all other electrons***
Can be recovered from the none occupied orbitals

partly recovered in MCSCF method but a lot still missing



$$E = E_{\text{scf}} + E_c = \langle \Psi / H / \Psi \rangle / \langle \Psi / \Psi \rangle$$

two type of approaches for correlation energy

•Variational methods : E is minimized

$$\Psi = \sum_{(k)} d_k \Phi_k$$

if Φ_k is the SCF determinant \rightarrow CIS, CISD, CCSD

if Ψ_{MC} rather than Φ_k \rightarrow MRCI

•Perturbational methods : a zero order solution is improved

$$\Psi = \Phi_0 + \lambda^1 \Phi_0^1 + \lambda^2 \Phi_0^2 + \lambda^3 \Phi_0^3 + \lambda^4 \Phi_0^4 + \dots$$

if Φ_0 is the SCF determinant \rightarrow MP2, MP3, MP4

if Ψ_{MC} rather than Φ_0 \rightarrow CASSPT2

CI and MP methods can be combined : CCSD(T), CCSD(T,Q), MC/P

Summary for wavefunction based methods

How **close** the calculated **wave function** will be to the **exact wave function** depends upon a quadruple choice that can be expressed in the form of four equations interlocked as a nest of Russian dolls:

- Choice of the atomic basis set

$$\chi_p = \sum_{(g)} G_g$$

G are Gaussian type functions centered on the atoms and previously determined in atomic calculations (# size : DZV, TZV, QZV... # type: polarization, Rydberg from # optimization : Pople, Dunning ..)

- Choice of the spin-orbital

$$\phi_i = \sum_{(p)} C_{pi} \chi_p$$

C_{pi} defines the contribution of the different atoms to the molecular levels

$$\delta E / \delta C_p$$

- Choice of the electronic wave function (1 to thousands configurations)

If SCF wave function $\Phi_k = (1/(n!)^2 | \phi_1(1) \phi_2(2) \dots \phi_n(n) |$

If MCSCF wavefunction : $\Psi_{MC} = \sum_{(i)} a_i \Phi_i$ and $\phi_i = \sum_{(p)} C_{pi} Xp$

$\delta E / \delta a_i$ together with $\delta E / \delta C_p$

- Choice of the basis of electronic configurations - correlation energy
(millions of configurations)

If variationally \Rightarrow CI and CCSD methods

$\Psi = \sum_{(k)} d_k \Phi_k$ and $\delta E / \delta d_k$

If perturbationally \Rightarrow MP and CASSPT2 methods

$\Psi = \Phi_0 + \lambda^1 \Phi_0^1 + \lambda^2 \Phi_0^2 + \dots$

CI and MP methods can be combined : CCSD(T), CCSD(T,Q), MC/P

DFT based methods

Density functional Theory : not necessary to know Ψ but only electronic density $\rho(r)$

kinetic energy, potential energy and total energy : functionals of the electronic density $\rho(r)$ (Hohenberg and Kohn)

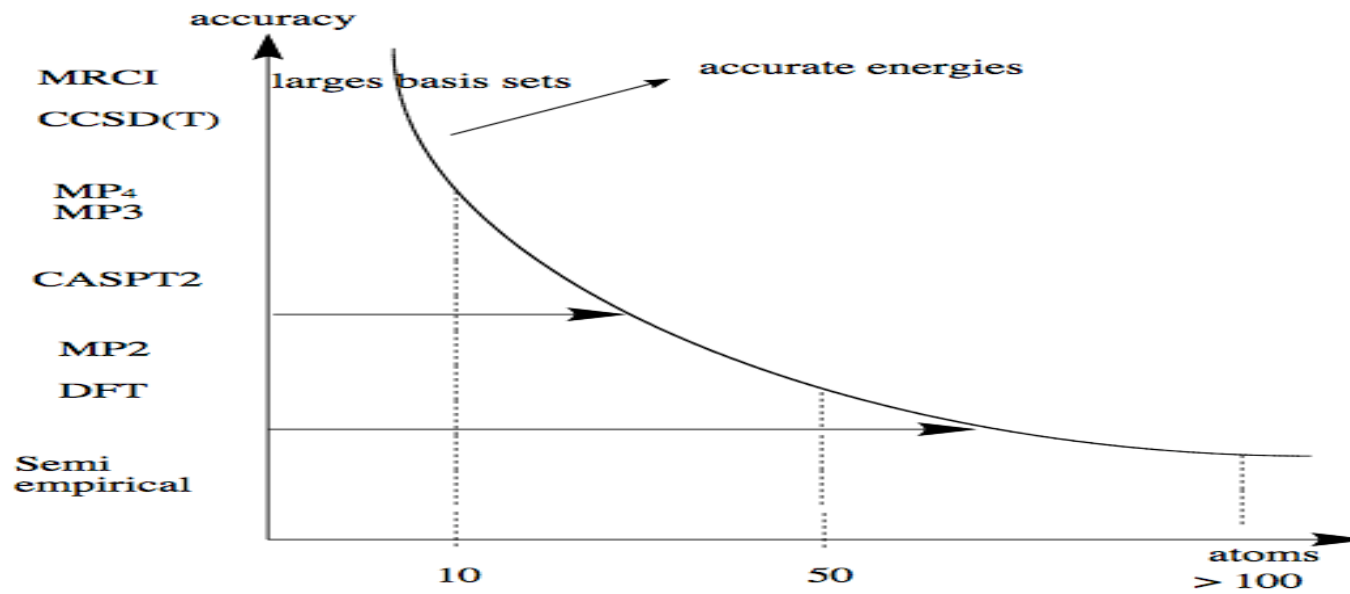
but ! no exact analytic expression for the energy functional

by analogy to the Hartree-Fock scheme : non interacting particles to which are associated set of orbitals from which is derived a $\rho(r)$. This introduces a new functional $E_{xc}[\rho]$: the exchange-correlation functional.

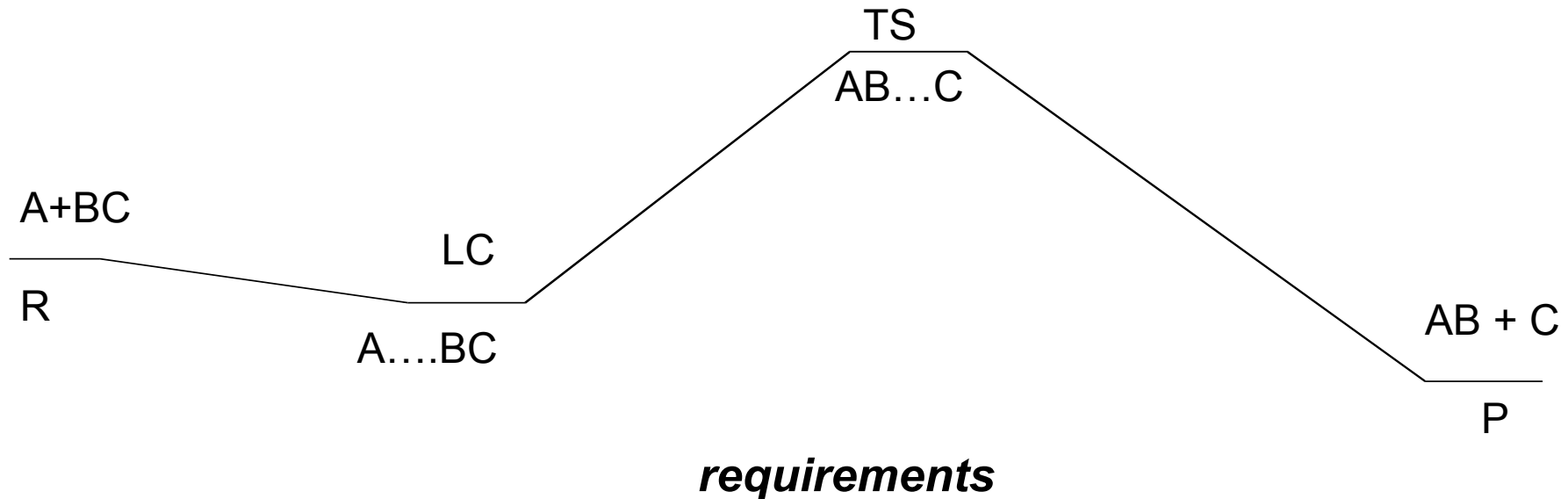
The correlation problem which is treated by interaction of configurations or perturbation in the wave function methods is replaced by the problem of finding the best approximation of the exchange-correlation $E_{xc}[\rho]$ in DFT methods; many are available ! B3LYP, PW91PW91, etc

Note : OK for stable structure optimization, careful for transition states and energy balances very dependent of the exchange-correlation used.

Compromising accuracy and size of the system



Potential energy calculations : choices not trivial : no unique recipe !



Basis set

- as large as possible to describe all intermediates : flexible enough for TS or LC

Wavefunction : SCF / MCSCF

- Closed shell systems : SCF wave function ok but not always for Ts !
- Open shell and excited state : MCSCF wave function

problem of the valence space that should be the same for TS, LC, R,P

Correlation energy : SCF/CCSD(T), SCF/MP_n, MRCI, CASSMPT2, ...

Complications

Size of the system

stationary points to locate, frequencies to calculate to check if minimum or transition states and to get zero point energies : first and second derivatives of the energy very expensive calculations !!!

- not always tractable with large basis set and at high level of correlation
- not tractable if MCSCF wave function (valence space *spanned by the union of the atomic orbitals that are occupied in the atomic ground states of the atoms*)

Compromise

1-optimisation at a lower level of correlation : MP2 (DFT) + reasonably sized basis set (DZV, TZV + polarization : 6-31G(p,d), cc-PVTZ)

if MCSCF optimizations : smaller valence active space but has to be balanced for all structures (Ts, LC, R, P)

compromise based on many test calculations. Convergence has to be studied with respect to the basis set and size of the active space in the case of MCSCF

2-single point calculations at high correlated level MP4 or CCSD(T), MRCI and MC/P and very large basis set (cc-PVQZ, cc-pV5Z, 6-311++G(3df,3pd))

BSSE : basis set superposition errors

$$\Delta E = E(AB\dots C) - E(AB) - E(C)$$

energy of AB...C artificially lowered because AB uses atomic basis set of C and vice versa : small energies (less than 1 kcal) but have to be considered when dealing with very small energies differences:

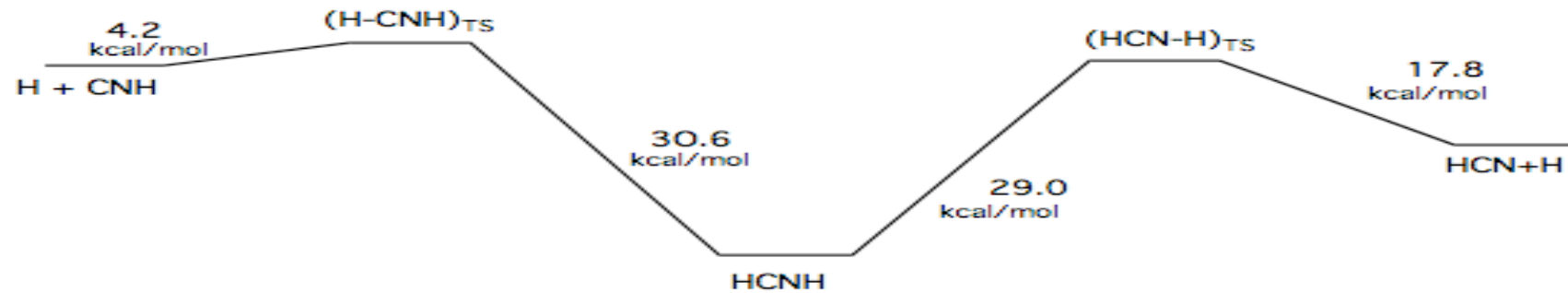
- **Spin contamination** problems for open-shell systems

two solutions : annihilation-projection method
use an mcscf wave function

- **Size consistency problems** : at infinite separation $E_{A\dots B} \neq E_A + E_B$

case of MRCI methods unless very large CI calculations (expensive not always possible if large system)

THE H+CNH \rightarrow HCN + H REACTION



SCF zero order wave function OK

MP2/6-31g(d,p) optimization, frequencies, zero point energies

Single point calculations at the MP4/6-311++G(3df,2pd)

H + HNC \rightleftharpoons HCNH \rightleftharpoons HCN + H
Convergence of relative energies with respect to correlation level

		SCF	MP2	MP3		MP4
H + CNH	E	0.0	0.0	0.0		0.0
	E ₀	0.0	0.0	0.0		0.0
(HNC-H)TS	E	8.7	5.07	4.09	(0.65)	3.44
	E ₀	9.3	5.65	4.67		4.02
HCNH	E	-29.8	-31.5	-35.8		-33.7
	E ₀	-22.5	-24.0	-28.3		-26.2
(HCN-H)TS	E	5.88	2.80	0.41	(0.53)	-0.12
	E ₀	8.05	5.03	2.64		2.11
HCN+H	E	-8.40	-17.5	-13.0		-15.4
	E ₀	-8.23	-17.3	-12.8		-15.2

E in kcal/mol at the optimized MP2/6-31G(d,p) geometries
E₀ includes scaled MP2/6-31G(d,p) zero-point vibrational energie

H + HNC \rightleftharpoons HCNH \rightleftharpoons HCN + H
Convergence of relative energies with respect to basis set

MP4

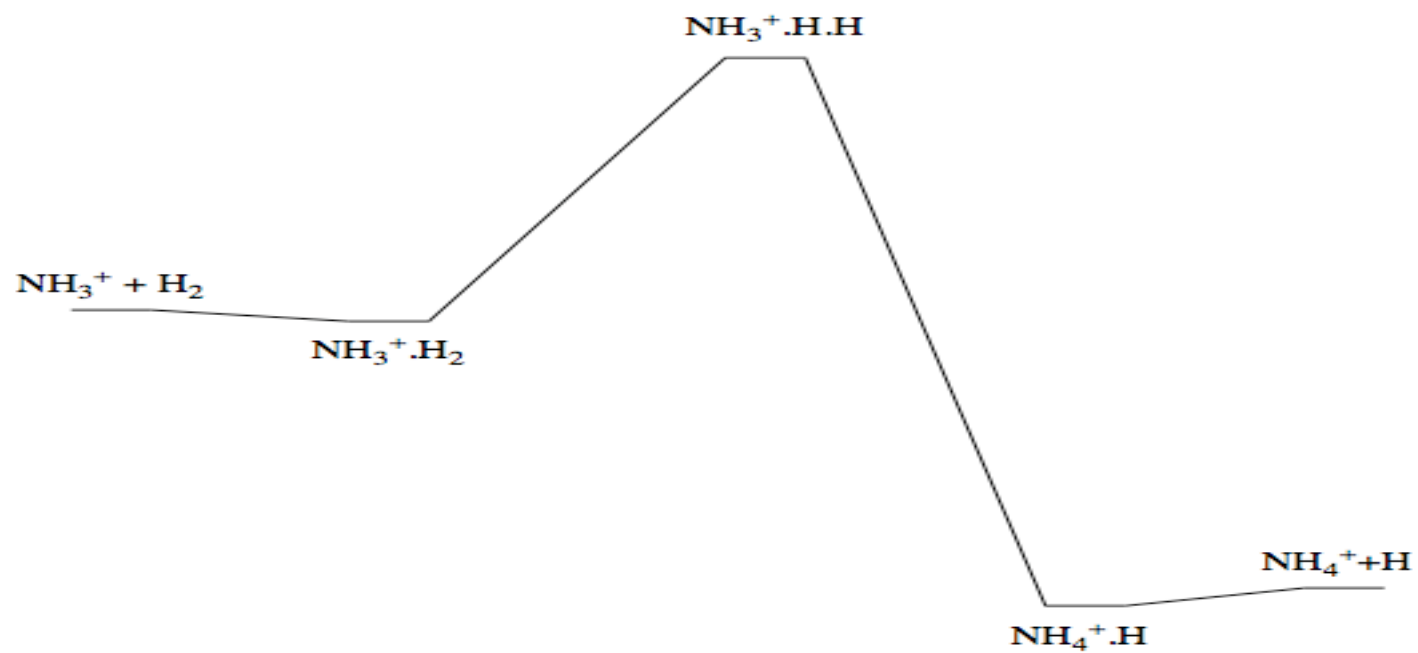
		6-311++G(3df,2pd)	6-311++G(3df,3pd)
H + CNH	E	0.0	0.0
	E ₀	0.0	0.0
(HNC-H)TS	E	3.44	(0.07) 3.37
	E ₀	4.02	3.95
HCNH	E	-33.7	-33.9
	E ₀	-26.2	-26.4
(HCN-H)TS	E	-0.12	(0.19) -0.31
	E ₀	2.11	1.92
HCN+H	E	-15.4	-15.4
	E ₀	-15.2	-15.2

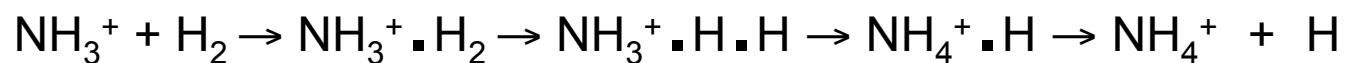
E are computed at the optimized MP2/6-31G(d,p) geometries
 E₀ includes scaled MP2/6-31G(d,p) zero-point vibrational energie

H + HNC \rightleftharpoons HCNH \rightleftharpoons HCN + H
Convergence of relative energies with respect to geometries

		MP4//MP2		MP4//MP3
H + CNH	E	0.0		0.0
	E ₀	0.0		0.0
(HNC-H)TS	E	3.37	(0.28)	3.65
	E ₀	3.95		4.23
BSSE				0.27
best estimate		4.5 ± 1.0	(0.65+0.07+0.28)	
HCNH	E	-33.9		-33.9
	E ₀	-26.4		-26.4
best estimate		-26.4		
(HCN-H)TS	E	-0.31	(0.29)	-0.02
	E ₀	1.92		2.21
BSSE				0.64
best estimate		2.85 ± 1.0	(0.53+0.19+0.29)	
HCN+H	E	-15.4		-15.4
	E ₀	-15.2		-15.2
best estimate		15.2		

MP2/6-31G(d,p) geometries
MP3/6-311++G(d,p) geometries.





SCF MP2 MP4 Best estimate

NH ₃ ⁺ ·H ₂	E	-2.2	-3.1	-3.2	-1.4±0.3
	E ^C	-2.1	-2.9	-3.0	
	E ₀ ^c	-0.5	-1.3	-1.4	
NH ₃ ⁺ ·H·H	E	11.8	2.6	2.2	-4.8±0.5
	E ^C	12.1	3.2	2.8	
	E ₀ ^c	14.1	5.2	4.8	
NH ₄ ⁺ ·H	E	-18.1	-30.6	-26.0	-21.4±2.
	E ^C	-18.0	-30.5	-25.9	
	E ₀ ^c	-13.5	-25.5	-21.4	
NH ₄ ⁺ + H	E	-17.3	-29.4	-24.7	-20.8±2.
	E ₀	-13.4	-25.5	-20.8	
	Exp	-19 ±3			

SUMMERY

Calculations of accurate potential energy surfaces is a delicate problem but feasible for ground state surfaces with accuracy of 10-20% :

- Basis set are well chosen flexible enough for all structure
- Wave functions are balanced all along the reaction path
- Correlation energy correctly evaluated in a balanced way all along reaction path

The quality of the calculations (error bar) can be checked by making sure that the results are stable with respect to any extension of both the atomic basis and the configuration space

For excited state surfaces : another story . Case dependent. Should at least insure a qualitative description possible with MRCI or MC/P.

Computed geometries

Molecule	MP2/6-31G(d,p)	MP3/6-311++G(d,p)	Experimental
HCN	r(CH)=1.064 r(CN)=1.176	r(CH)=1.066 r(CN)=1.150	r(CH)=1.065 r(CN)=1.153
HNC	r(NH)=0.997 r(CN)=1.186	r(NH)=0.996 r(CN)=1.168	r(NH)=0.986 r(CN)=1.173
(HCN-H)TS	r(NH)=1.418 r(CH)=1.065 r(CN)=1.157 <(CNH)=124.93 <(NCH)=190.15	r(NH)=1.461 r(CH)=1.067 r(CN)=1.151 <(CNH)=122.18 <(NCH)=188.58	
(H-CNH)TS	r(NH)=0.997 r(CH)=1.744 r(CN)=1.187 <(CNH)=188.84 <(NCH)=122.56	r(NH)=0.996 r(CH)=1.784 r(CN)=1.171 <(CNH)=184.66 <(NCH)=120.38	
HCNH	r(NH)=1.014 r(CH)=1.095 r(CN)=1.214 <(CNH)=122.14 <(NCH)=123.99	r(NH)=1.016 r(CH)=1.098 r(CN)=1.215 <(CNH)=119.64 <(NCH)=125.99	

Experimental geometries are from Herzberg (1966) for HCN and Harmony et al. (1979) for HNC