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The use of Symmetry-Adapted Perturbation Theory (*SAPT*) Methods for the Decomposition of Hydrogen Bonding and other Intermolecular Interactions

José A. Sordo

Theoretical methods can be helpful to *COMPLEMENT* the experimental work on weakly-bound systems

Ab initio methodologies: $A \cdots B$

Supermolecular Approach

(variational theory)

$E_{int} = E(AB) - E(A) - E(B)$

SAPT Approach

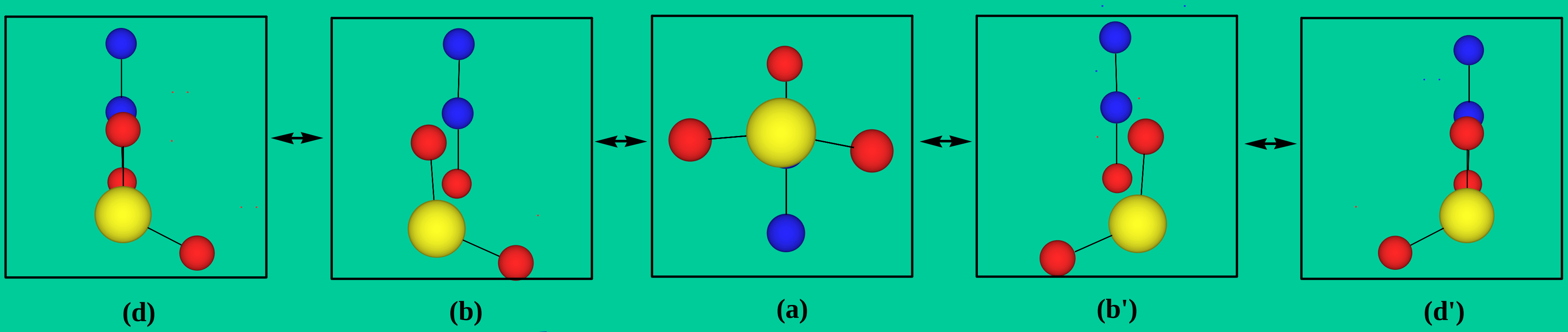
(perturbation theory)

E_{int}: Direct evaluation

Prof. Kuczkowski's group (J. Phys. Chem. A 2000, 104, 4968)

- $N_2O \cdots SO_2$ lacks a symmetry plane.
- Tunneling motion splits the transitions into doublets.

Dynamic definition of the $N_2O \cdots SO_2$ dimer



Cluster nonrigidity

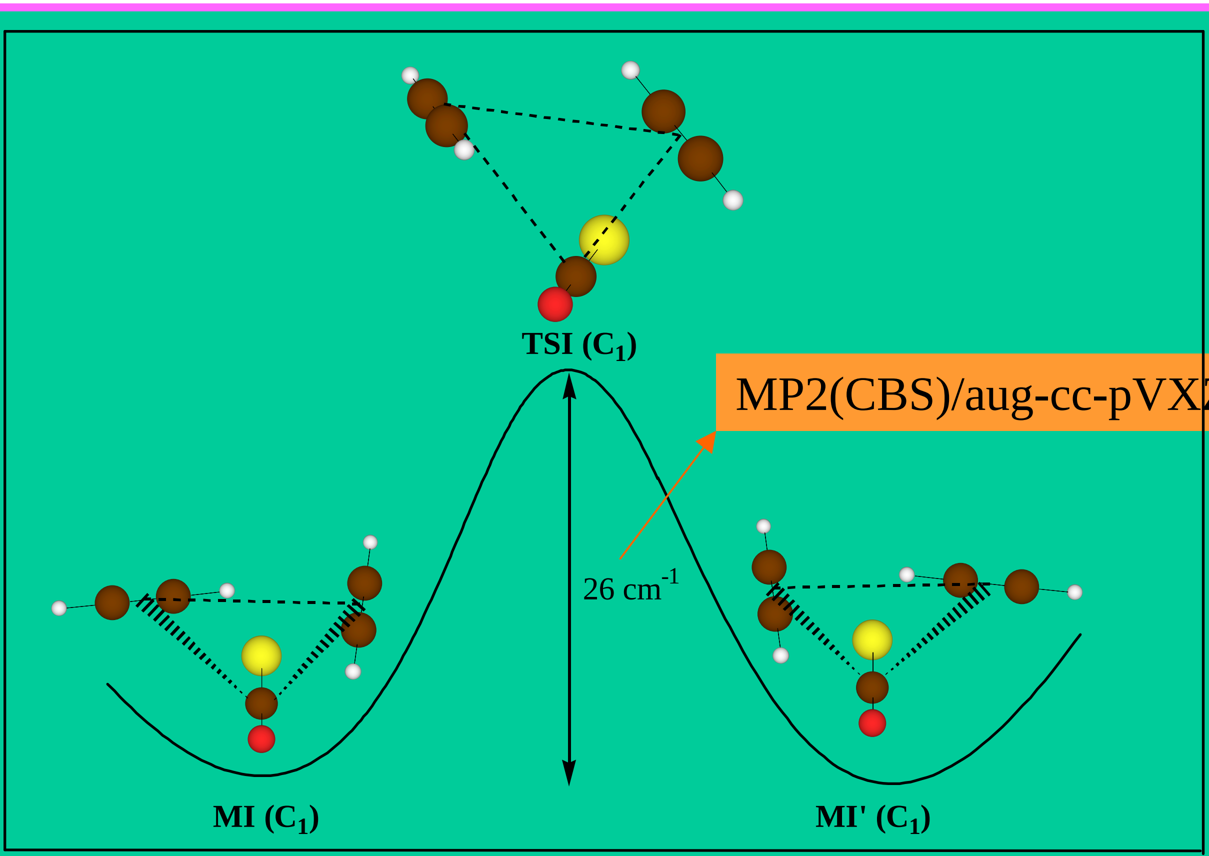
H. Valdés, J.A. Sordo J. Phys. Chem. A 2004, 108, 2062

$(HCCH)_2\cdots OCS$

DYNAMICS OF INTERCONVERSION

S.A. Peebles, R.L. Kuczkowski J. Mol. Struct. (Theochem) 2000, 500, 391

- Failure in observing some isotopomers ⇒ Structure cannot be resolved.
- Responsible: High amplitude motions sensitive to the masses of the HCCH monomers



MP2(CBS)/aug-cc-pVXZ (X = D, T, Q)

Interconversion tunneling motion perturbing the spectrum

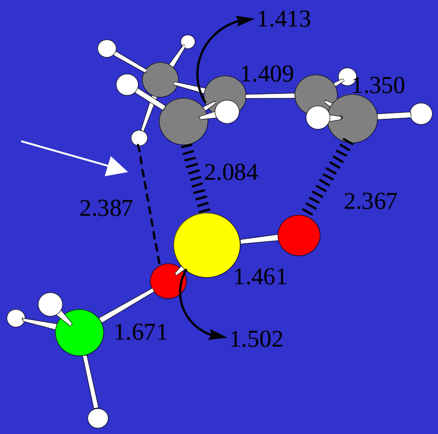
H. Valdés, J.A. Sordo Chem. Phys. Lett. 2004, 387, 428

Prof. Desiraju's group (Acc. Chem. Res. 1991, 24, 290)

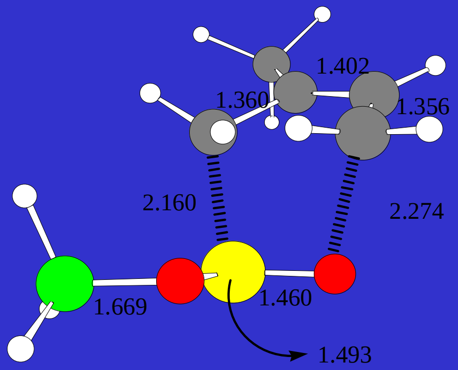
Isoprene + SO_2 Diels-Alder cycloaddition

ENDO preference: Alder's rule (B.Deguin, P. Vogel J. Am Chem. Soc. 1992, 114, 9210)

C-H···O interaction



ENDO



EXO

D. Suárez, T.L. Sordo, J.A. Sordo J. Am. Chem. Soc. 1994, 116, 763

Prof. Legon’s group (Chem. Soc. Rev. 1987, 16, 467)

Legon-Millen’s rules

Legon and Millen proposed the two following rules, based on electrostatic arguments, in order to make geometry predictions on hydrogen bonded complexes (B···HX):

- HX interacts either through non-bonding pairs (n) or through π pairs existing in B.
- Should B contain both n and π pairs, the former determine the geometry.

Sometimes these rules are VIOLATED (Legon *et al*. Chem. Soc. Faraday Trans. 1998, 94, 1565)

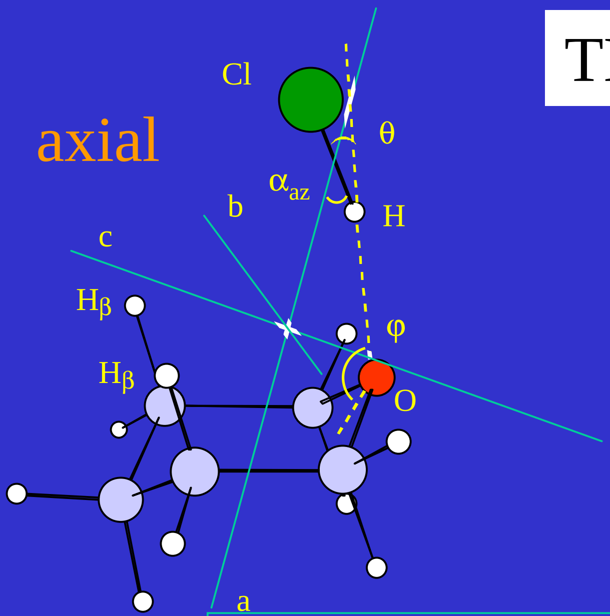
(theoretical justification)

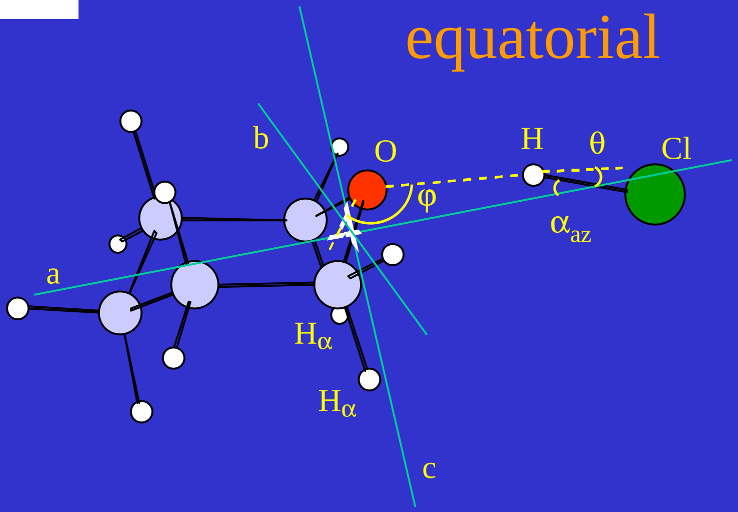
H. Valdés, V.M. Rayón, J.A. Sordo Chem. Phys. Lett. 1999, 309, 265

Prof. Alonso’s group (Angew. Chem. Int. Ed. 1999, 38, 1772)

The **FIRST** experimental observation of axial and equatorial conformers of hydrogen bonded complexes was reported in 1999

THP···HCl





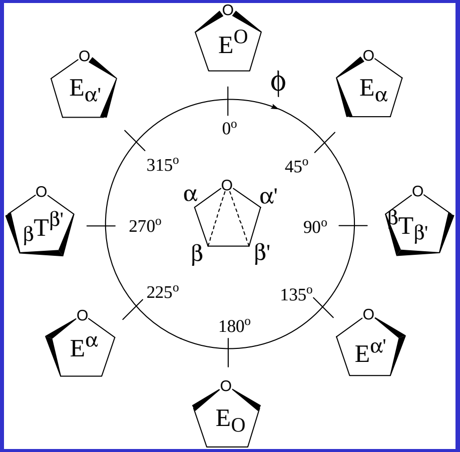
The axial conformer is more stable

(theoretical justification)

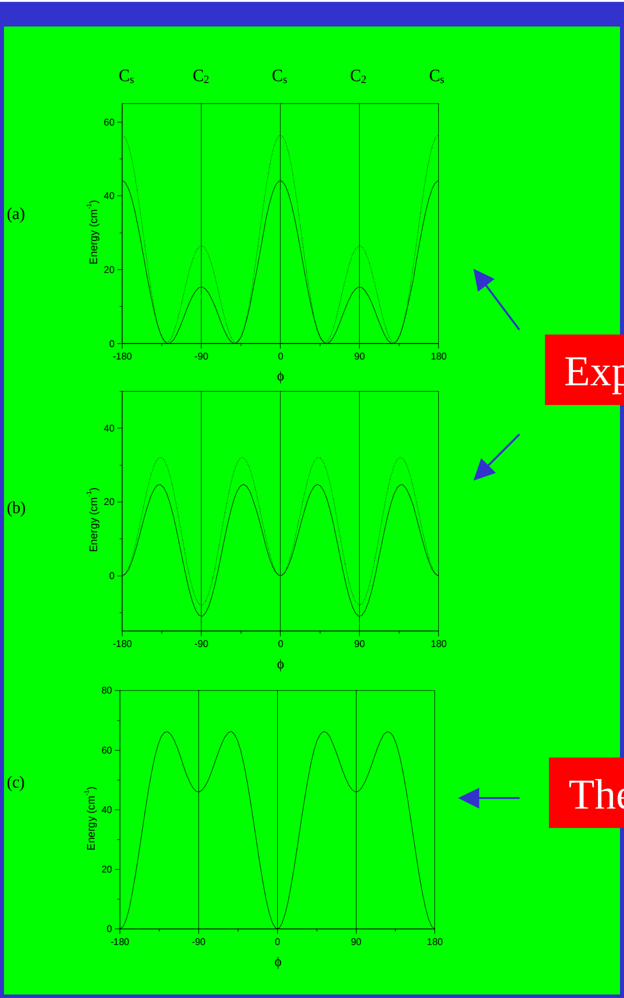
H. Valdés, J.A. Sordo Chem. Phys. Lett. 2001, 333, 169

Prof. Caminati’s group (J. Chem. Phys. 1999, 111, 7871)

pseudorotation



THF



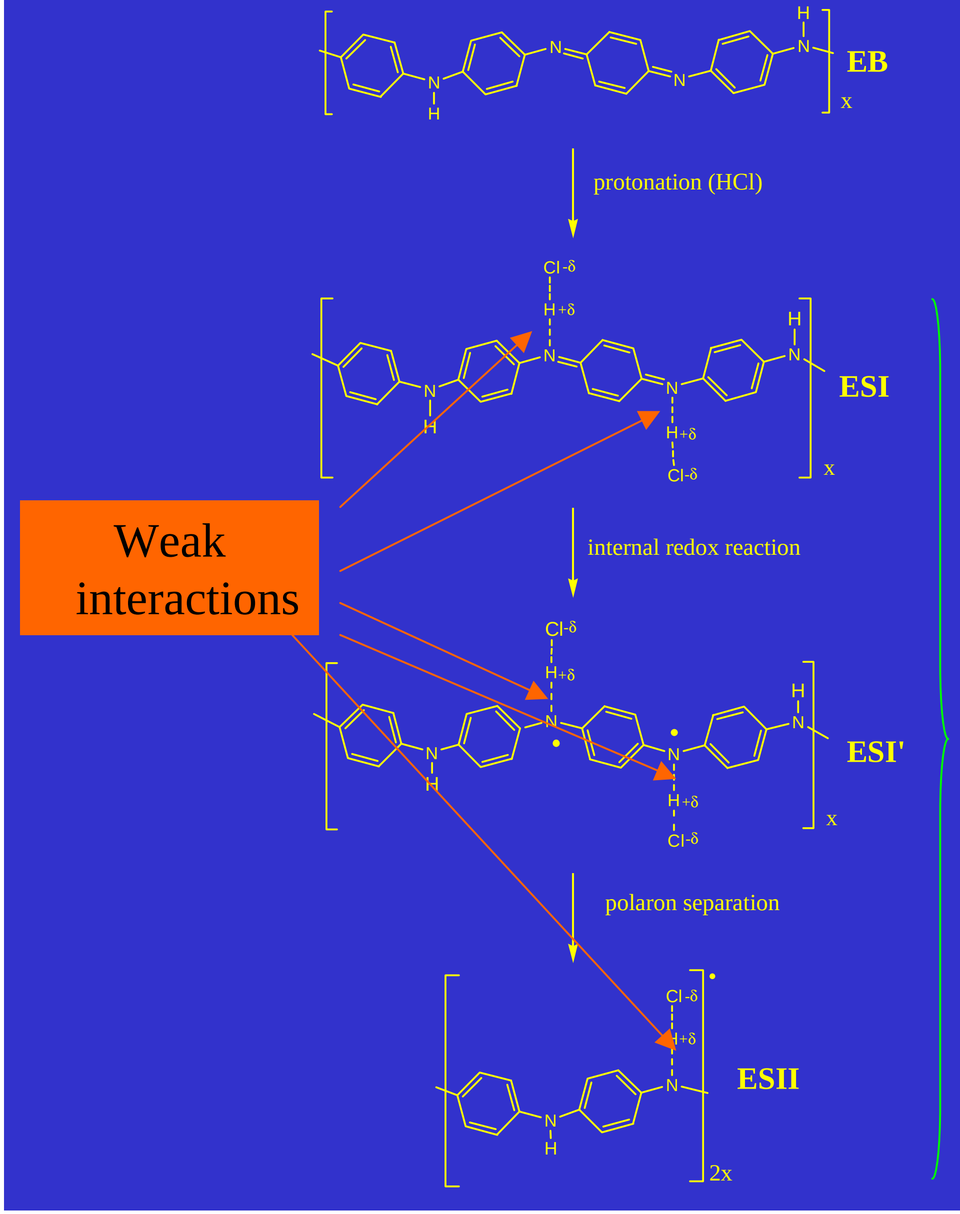
Experimental results

Theoretical prediction

V.M. Rayón, J.A. Sordo J. Chem. Phys. 2005, 122, 204303

ROLE OF WEAKLY-BOUND SYSTEMS IN CHEMICAL REACTIVITY

Heeger-MacDiarmid-Shirakawa (Nobel Prize, 2000) Phys. Rev. Lett. 1987, 59,1464



Emeraldine base

$10^{-10}\ \Omega^{-1}\cdot cm^{-1}$

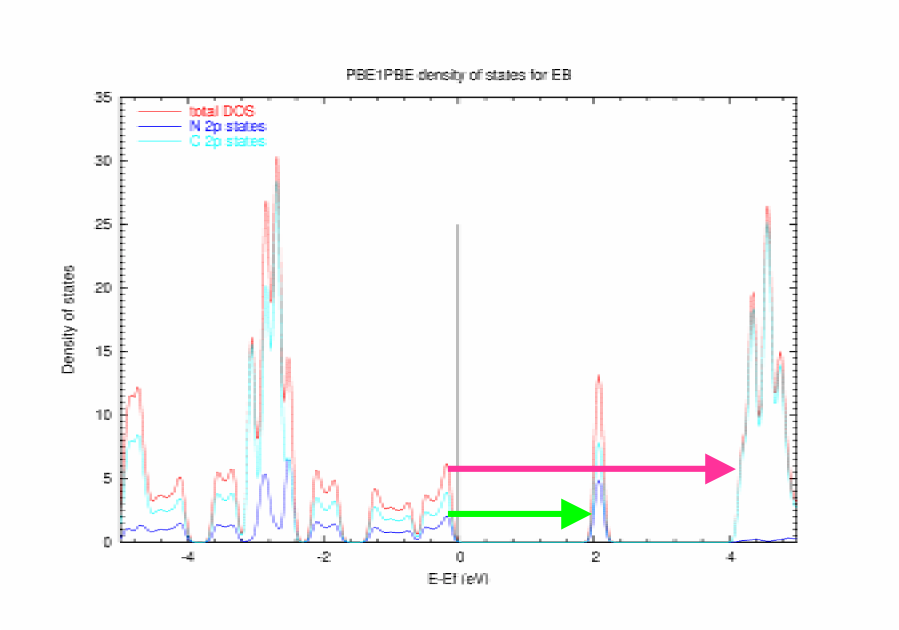
proton-doping (HCl)

Emeraldine salt

$10^{2}\ \Omega^{-1}\cdot cm^{-1}$

(Copper: $10^{6}\ \Omega^{-1}\cdot cm^{-1}$)

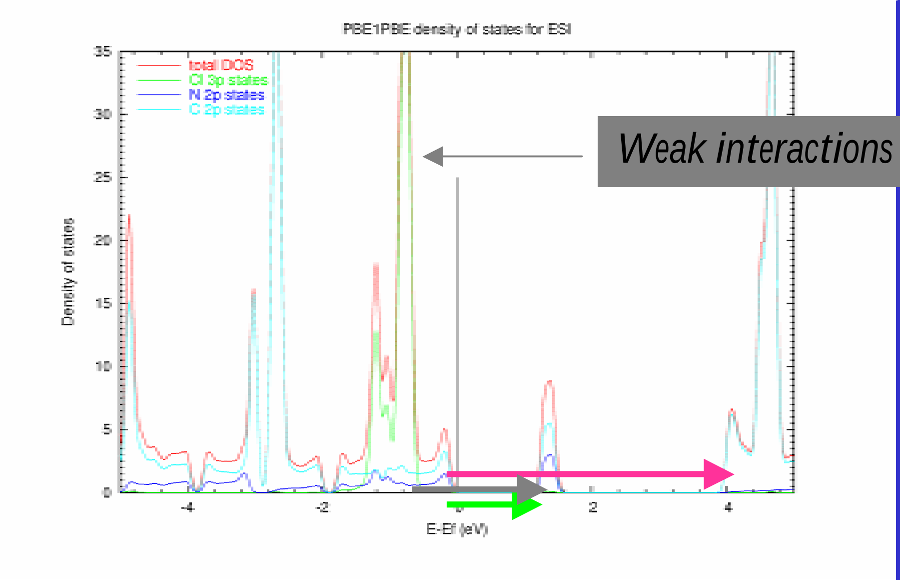
I. Prodan, J.A. Sordo, G.E. Scuseria, R.L. Martin J. Chem. Phys. 2005, 123, 014703



EB

PBC methodology

Theor	Exp
2.1 eV →	2.0 eV
4.0 eV →	3.8 eV



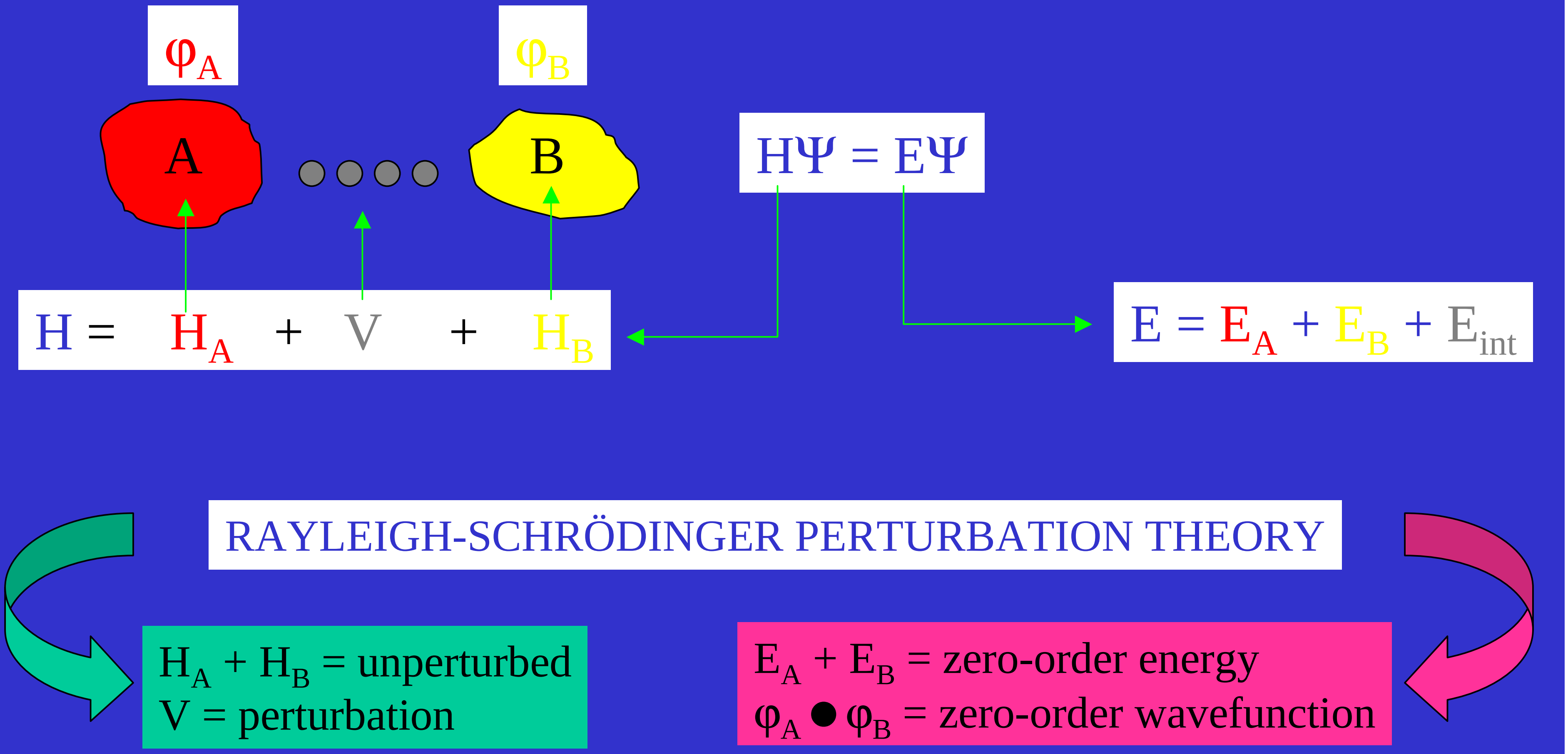
Weak interactions band

ESI

Theor	Exp
1.4 eV →	1.5 eV
2.0 eV →	2.8 eV
4.0 eV →	4.1 eV

A. Varela, G.E. Scuseria, J.A. Sordo J. Am. Chem. Soc. 2005, 127, 11318

SAPT METHODOLOGY



$H = H_A + V + H_B$

$H\Psi = E\Psi$

$E = E_A + E_B + E_{int}$

RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

$H_A + H_B$ = unperturbed
V = perturbation

$E_A + E_B$ = zero-order energy
$\varphi_A \bullet \varphi_B$ = zero-order wavefunction

PROBLEMS:

(a) φ_A, φ_B unknown (intramolecular correlation)
(b) $\varphi_A \bullet \varphi_B$ violates the Pauli exclusion principle

SOLUTION: Szalewicz et al. Chem. Rev. 1994, 94, 1887

(a) Appropriate partitioning scheme

$$H = F_A + F_B + W_A + W_B + V$$

F = Fock operators (unperturbed Hamiltonian with known eigenfunctions: Hartree-Fock wavefunction)

W = Moeller-Plesset operators (intramolecular correlation)

V = Intermolecular interaction

⇒ Double perturbation theory: $\lambda W + \zeta V$

(b) Symmetry-adapted, $A\,\varphi_A\varphi_B$, wavefunctions

SAPT METHODOLOGY

$$E_{\text{int}} = E^{(1)}_{elec} + E^{(1)}_{exch} + E^{(2)}_{ind} + E^{(2)}_{dis} + E^{(2)}_{exch} + \cdots$$

elec, ind, dis: $\varphi_A \varphi_B$
exch: $A\, \varphi_A \varphi_B$

elec, ind: Classical
dis, exch: Quantum

Notation: $$E^{(n)}_{\alpha} = \sum_{l=0}^{\infty} E^{(nl)}_{\alpha}$$

n → *interaction* (V)
l → *intramolecular correlation* (W)

Levels of Accuracy

HF → $$E_{\text{int}}(HF) = E^{(10)}_{elec} + E^{(10)}_{exch} + E^{(20)}_{ind} + E^{(20)}_{exch-ind} + \delta E^{HF}_{\text{int}}$$

MP2 → $$E_{\text{int}}(SAPT2) = E_{\text{int}}(HF) + E^{(12)}_{elec} + E^{(11)}_{exch} + E^{(12)}_{exch} + E^{(22)}_{ind} + E^{(22)}_{exch-ind} + E^{(20)}_{dis} + E^{(20)}_{exch-dis}$$

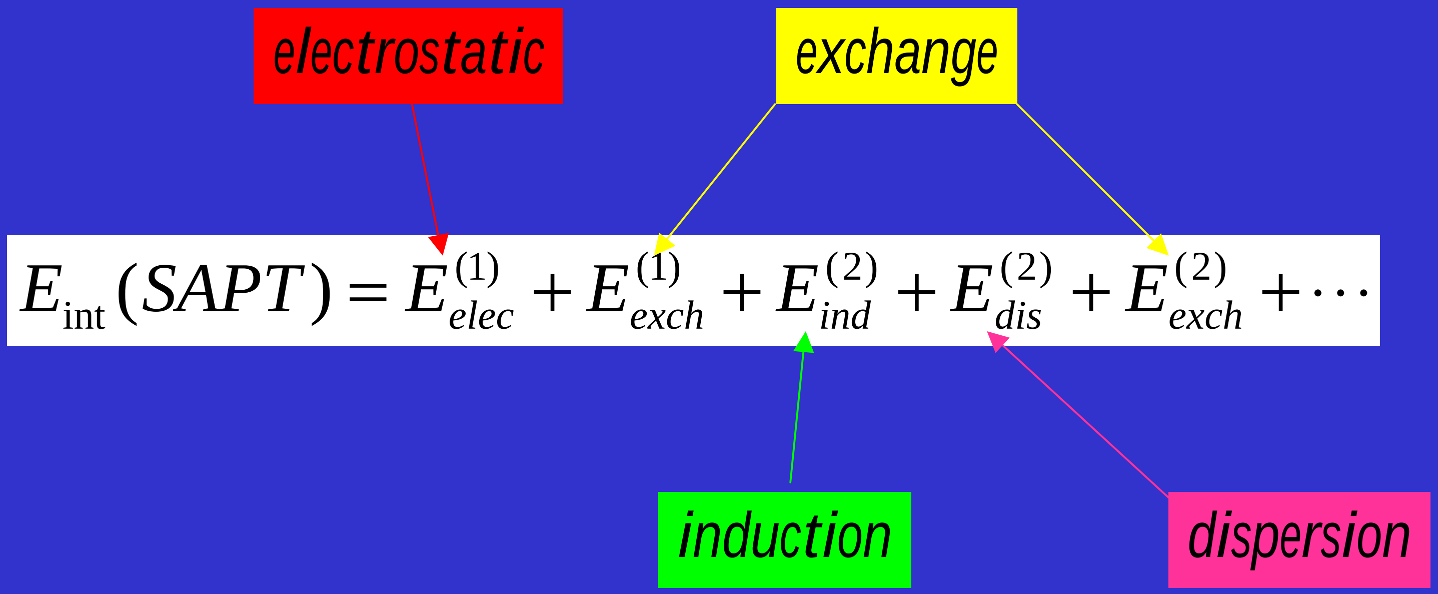
MP4 → $$E_{\text{int}}(SAPT4) = E_{\text{int}}(SAPT2) + E^{(13)}_{elec} + E^{(13)}_{exch} + \cdots + E^{(1\infty)}_{exch} + E^{(21)}_{dis} + E^{(22)}_{dis}$$

SAPT METHODOLOGY

SAPT allows for the *INTERPRETATION* of the mechanisms

of formation of molecular associations in terms of the

four FUNDAMENTAL FORCES in Chemistry



electrostatic

exchange

$$E_{\text{int}}(SAPT) = E^{(1)}_{elec} + E^{(1)}_{exch} + E^{(2)}_{ind} + E^{(2)}_{dis} + E^{(2)}_{exch} + \cdots$$

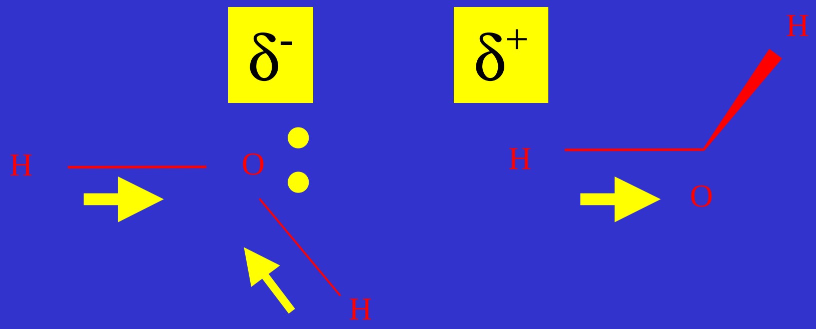
induction

dispersion

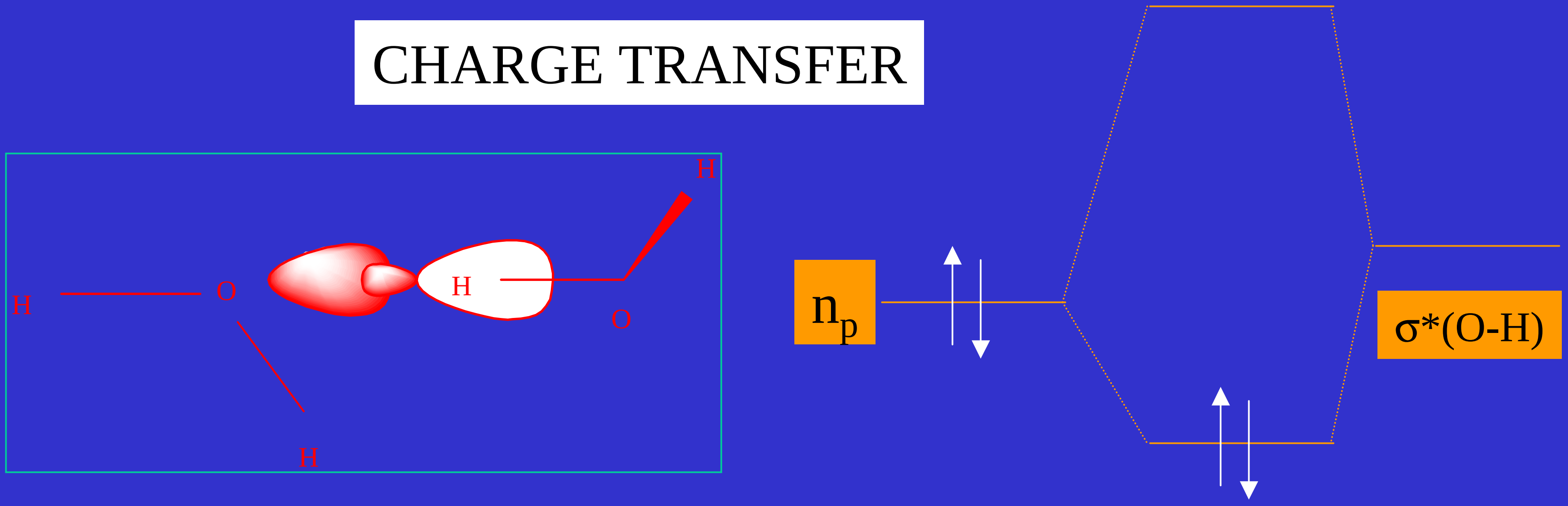
IMPORTANCE OF ELECTROSTATIC AND INDUCTION FORCES

ELECTROSTATIC INTERACTIONS

(Legon-Millen's rules)

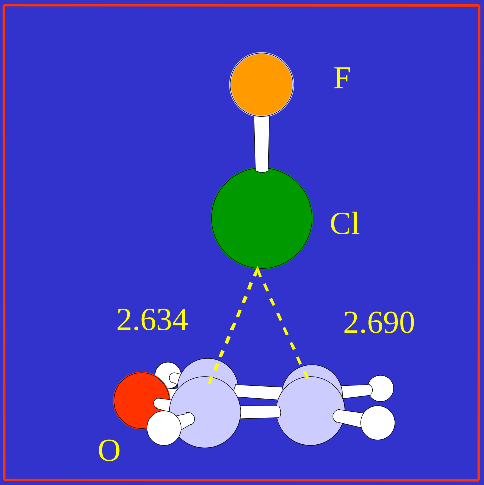


CHARGE TRANSFER

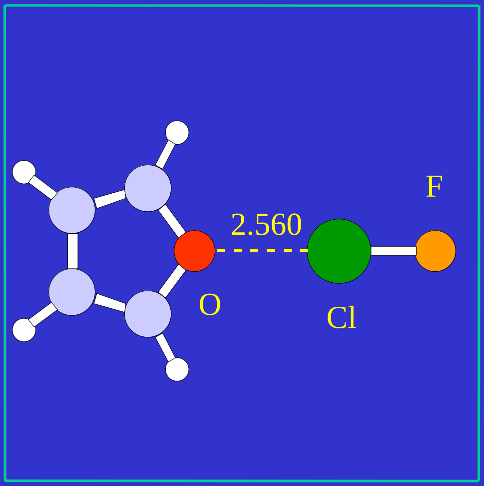


Violation of the Legon-Millen's rules

π interaction



n interaction



Experiment

Prediction

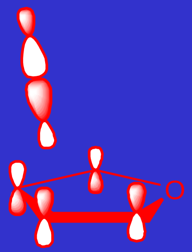
Legon *et al*. Chem. Soc. Faraday Trans. 1998, 94, 1565

Furan ··· ClF

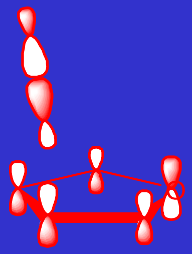
Justification in terms of charge transfer

SAPT suggests the induction forces to be more relevant in the π complex

π interaction $c_i = 0.1\text{-}0.2$

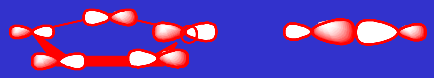


HOMO (Furano) ⟶ LUMO (ClF)

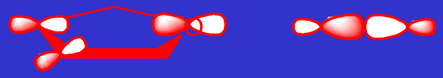


NHOMO (Furano) ⟶ LUMO (ClF)

n interaction $c_i = 0.04\text{-}0.06$



N'HOMO (Furano) ⟶ LUMO (ClF)



N"HOMO (Furano) ⟶ LUMO (ClF)

H. Valdés, V.M. Rayón, J.A. Sordo Chem. Phys. Lett. 1999, 309, 265

EXCHANGE AND DISPERSION CONTRIBUTIONS

System	ΔE(theor)[a]	CT(exp)[b]	CT(theor)[a]	k_σ(exp)[b]	k_σ(theor)[a]
$H_3P\cdots BrCl$	-7.2	0.101 e	-50.1	11.56(7)	11.9
$H_3N\cdots BrCl$	-11.2	0.064 e	-35.2	26.6(3)	31.6

ΔE y CT(theor) in kcal/mol, k_σ en $N \cdot m^{-1}$

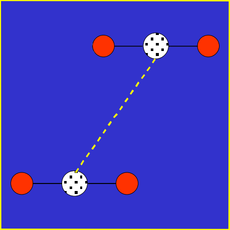
[a] H. Valdes, J.A. Sordo Chem. Phys. Lett. 2003, 371, 386

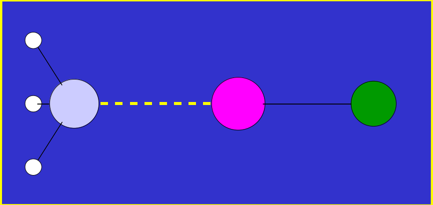
[b] A. C. Legon *et al.* J Chem. Phys. 2000, 113, 5278

⇩

How can one justify the greater strength of the $H_3N\cdots BrCl$ complex?

IMPORTANCE OF EXCHANGE AND DISPERSION FORCES





	vdW	X-bond	
E (cm^{-1})	$CO_2 \cdots CO_2$	$H_3P \cdots BrCl$	$H_3N \cdots BrCl$
$E_{pol}(1)$	-559	-10612	-11441
$E_{ind}(2)$	-394	-45757	-31116
$E_{dis}(2)$	-707	-4028	-3263
$E_{exc}(1)$	920	18768	16172
$E_{exc}(2)$	353	40676	27752
$E_{int}(HF)$	-9	-30	-1563
$E_{int}(corr)$	-398	-2411	-2289
$E_{int}(SAPT)$	-407	-2441	-3851

X-bond >> vdW

vdW >> X-bond

Exchange forces responsible for the greater strength of $H_3N \cdot BrCl$

H. Valdés, J.A. Sordo Chem. Phys. Lett 2003, 371, 386

SUMMARY

Theoretical methods can be helpful tools to *COMPLEMENT* the experimental work on weakly-bound systems

SAPT allows for the *INTERPRETATION* of the mechanisms of formation of molecular associations in terms of the four *FUNDAMENTAL FORCES* in Chemistry

2005

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