

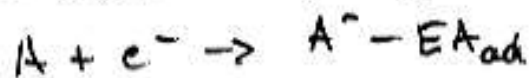
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Electron Affinities

play a key role together with IE in the theory of chemical reactivity, Parr, Pearson, JACS, 1983, 105, 7512

hardness, softness, chemical potential

Adiabatic electron affinity EA_{ad}



equilibrium geometries of A , A^- needed and energy differences in their equilibrium ground states

Adiabatic electron affinities (eV)

	HF	CISD	EOM	HFS	LDA	LDA/NL	Exp.
CN	2.93	3.70	4.15	2.78	3.25	3.51	3.89
BO	1.41	2.35	2.97	1.25	1.96	2.33	$\left\{ \begin{array}{l} 3.1 \\ 2.2 \end{array} \right.$
DCN	2.28	3.21	-	2.83	3.19	3.35	3.60
N ₃	0.89	2.15	-	2.12	2.50	2.65	2.70
NO ₂	1.54	2.00	-	1.02	1.43	1.90	2.32

EOM equation of motion approach

flexible basis sets needed (extensive basis sets)

HF, HFS underestimate EA_{ad} : lack of correlation is more crucial (destabilizing) for A^- than A^0

A^- has one more electron pair than A CISD, EOM inclusion of electron correlation (explicit) greatly improves EA_{ad} , DFT based LDA also

LDA/NL further improves: local correlation and nonlocal correlation needed comparable with ab-initio (CISD and EOM) but much more accurate.

Miscellaneous

Electron density from approximate DFT more adequate than HF density

dipole moments and polarizabilities of H_2O
(atomic units)

	LDA	HF	CI	CEPA-1	expt
μ_z	0.721	0.787	0.785	0.723	0.728
α_{xx}	9.403	7.83	9.02	9.59	9.26
α_{yy}	10.15	9.10	9.84	9.81	10.01
α_{zz}	9.25	8.36	9.33	9.64	9.62

Calculated dipole moments in Debye

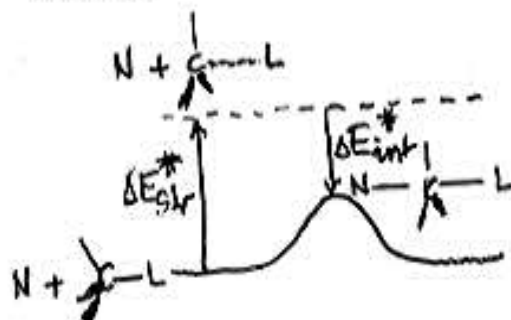
	LDA	LDA/NL	HF	expt
CO	-0.174	-0.153	0.33	-0.11
CS	2.107	2.014	1.26	1.98
Lit	5.65	5.74	6.77	5.83
HF	1.86	1.80	1.98	1.82

LDA much better results than HF, similar to CEPA-1 (Configuration interaction)

polarizabilities (HFS) also OK. Introduction of non-local exchange and correlation has small but important contribution.

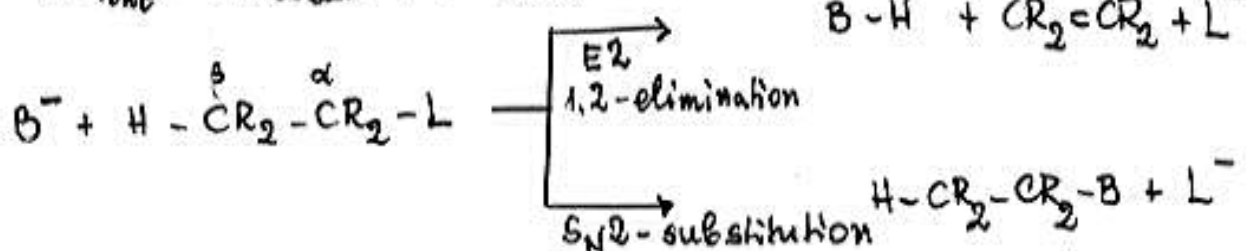
Conclusion: μ and α are accurately represented; in addition to accurate vibr. frequencies we are also able to calculate accurate IR and Raman intensities.

Reaction mechanisms: the activation strain model

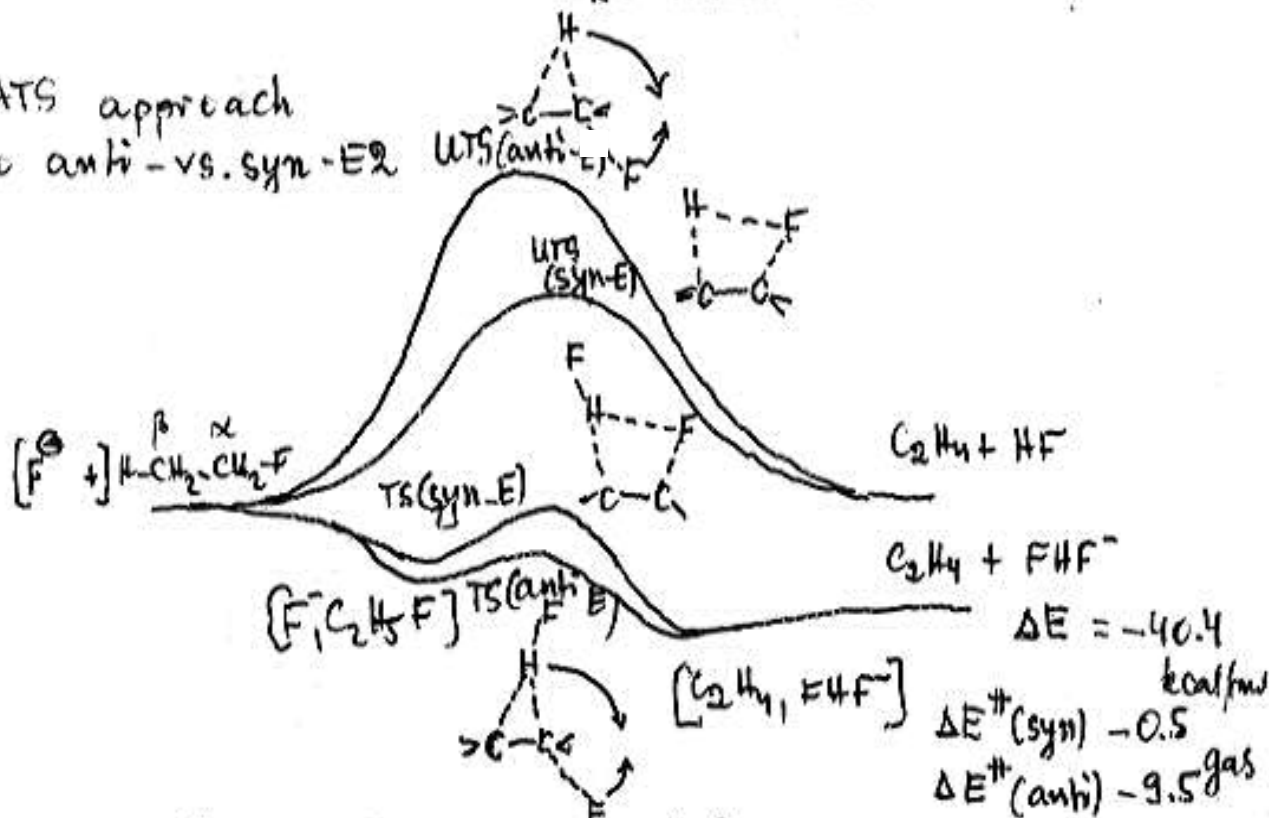


The activation strain
- TS interaction (ATS)

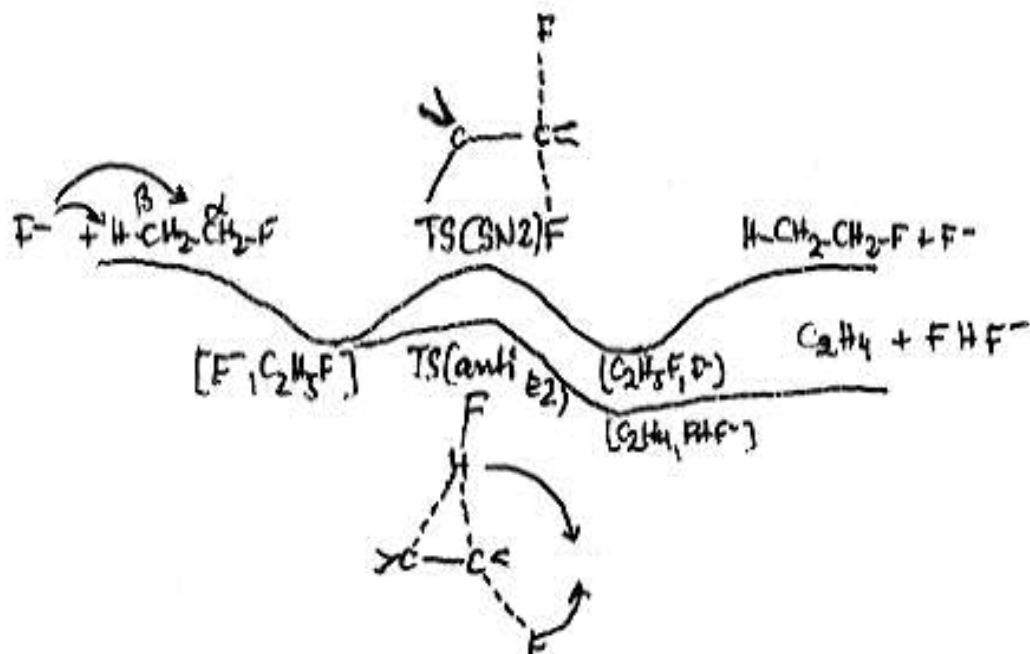
$$\Delta E_{int}^* = \Delta V_{elstat} + \Delta E_{pauli} + \Delta E_{oi}$$



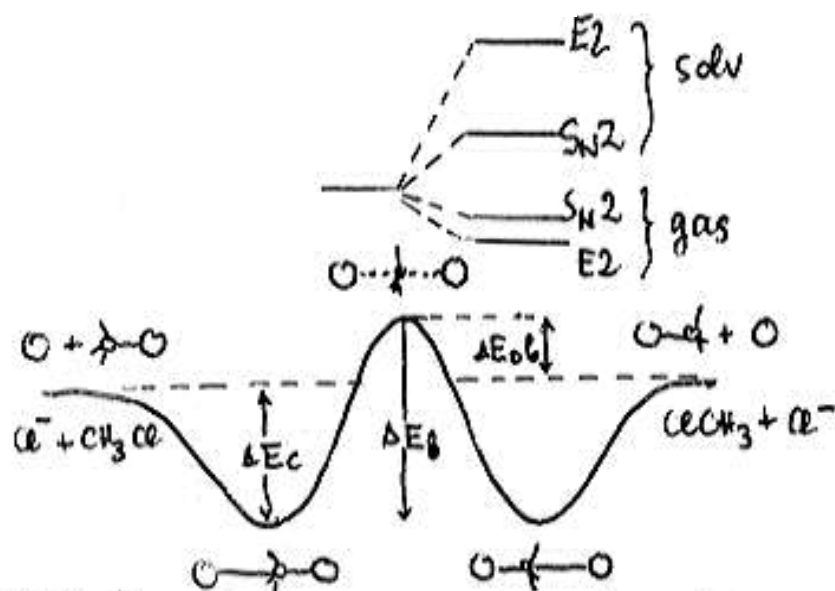
ATS approach to anti- vs. syn-E2



	$F^- + C_2H_5F$ E2	SN2
gas phase	$\Delta E^\ddagger = -9.5$	-0.5
monosolvated	$\Delta E^\ddagger = 31.6$	23.0
dissolved	$\Delta E^\ddagger = 54.4$	34.4



Reaction energy profiles to SN2 vs E2 competition in the gas phase



G-311 + G (d,p) gas phase reaction exp	Zero-point vibr. included			Zero-point vibr. included	
	G2	HF	BVWN	BLYP	B3LYP
ΔE_c	-12 ± 2	-11	-9	-10	-10
ΔE_{ob}	$3/1 \pm 1$	3	7	-6	-2
ΔE_0	13 ± 2	13	16	5	8

TDDFT

review:

A. Dreuw, M. H. Gordon

Chem. Rev. 2005, 105, 4009Runge-Gross Theorem

time-dependent analogue of the first Hohenberg-Kohn theorem;

The exact, time dependent electron density $\rho(r, t)$ determines the time dependent external potential $V(r, t)$, up to a spacially time-dependent function $C(t)$

$$V(r, t) = \sum_i^N \hat{v}(r_i, t) - \text{one particle potentials}$$

$$AX = \omega^2 X$$

$$A_{ia, j\ell} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (ia|j\ell) + (ia|f_{xc}|j\ell)$$

i, j correspond to occupied orbitals

a, ℓ correspond to virtual orbitals

exchange
correlation
kernel

$$(ia|j\ell) = \iint d^3r d^3r' (\phi_i^*(r) \phi_a(r) \phi_j(r') \phi_\ell^*(r')) / |r-r'|$$

$$(ia|f_{xc}|j\ell) = \int d^3r d^3r' \phi_i^*(r) \phi_a(r) \frac{\delta^2 E_{xc}}{\delta \rho(r) \delta \rho(r')} \left\{ \phi_\ell^*(r') \phi_j(r') \right\}$$

\hookrightarrow corresponds to the response of the chosen XC functional, which replaces the HF exchange potential; in the ALDA approximation

adiabatic local density approximation the non local (in time) time dependent XC kernel is replaced

with a time-independent local ene, based on the assumption, the density varies only slowly with time.

$$V_{xc}[\rho(\vec{r}, t)] = \frac{\partial A_{xc}[\rho]}{\partial \rho(\vec{r}, t)} \approx \frac{\partial E_{xc}[\rho]}{\partial \rho_t(\vec{r})} = V_{xc}[\rho_t(\vec{r})]$$

A_{xc} exchange correlation action

$$A = \int_{t_0}^{t_1} dt \langle \psi(r, t) | i \frac{\partial}{\partial t} - \hat{H}(r, t) | \psi(r, t) \rangle$$

Runge-Gross theorem

$$A[\rho] = \int_{t_0}^{t_1} dt \langle \psi[\rho](r, t) | i \frac{\partial}{\partial t} - \hat{H}(r, t) | \psi[\rho](r, t) \rangle$$

The basic equation of TDFT

$$\boxed{AX = \omega^2 X}$$

The dimension of A : $N_{\text{virt}} \times N_{\text{occup}}$

direct diagonalization is not possible

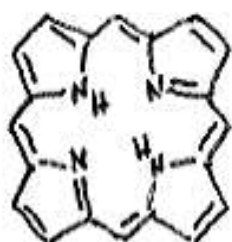
Davidson procedure is invoked to obtain a few lowest excitation energies and oscillator strengths of each irrep

oscillator strengths are calculated from the eigen vectors X

A contains information (Coulomb, XC terms) needed for the polarizability tensor as well

average dipole polarizability and its frequency dependence (determined by Cauchy coefficients).

ADF Response
module



FBP free base porphyrin

Fe^{II} hemin hemoglobin
Co^{III} vitamin B₁₂

Gouterman four-orbital model

	TDDFT (BP86/ALDA)	ΔE (eV)	f osc. strength
	TDDFT ΔE	f	exp. f (exp)
1 ¹ B _{3u}	2.16	0.01	1.98-2.02 (Q _x) 0.01
1 ¹ B _{2u}	2.29	0.0005	2.33-2.42 (Q _y) 0.06
2 ¹ B _{3u}	3.01	0.04	3.13-3.33 (B) 1.15
2 ¹ B _{2u}	2.98	0.1338	-
3 ¹ B _{2u}	3.41	0.8962	3.65 (N) < 0.1
3 ¹ B _{3u}	3.47	0.7283	
4 ¹ B _{3u}	3.77	0.1688	4.25 (L) ~ 0.1
4 ¹ B _{2u}	3.76	0.1272	

TM: Mg²⁺, Ni²⁺, ect. Zr⁴⁺ non-linear optical properties

Functionals in use:

SVWN Slater - Vosko - Wilk - Nussair

gradient-corrected GGA, NL - non-local:

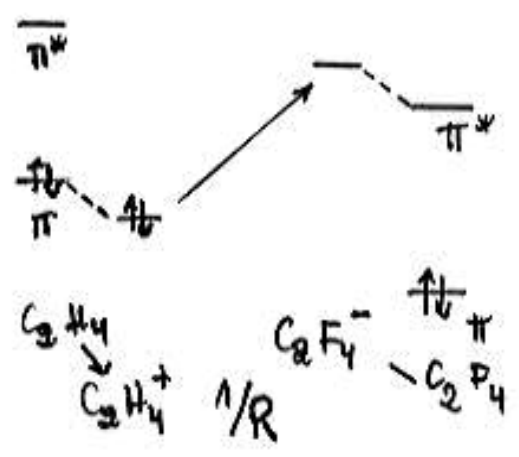
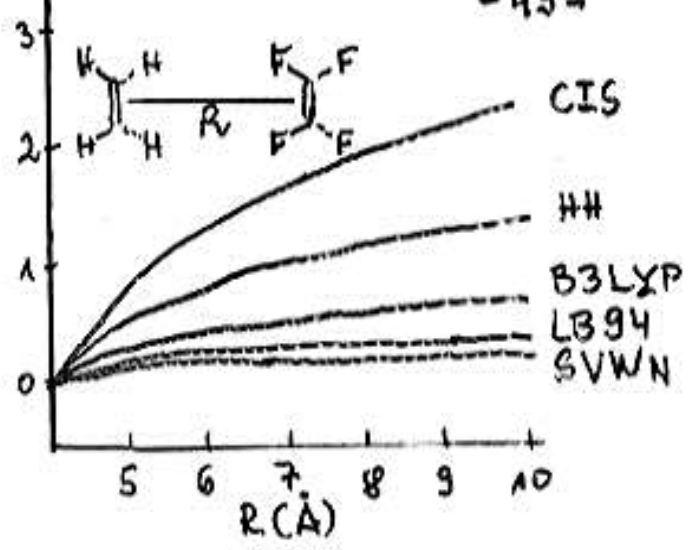
BLYP - Becke - Lee - Yang - Parr
(X) (C)

PBE Perdew - Burke - Ernzerhof

BP86 Becke - Perdew ; PW91 - Perdew - Wang 1991
(X) (C)

B3LYP Becke3 - Lee - Yang - Parr

↳ the most popular



Properties and Limitations:

- 1) TDDFT results sensitive to choice of XC funct. check in comparison with WV based benchmark, or experiment
- 2) yields accurate results for valence excited states with ΔE below IE

typical error 0.1-0.5eV comparable to high-level correlated EOM-CCSD or CASPT2 eq. of motion

to get this one needs to include large sets of virtual orbitals

- 3) RI (pure functionals) reduces the comp. costs $N^4 \rightarrow N^3$

$$1 = \sum |\varphi_i\rangle \langle \varphi_i|$$

up to 3000 basis functions (200 first row atoms) (standard)

4000 Basis funct. (300 atoms) RI

4) Reason for the accuracy: (0.1-0.5eV)

$$\Delta E_{i \rightarrow a}^{KS} \approx \epsilon_a^{KS} - \epsilon_i^{KS} : \text{leading term of}$$

the diagonal elements of matrix A

virtual KS ϵ_a^{KS} evaluated for N-electr. system

correspond more to the single particle energy of an excited electron: $\begin{matrix} \text{v-el.} \\ \vdots \\ \dots \end{matrix} (N-1) \text{ occ.}$

HF: virtual orbital energies evaluated for $N+1$ particles

$$\Delta E_{i \rightarrow a}(\text{HF}) \gg \Delta E_{i \rightarrow a}(\text{KS})$$

5) TDDFT has severe problems for:

- Rydberg states

- valence states of molecules with extended π -systems

- doubly excited states

- charge transfer excited states (see example above)

6) Rydberg states; extended π -systems:

wrong long range behaviour of current standard XC-functionals, decay faster than $1/r$ (electr. nucl. distance)

Leewen-Baerends (LB94)

statistical averaging of orbital potentials (SAOP)

local exact exchange potentials \rightarrow improved Ryd. state exc. energies

7) States with substantial double excitation character cannot be treated within linear response theory in the ALDA approximation exchange-correlation kernel

$$K = \frac{\partial^2 E_{xc}}{\partial \rho(\mathbf{r}) \partial \rho(\mathbf{r}')} \text{ does not depend on the energy (frequency)}$$

but K is strongly frequency dependent close to double excitation.

example! $Ni(H_2O)_6^{2+}$ 3A_2 gr. state $\rightarrow \frac{1}{2} e_g$
 another theory of description! ${}^3T_2 (t_{2g} \rightarrow e_g)$ $\frac{1}{2} t_{2g}$
 ${}^3T_1 (t_{2g} \rightarrow e_g)$
 ${}^3T_1 (t_{2g}^2 e_g^2 \rightarrow t_{2g}^4 e_g^4)$

8) Since 2002

analytic first geometric derivatives of excitation energies given by hybrid expression of TDDFT; allow efficient calculation of first order properties of excited states: equilibrium geometries
 dipole moments
 harmonic frequencies

programs: CAD-PAC

TURBOMOLE