Block-Localized Wavefunction (BLW) Method and Its Applications

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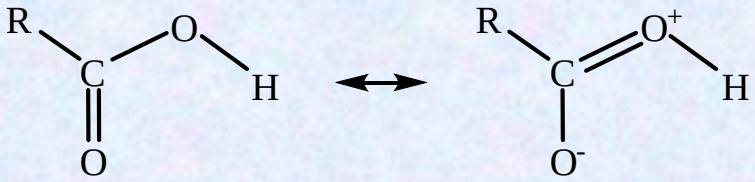
Introduction

Lewis structure:

A molecule can be visualized with a dot diagram where each pair of electrons (dots) locates on one atom (lone pair) or between two atoms (chemical bond).

Resonance theory:

When one Lewis structure is not enough to describe the structure and properties of a molecule, more Lewis (often ionic) structures are called.



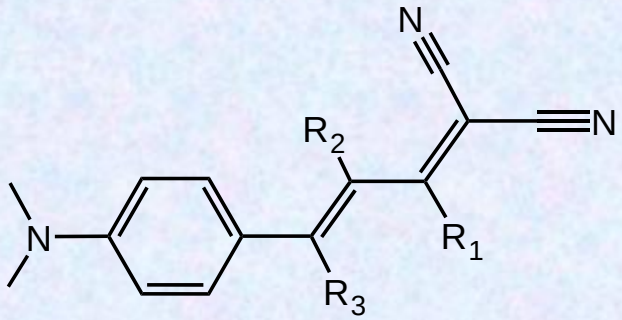
Resonance energy:

"obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure."

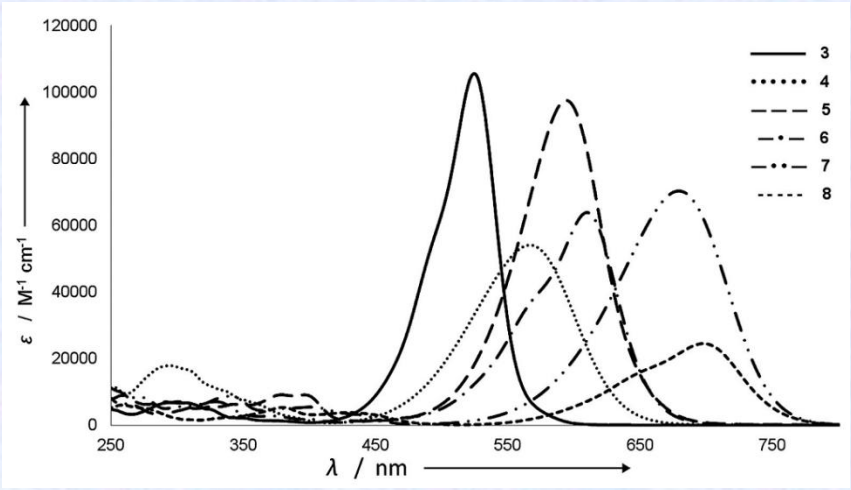
Wheland, *The Theory of Resonance*, John Wiley & Sons, New York, 1944.

Introduction

π-Conjugated donor-acceptor chromophores:

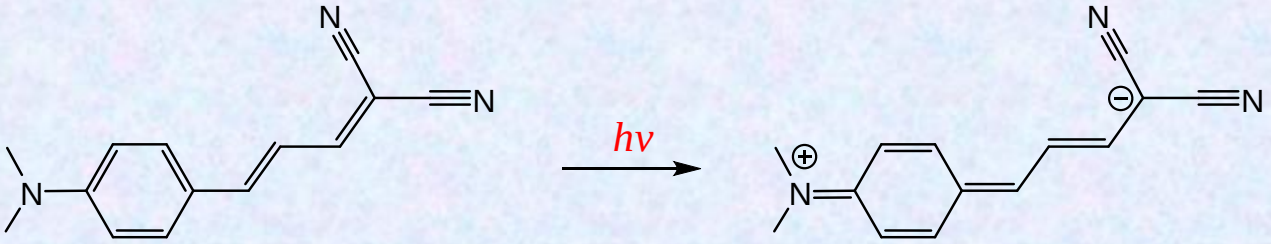


1: $R_1 = R_2 = R_3 = H$
2: $R_1 = CN, R_2 = R_3 = H$
3: $R_1 = H, R_2 = CN, R_3 = H$
4: $R_1 = R_2 = H, R_3 = CN$
5: $R_1 = R_2 = CN, R_3 = H$
6: $R_1 = H, R_2 = R_3 = CN$
7: $R_1 = CN, R_2 = H, R_3 = CN$
8: $R_1 = R_2 = R_3 = CN$



Tancini, et al. *Eur. J. Org. Chem.*, 2756-2765 (2012).

How to understand the intramolecular charge-transfer (ICT) in terms of donor, acceptor and π-conjugated spacer?



Introduction

Mulliken two-state theory (1952):

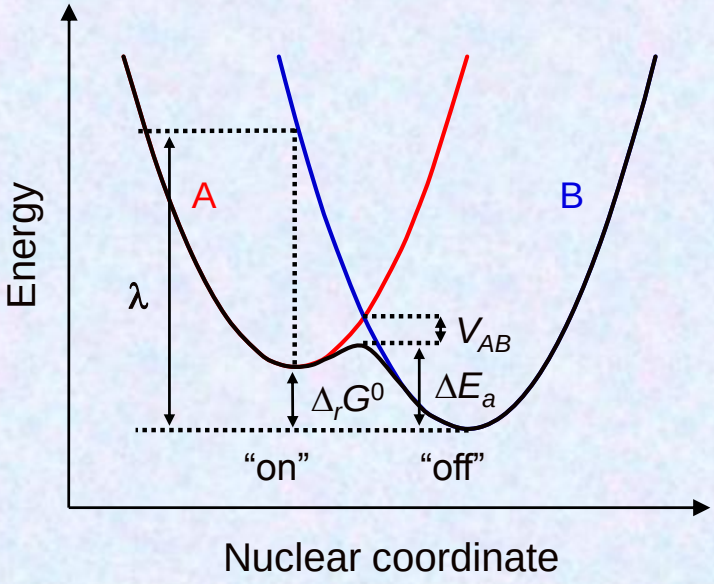
For charge-transfer (donor-acceptor complexes)

$$\begin{cases} \Psi_{GS} = c_a \psi_{D,A} + c_b \psi_{D^+A^-} \\ \Psi_{ES} = c_b \psi_{D,A} - c_a \psi_{D^+A^-} \end{cases}$$

$$H_{DA} = \left\langle \psi_{D,A} \middle| \hat{H} \middle| b\psi_{D^+A^-} \right\rangle$$

(**Assuming $S_{DA} = 0$**)

Marcus-Hush two-state theory (1963):



The rate constant for nonadiabatic ET reactions (i.e., $V_{AB} < 200\ cm^{-1}$)

$$k_{ET} = \frac{2\pi}{\hbar} |V_{AB}|^2 \left(\frac{1}{4\pi\lambda k_B T} \right)^{1/2} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right)$$

$$\lambda = \lambda_{int} + \lambda_s$$

Illustration of the Marcus-Hush two-state model.

Methodology: Constrained DFT (CDFT)

To study the electron transfer effect, both the non-ET and ET states better be defined explicitly.

Constrained density functional theory (CDFT) method

Kohn-Sham method

$$E[\rho] = 2\sum_{i}^{N/2}\left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle + \int v_n(\vec{r})\rho(\vec{r})d\vec{r} + J[\rho] + E_{xc}[\rho]$$

Adding a general constraint

$$\int_C \rho(\vec{r})d\vec{r} = \int w_C(\vec{r})\rho(\vec{r})d\vec{r} = N_C$$

$$\rightarrow \left[-\frac{1}{2}\nabla^2 + v_n(\vec{r}) + \int \frac{\rho(\vec{r}')}{\left|\vec{r} - \vec{r}'\right|}d\vec{r}' + v_{xc}[\rho](\vec{r}) + v_C w_C(\vec{r}) \right] \phi_i = \varepsilon_i \phi_i$$

Dederichs, Bluegel, Zeller, Akai, *Phys. Rev. Lett.*, 53, 2512-2515 (1984);
Wu, Van Voorhis, *Phys. Rev. A: At., Mol., Opt. Phys.*, 72, 024502 (2005).

Methodology: Valence Bond (VB)

Ab initio Valence Bond (VB) method

Heitler-London-Slater-Pauling (HLSP) function

$$\Psi_K = N_K \hat{A}\left[\phi_1(1)\phi_2(2)\cdots\phi_N(N)\prod_{(ij)} 2^{-1/2}[\alpha(i)\beta(j) - \beta(i)\alpha(j)]\prod_k \alpha(k)\right]$$

Software

XMVB – An ab initio non-orthogonal VB program.

HLSP in an alternative form:

$$\Psi_K = N_K \hat{A}\left(\varphi_{12}\varphi_{34}\cdots\varphi_{n-1n}\right)$$

where the bond function:

$$\varphi_{ij} = \hat{A}\left\{\phi_i\phi_j\left[\alpha(i)\beta(j) - \beta(i)\alpha(j)\right]\right\}$$

Methodology: Valence Bond (VB)

Approximate Valence Bond (VB) Methods:

GVB method:

$$\psi_K = \hat{A}\left\{\varphi_1^2\varphi_2^2\cdots\varphi_{n/2-1}^2\phi_i\phi_j[\alpha(i)\beta(j)-\beta(i)\alpha(j)]\right\}$$

Bond function method:

$$\varphi_{ij} = \hat{A}\left\{\phi_{ij}\phi_{ij}\alpha(i)\beta(j)\right\} \longrightarrow \boxed{\psi_K = \hat{A}\left\{\varphi_1^2\varphi_2^2\cdots\varphi_{n/2-1}^2\varphi_{n/2}^2\right\}}$$

One Slater determinant

Methodology: Block-Localized Wavefunction (BLW)

Block-localized wavefunction (BLW) Method

Mo, Peyerimhoff, *J. Chem. Phys.* 109(5), 1687-1697(1998).
Mo, Gao, Peyerimhoff, J. Chem. Phys. 112(13), 5530-5538(2000).
BLW-DFT: Mo, Song, Lin, *J. Phys. Chem. A* 111(34), 8291-8301 (2007).
Cembran, Song, Mo, Gao, JCTC, 5(10), 2702-2716(2009).

For a diabatic state with N electrons and M primitive orbitals which are partitioned into *k* subgroups, the BLW is

$$\Psi_I^{BLW} = \hat{A}\{\Phi_1\Phi_2\cdots\Phi_k\}$$

where

$$\Phi_i = \varphi_{i1}\alpha(1)\varphi_{i1}\beta(2)\varphi_{i2}\alpha(3)\cdots\varphi_{i\frac{n_i}{2}}\beta(n_i)$$

$$\varphi_{ij} = \sum_{\mu=1}^{m_i} C_{ij\mu}\chi_{i\mu}$$

Block-Localized Wavefunction (BLW)

Overlap integrals:

$$\left\langle \varphi_{ij} \middle| \varphi_{kl} \right\rangle = \begin{cases} \delta_{jl} & i = k \\ s_{jl}^{ik} & i \neq k \end{cases}$$

The difference between HF and BLW lies in the transformation matrix:

$$C^{BLW} = \begin{pmatrix} C_1 & 0 & \cdots & 0 \\ 0 & C_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & C_k \end{pmatrix} \qquad C^{HF} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1k} \\ C_{21} & C_{22} & \cdots & C_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ C_{k1} & C_{k2} & \cdots & C_{kk} \end{pmatrix}$$

Methodology: Block-Localized Wavefunction (BLW)

The energy for a diabatic state

$$E_I = \left\langle \Psi_I^{BLW} \mid \hat{H} \mid \Psi_I^{BLW} \right\rangle = \sum_{\mu,\nu} D_{\mu\nu}(h_{\mu\nu} + F_{\mu\nu})$$

where $D = C(C^+ SC)^{-1} C^+$

For the example of two-block case:

$$C = \begin{pmatrix} C_a & 0 \\ 0 & C_b \end{pmatrix} \rightarrow S = \begin{pmatrix} S_{aa} & S_{ab} \\ S_{ba} & S_{bb} \end{pmatrix}$$

By defining

$$S_a' = S_{aa} - S_{ab} D_b S_{ba} \qquad F_a' = \left(1_a \mid -S_{ab} D_b\right) F \begin{pmatrix} 1_a \\ -D_b S_{ba} \end{pmatrix}$$

$$\rightarrow \begin{cases} F_a' C_a = F_a' C_a L_a \\ C_a^+ S_a' C_a = 1_a \end{cases}$$

Gianinetti, E., Raimondi, R., Tornaghi, E. J. Int. J. Quantum Chem. 60, 157-166(1996).

Block-Localized Wavefunction (BLW)

First-order derivative of E_{BLW} with respect to $\{\boldsymbol{q}_i\}$:

$$\frac{\partial E_I}{\partial q_i} = 2\sum_{\mu\nu}^{m} d_{\mu\nu}\frac{\partial h_{\mu\nu}}{\partial q_i} + \sum_{\mu\nu\rho\sigma}^{m}[2d_{\mu\nu}d_{\rho\sigma} - d_{\mu\rho}d_{\nu\sigma}]\frac{\partial(\mu\nu\,|\,\rho\sigma)}{\partial q_i} - 2\sum_{\mu\nu}^{m} W_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial q_i}$$

Mo, Y. *J. Chem. Phys.* 119(3), 1130-1136 (2003).

BLW at the DFT level:

$$\boldsymbol{F}^{\alpha} = \boldsymbol{H} + \boldsymbol{J} + \boldsymbol{F}^{XC\alpha}$$

BLW-DFT has been ported to GAMESS.

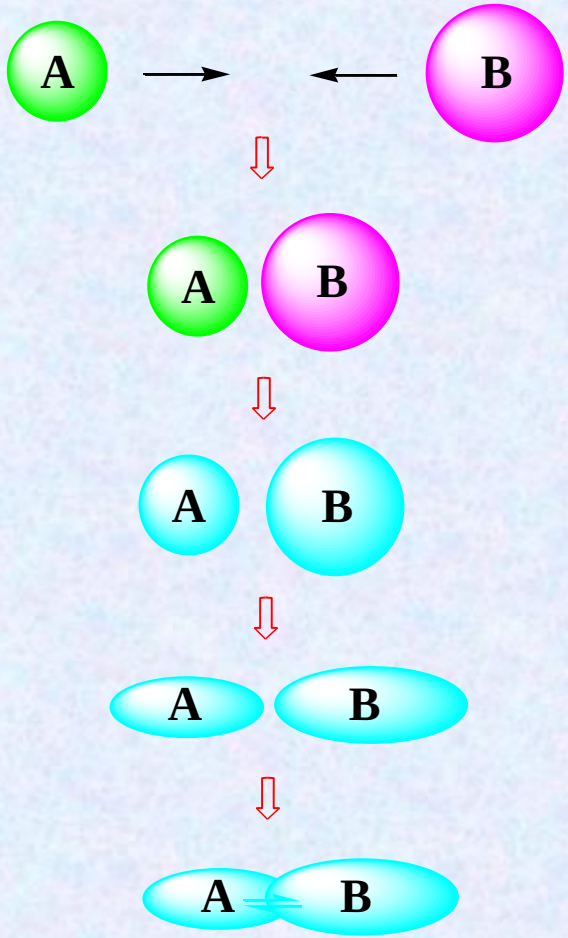
Mo, Y., Song, L., Lin, Y. *J. Phys. Chem.* A, 111, 8291-8301 (2007) (Feature Article).

BLW Energy Decomposition (BLW-ED)

Block-localized wavefunction energy decomposition (BLW-ED):

Mo, Gao, Peyerimhoff, *J. Chem. Phys.* 112, 5530-8 (2000).

$$\Delta E_{\text{int}} = E(AB) - E(A) - E(B) + BSSE \quad = \Delta E_{def} + \Delta E_{HL} + \Delta E_{pol} + \Delta E_{ct}$$



$$\Delta E_{el} = \langle \Psi_A^0 \Psi_B^0 \,|\, \hat{H} \,|\, \Psi_A^0 \Psi_B^0 \rangle - E(\Psi_A^0) - E(\Psi_B^0)$$

$$\Psi_{AB}^{BLW-ini} = \hat{A}(\Psi_A^0 \Psi_B^0)$$

$$\Delta E_{ex} = E(\Psi_{AB}^{BLW-ini}) - \langle \Psi_A^0 \Psi_B^0 \,|\, \hat{H} \,|\, \Psi_A^0 \Psi_B^0 \rangle$$

$$\Delta E_{pol} = E(\Psi_{AB}^{BLW}) - E(\Psi_{AB}^{BLW-ini})$$

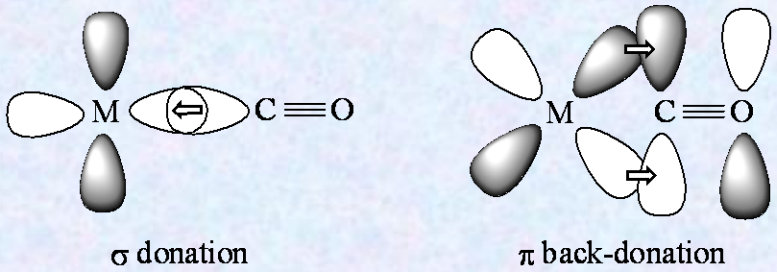
$$\Delta E_{ct} = E(\Psi_{AB}^{HF}) - E(\Psi_{AB}^{BLW}) + BSSE$$

BLW Energy Decomposition (BLW-ED)

σ/π interactions in metal-carbonyl bonding:

Nakashima, Zhang, Xiang, Lin, Lin, Mo, *J. Theo. Chem. Comput.* 7, 639 (2008).

SCHEME 1

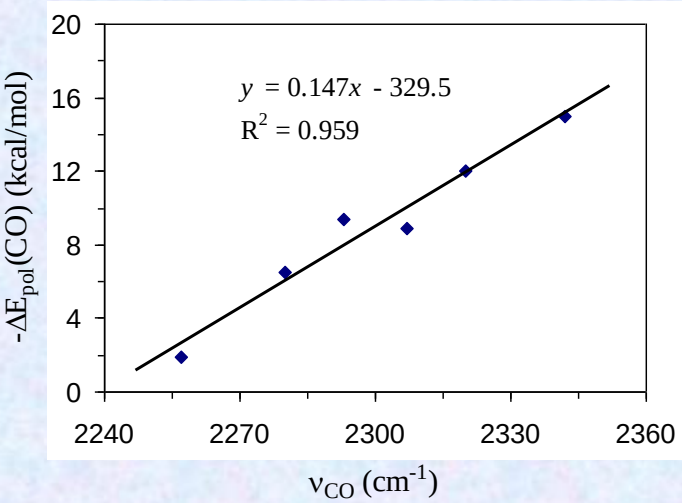


σ donation π back-donation

Optimal bond distances and stretching frequencies of CO for MCO (M = Ni, Pd, Pt, Cu^+, Ag^+ and Au^+)

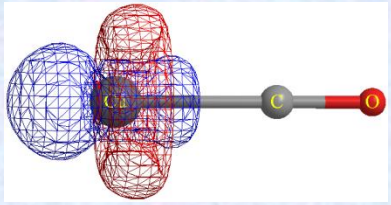
M	DFT				BLW-DFT			
	R_{MC}	R_{CO}	ν_{CO}	$\Delta\nu_{CO}$	R_{MC}	R_{CO}	ν_{CO}	$\Delta\nu_{CO}$
Ni	1.672	1.151	2079	-133	2.044	1.120	2293	+81
Pd	1.879	1.142	2112	-100	2.406	1.123	2257	+45
Pt	1.791	1.146	2120	-92	2.360	1.121	2280	+68
Cu^+	1.884	1.116	2316	+104	2.177	1.114	2342	+130
Ag^+	2.199	1.116	2314	+102	2.570	1.117	2307	+95
Au^+	1.968	1.116	2310	+98	2.517	1.116	2320	+108

Correlation between ν_{CO} in diabatic states and $\Delta E_{pol}(CO)$

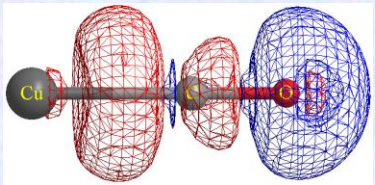


BLW Energy Decomposition (BLW-ED)

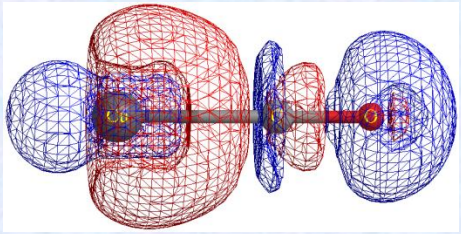
Electron density difference (EDD) maps for $CuCO^+$:



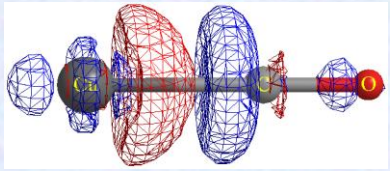
Cu^+ polarization



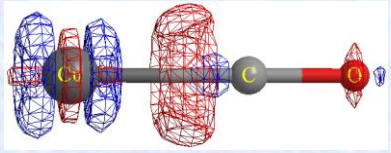
CO polarization



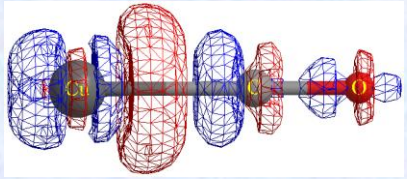
overall polarization



σ charge transfer



π charge transfer



overall charge transfer

Block-Localized Wavefunction (BLW)

Applications and further development of the BLW method:

- Resonance or conjugation;
- Hyperconjugation;
- Two-state model for electron transfer;
- Intermolecular interaction (BLW-ED);
- Reactions in condensed states within the combined QM(MOVB)/MM theory.

Limitations of the BLW method?

Basis set artifact!

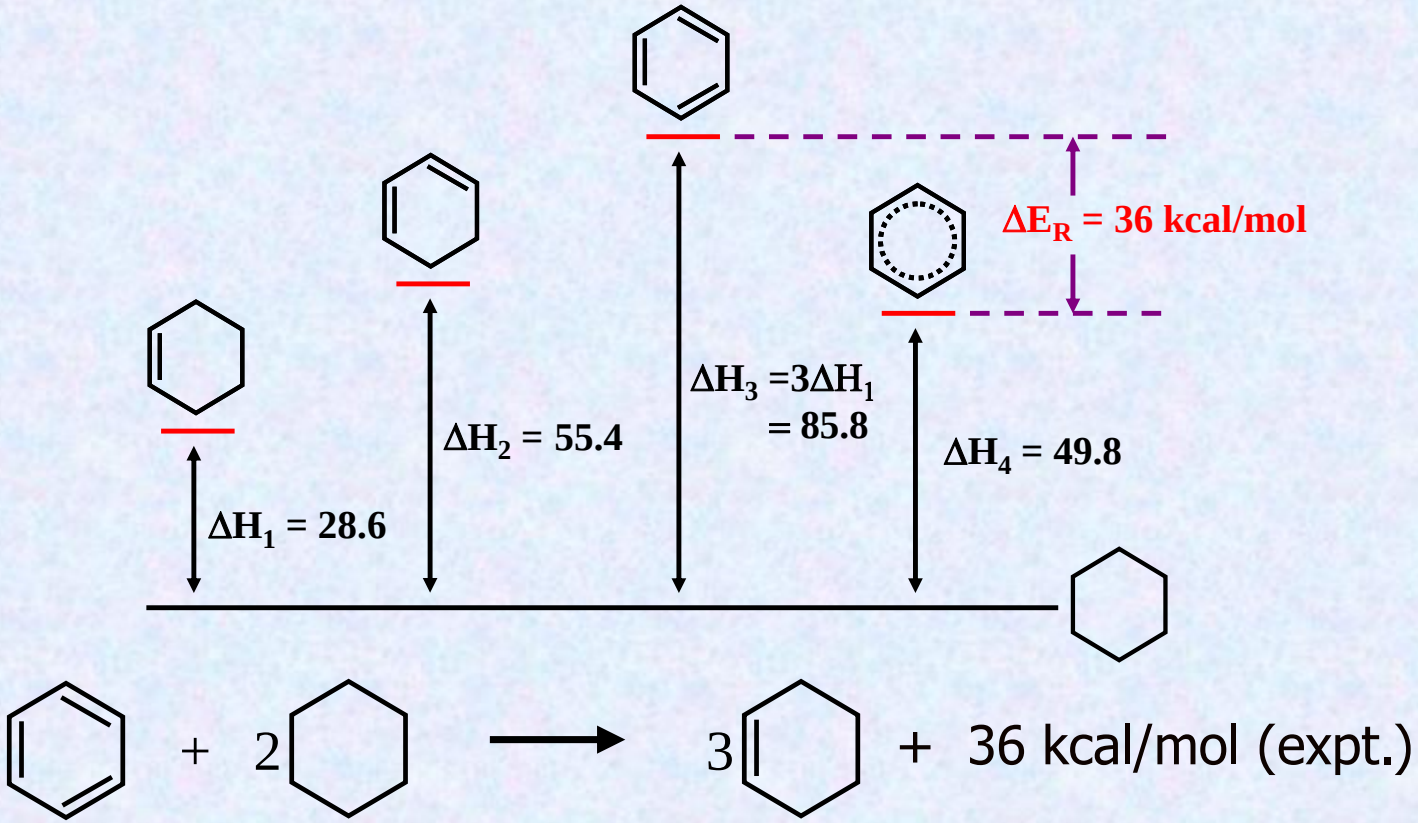
Computational results must be justified by viable experimental data.

BLW results are stable with small to mid-size basis sets.

Mo, *J. Phys. Chem. A* 113, 5163 (2009);
Mo, Hiberty, Schleyer, *Theor. Chem. Acc*., 127, 27 (2010).

Applications of BLW: Resonance in Benzene

Experimental resonance energy:



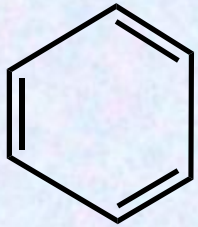
Isodesmic evaluation:

$$3C_2H_6 + 3CH_2{=}CH_2 \rightarrow C_6H_6 + 6CH_4 + 65.5 \text{ kcal/mol}$$

Wodrich, Wannere, Mo, Jarowski, Houk, Schleyer, *Chem. Eur. J.* 13, 7731 (2007)

Applications of BLW: Resonance in Benzene

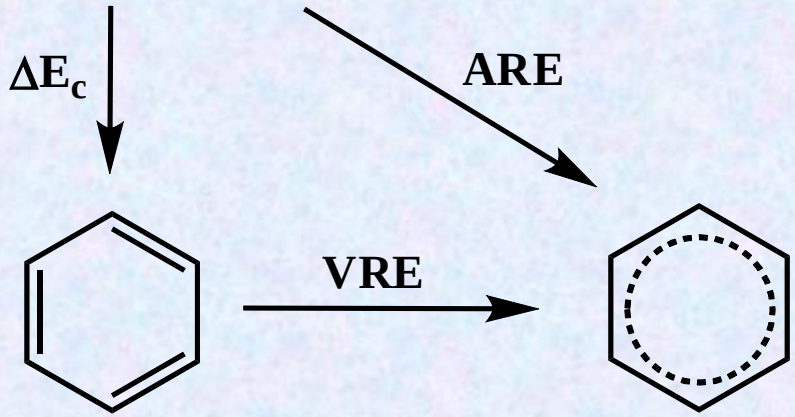
Computational analysis:



optimal 1,3,5-cyclohexatriene

6-31G(d)	1.329/1.528
6-311+G(d,p)	1.325/1.523
cc-pVTZ	1.322/1.523
aug-cc-pVTZ	1.324/1.513

VRE	ARE	ΔE_c
88.76	61.79	26.97
92.19	63.15	29.04
89.10	62.45	26.65
80.92	57.81	23.11



rigid 1,3,5-cyclohexatriene

benzene

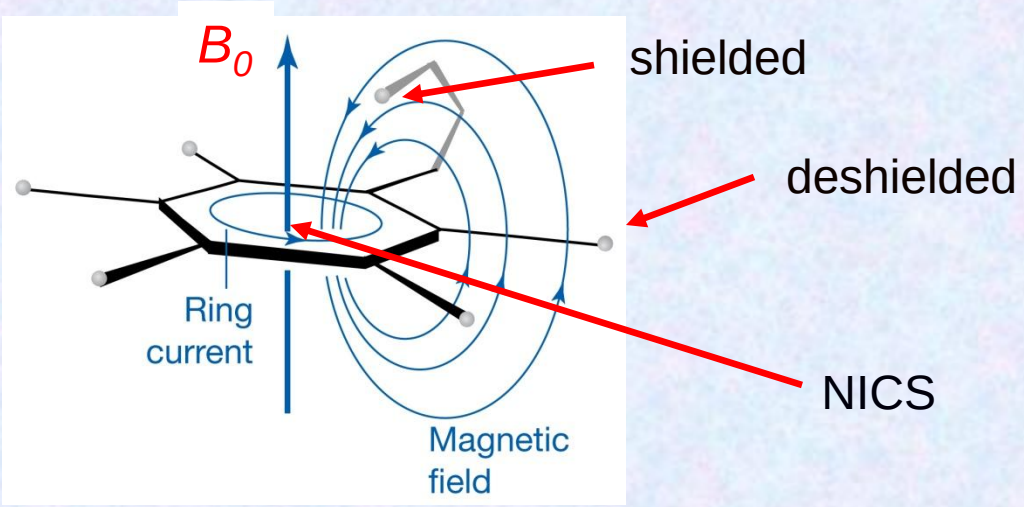
6-31G(d)	1.397
6-311+G(d,p)	1.395
cc-pVTZ	1.391
aug-cc-pVTZ	1.392

Mo, Y., Schleyer, P. v. R. *Chem. Eur. J.* 12, 2009 (2006);
Mo, Y. *J. Phys. Chem. A* 113, 5163 (2009);
Mo, Y., Hiberty, P., Schleyer, P. v. R. *Theor. Chem. Acc.*, 127, 27 (2010).

BLW-NMR: A Proof of Concept

Aromatic current ring:

Benzene C_6H_6



Chemical shift:

Schleyer, et al. *J. Am. Chem. Soc.*118, 6317(1996).

$$\nu_i = \frac{\gamma B_0}{2\pi}(1-\sigma_i)$$ ← **shielding constant**

Reference compound TMS: $(CH_3)_4Si$

$$\frac{\nu_i - \nu_{ref}}{\nu_{ref}} = (\sigma_{ref} - \sigma_i) = 10^{-6}\delta_i$$ ← **chemical shift (in ppm)**

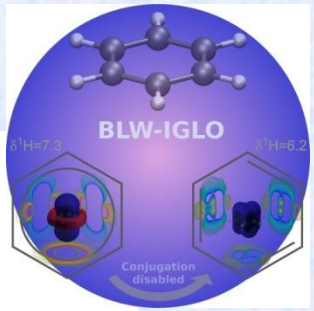
BLW-NMR: A Proof of Concept

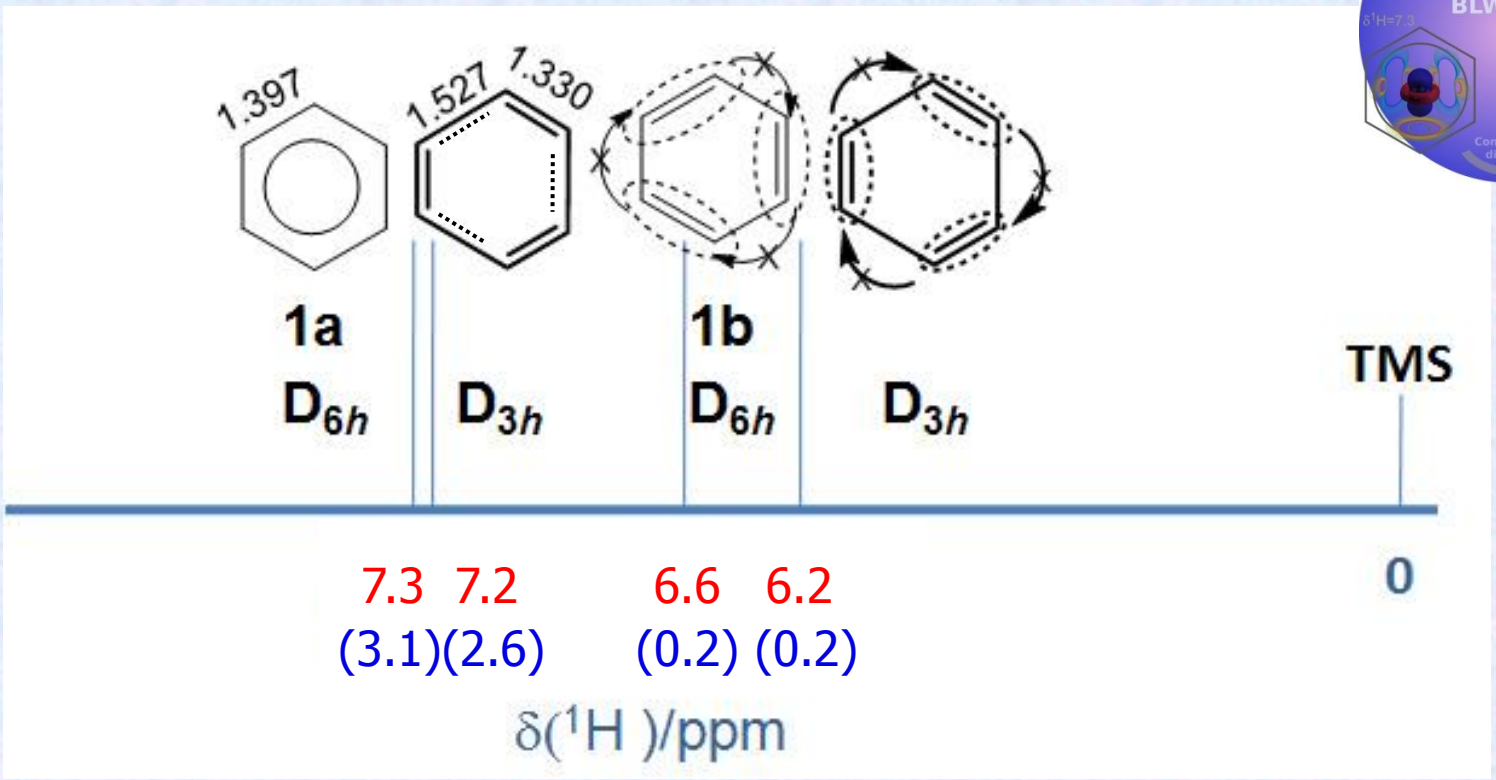
BLW-NMR:

A combination of our BLW method with Kutzelnigg's IGLO method.

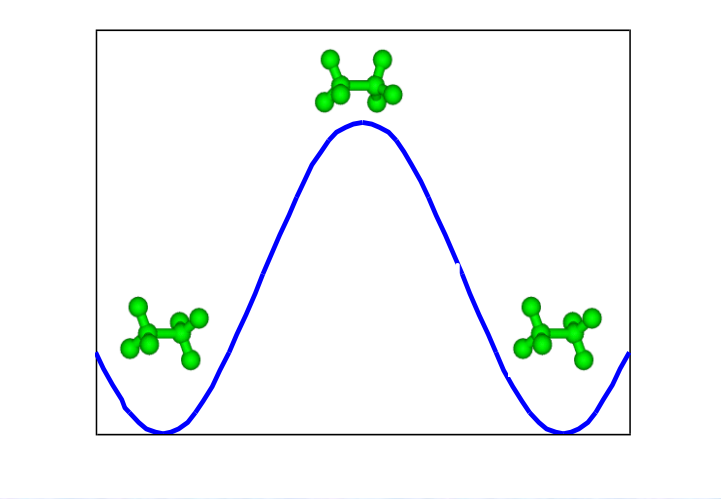
Steinmann, Jana, Wu, Schleyer, Mo, Corminboeuf, *Angew. Chem. Int. Ed.*, 48, 9828 (2009).

A direct assessment of electron delocalization on NMR:





Applications of BLW: Ethane



Existing explanations:

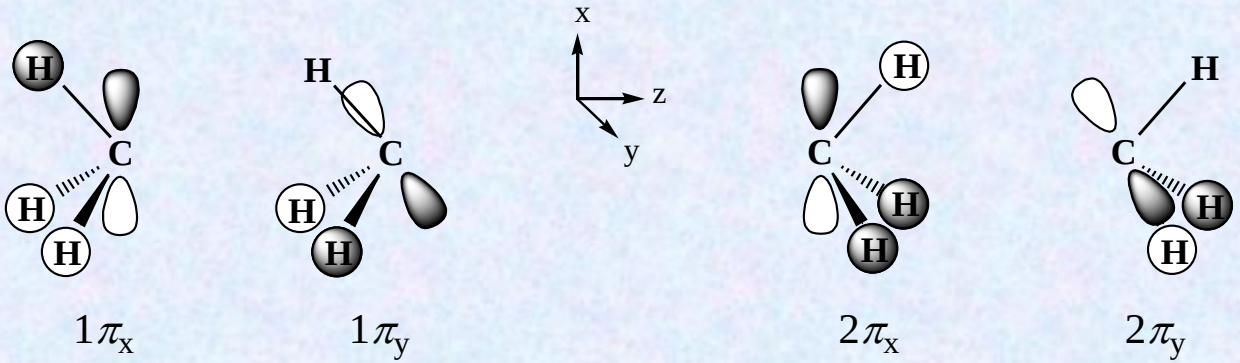
- Steric repulsion;
- Brunck-Weinhold: Vicinal σ_{CH} and σ_{CH}^{*} interactions;
- Bader et al: Weakening (polarization) of the CC bond;
- Goodman: Hyperconjugation model.

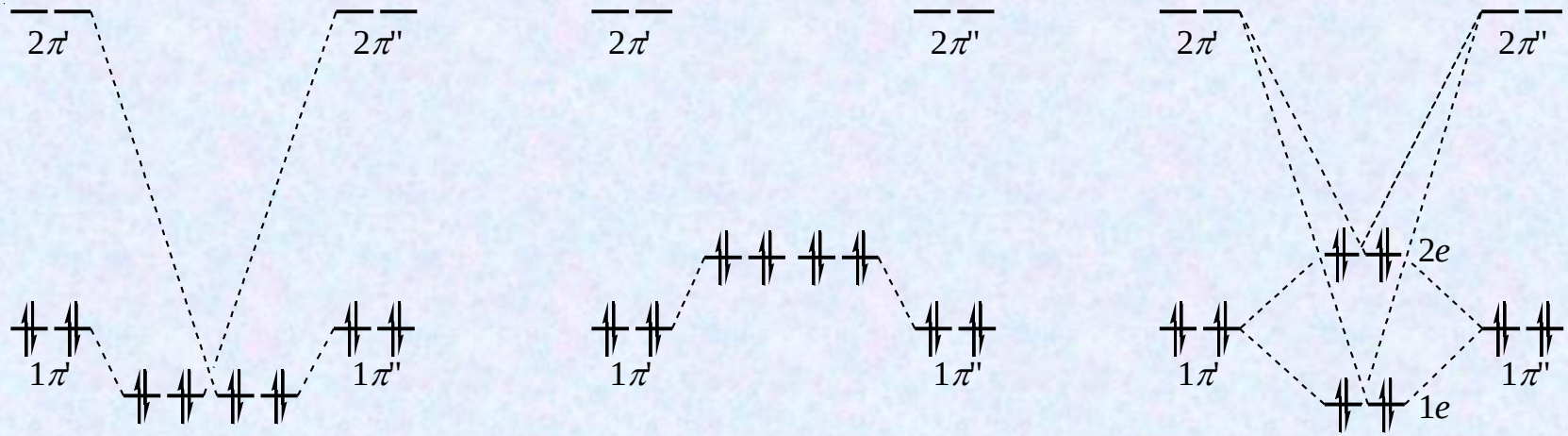
Mulliken (1939): "Hyperconjugation in ethane is only of second order" and "should have little or no direct effect in restricting free rotation".

Mulliken, R. S. *J. Chem. Phys.*, 7, 121 (1939)

Applications of BLW: Ethane

Considering C_2H_6 constructed from two CH_3 groups of C_{3v} symmetry:





Hyperconjugative interaction

Steric repulsion

Overall interaction

Figure. Diagrams for molecular orbital interactions.

Applications of BLW: Ethane

HF wavefunction:

$$\Psi = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1e^4 2e^4)$$

Molecular orbitals;
Orthogonal

BLW wavefunction:

$$\Phi_L = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1\pi'^4 1\pi''^4)$$

Group orbitals;
Nonorthogonal

Hyperconjugation energy:

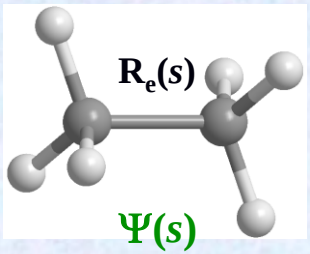
$$E_{hc} = E(\Psi) - E(\Psi_L)$$

Steric energy:

ΔE_s = Energy change with group orbitals frozen in rotation.

Applications of BLW: Ethane

With 6-311+G(d,p) basis set

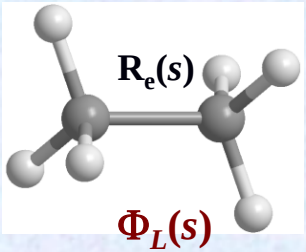


$\Psi(s)$

electronic localization

$-E_{hc}(s)$

7.33

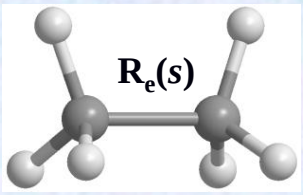


$\Phi_L(s)$

rigid rotation orbitals frozen

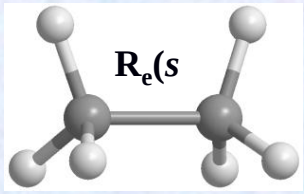
ΔE_s

2.87



$\Phi_L'(e)$

electronic relaxation ΔE_e -0.03

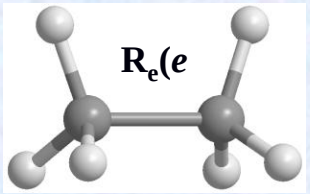


$\Phi_L''(e)$

geometric relaxation

ΔE_g

-0.54

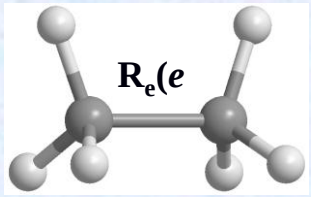


$\Phi_L(e)$

electronic delocalization

$E_{hc}(e)$

-6.57



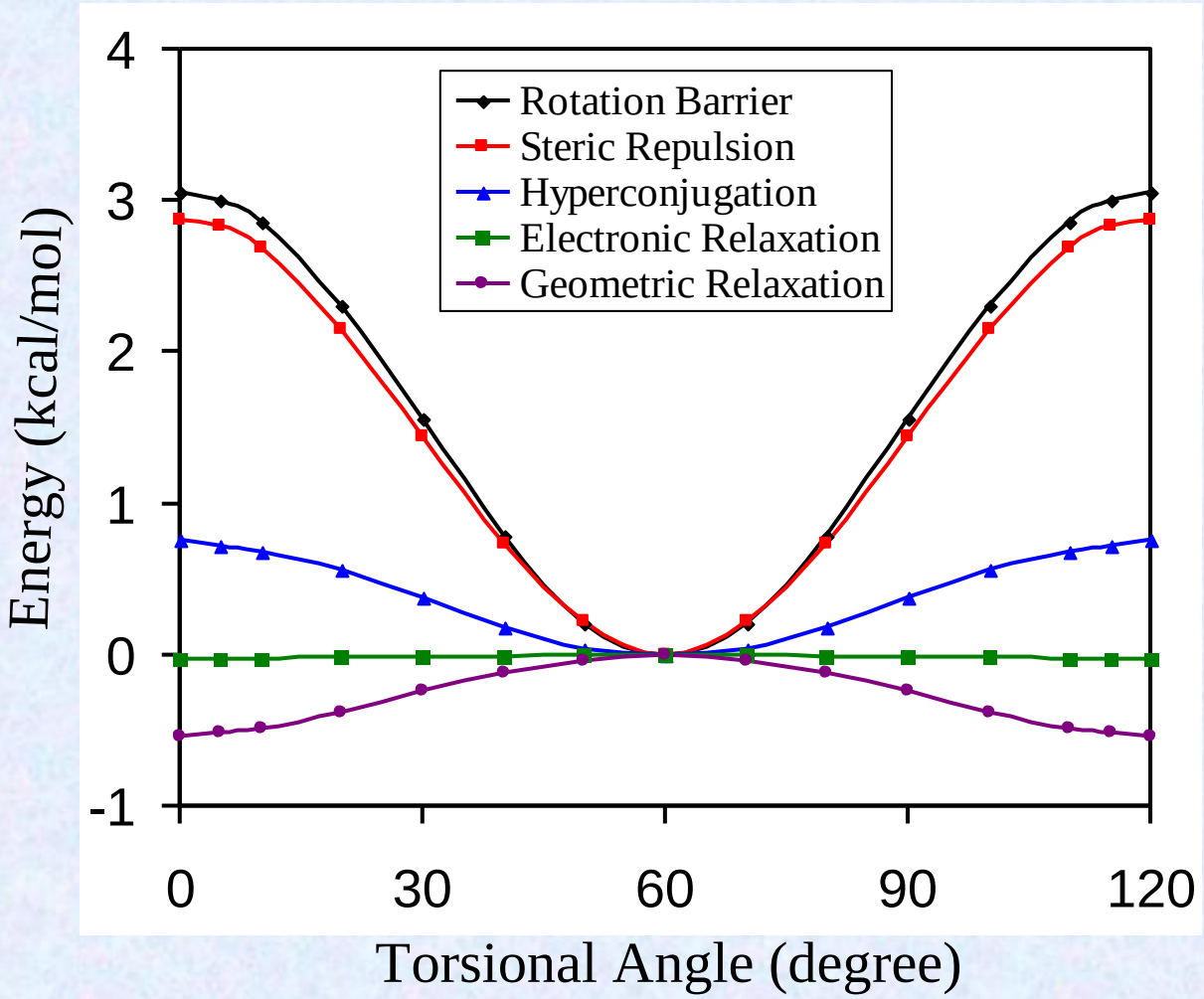
$\Psi(e)$

ΔE_b 3.06

$$\Delta E_b = -E_{hc}(s) + \Delta E_s + \Delta E_e + \Delta E_g + E_{hc}(e) = \Delta E_{hc} + \Delta E_s + \Delta E_e + \Delta E_g$$

3.06 0.76 2.87 -0.03 -0.54

Applications of BLW: Ethane



Mo, Gao, *Acc. Chem. Res.* 40, 113 (2007).

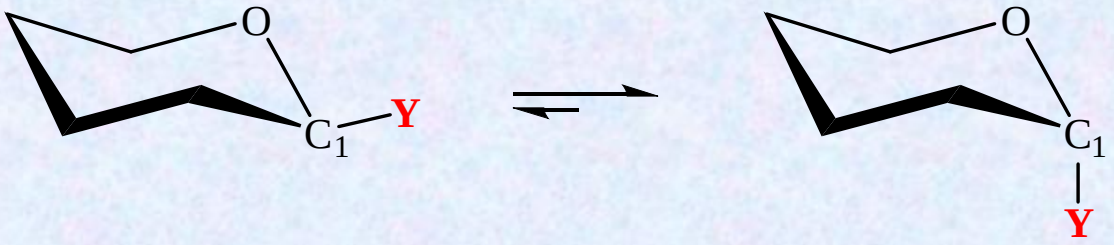
Applications of BLW: Ethane

Energy decomposition of the rotational barriers from staggered conformations to eclipsed conformations (kcal/mol):

Molecule	Basis Set	ΔE_{hc}	ΔE_s	ΔE_e	ΔE_g	ΔE_b
CH_3CH_3	6-31G(d)	0.76	2.73	-0.01	-0.50	2.98
	6-311+G(d,p)	0.76	2.87	-0.03	-0.54	3.06
SiH_3SiH_3	6-31G(d)	0.30	0.71	0.00	-0.06	0.95
	6-311+G(d,p)	0.26	0.77	-0.01	-0.04	0.98
GeH_3GeH_3	6-31G(d)	0.09	0.78	-0.01	-0.05	0.81
	6-311+G(d,p)	0.14	0.67	0.00	-0.08	0.73
CH_3SiH_3	6-31G(d)	0.38	1.16	-0.01	-0.13	1.40
	6-311+G(d,p)	0.37	1.27	-0.02	-0.16	1.46

Applications of BLW: Anomeric Effect

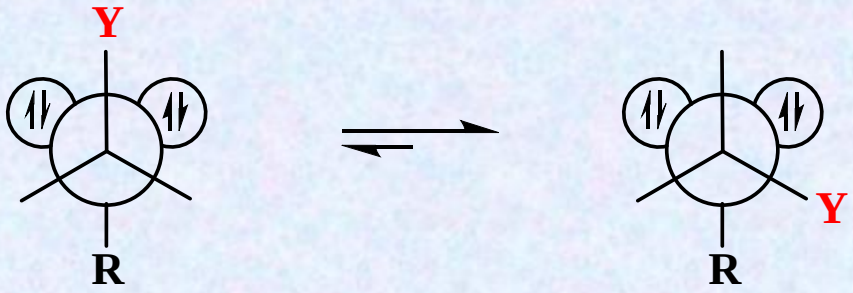
Concept: with the example of substituted tetrahydropyrans



β-anomer α-anomer

The preference of α increases with the increasing electronegativity of Y.

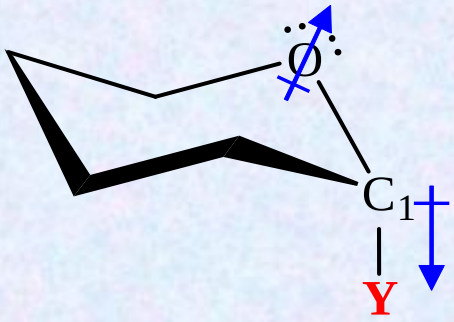
Newman projections of the R-O-C-Y moiety



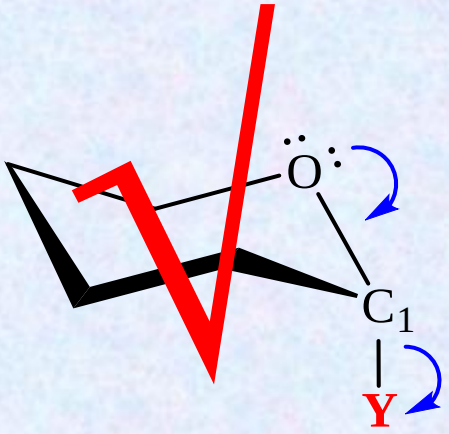
anti-anomer *gauche*-anomer

Applications of BLW: Anomeric Effect

Two explanations for the anomeric effect:



Electrostatic model



Hyperconjugation model

Experimental evidence:

Aqueous solvation effects stabilize the β-anomer.

Experimental evidence:

Shortened O-C_1 bond and the lengthened C_1-Y bond.

Applications of BLW: Anomeric Effect

Extended block-localized wavefunction method:

Allow basis orbitals to appear in more than one block.

Under development.

$$\Phi_L = N_L \hat{A}\{\Omega^1\Omega^2\cdots\Omega^K\}$$

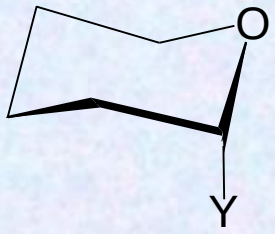
$$\mathrm{DE} = E(\Phi_L) - E(\Psi^{\mathrm{Del}})$$

Examples:

Dimethoxymethane

CH_3-O-CH_2-O-CH_3

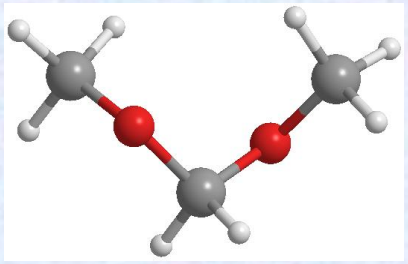
Substituted tetrahydropyrans



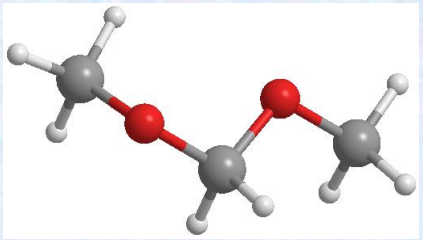
Y = F, Cl, OH, NH_2 and CH_3

Applications of BLW: Anomeric Effect

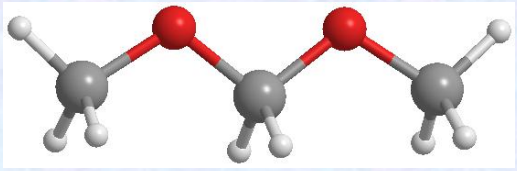
Dimethoxymethane:



(**a**) gauche-gauche (GG)

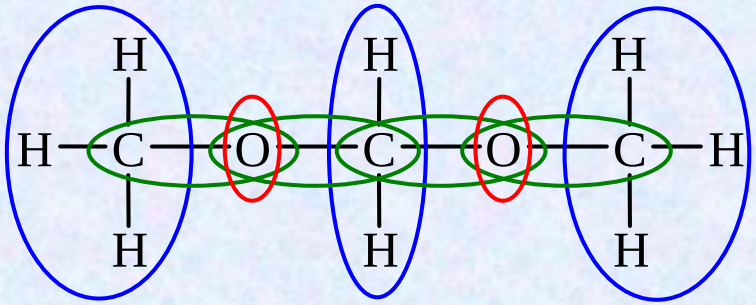


(**b**) gauche-anti (GT)



(**c**) anti-anti (TT)

BLW partition scheme:

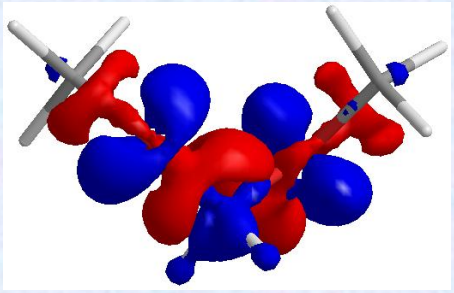


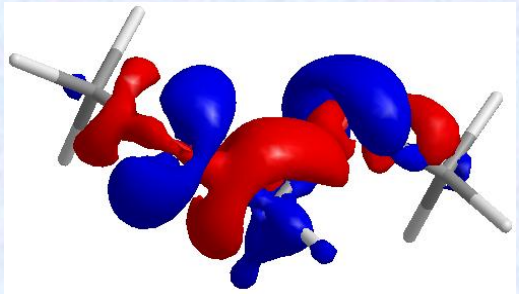
Applications of BLW: Anomeric Effect

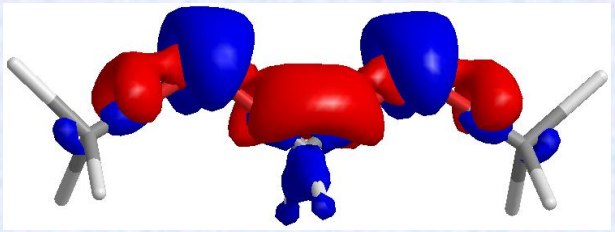
Energies (kcal/mol) with the 6-311+G(d,p) basis set:

	GG	GT	TT
RE(MP2)	0.00	2.74	6.56
RE(HF)	0.00	2.07	5.20
RE(BLW)	0.00	2.94	7.02
DE	56.72	57.59	58.55

Electron density difference (EDD) maps:

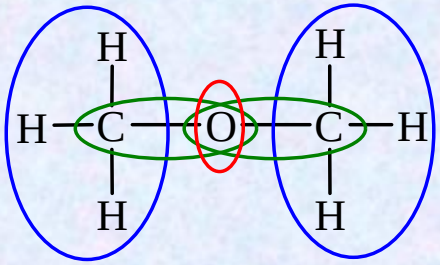






Applications of BLW: Anomeric Effect

Dimethyl ether as a reference:



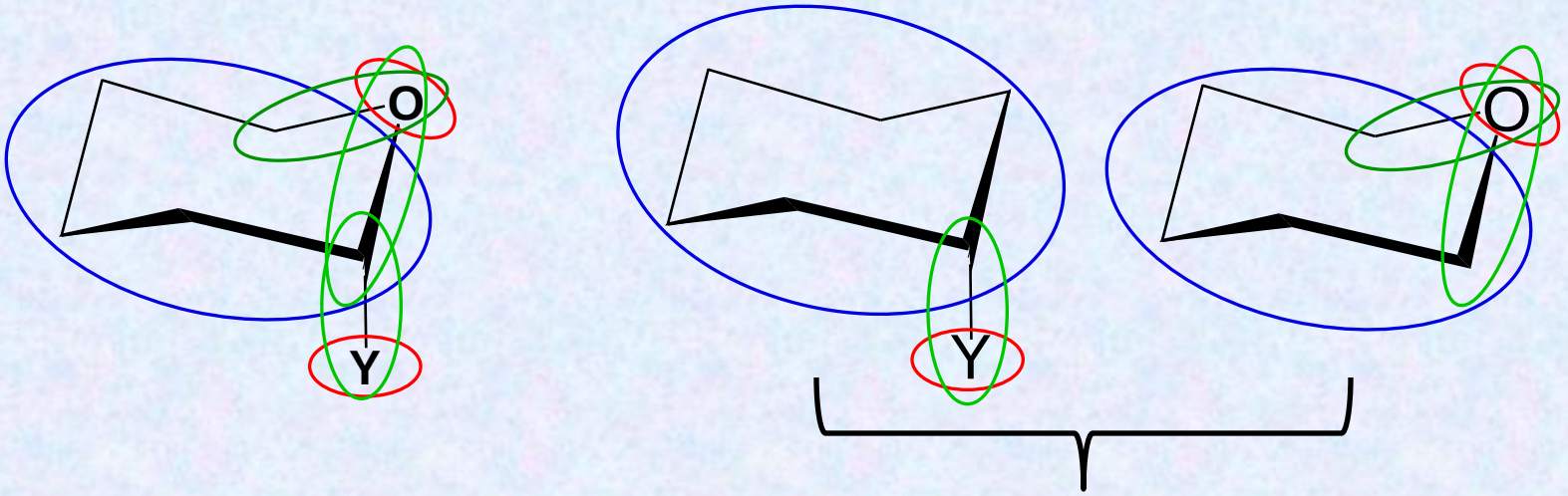
DE = 28.6 kcal/mol

There is no remarkable difference between the n→σ_{CO}* and n→σ_{CH}* hyperconjugative interactions in dimethoxymethan.

Calculations strongly disapprove the hyperconjugation model.

Applications of BLW: Anomeric Effect

Substituted tetrahydropyrans:



Reference molecules

Applications of BLW: Anomeric Effect

Computational results for substituted tetrahydropyrans and cyclohexane (kcal/mol):

$\Delta E_{\alpha\rightarrow\beta}$

$= E_\beta(MP2) - E_\alpha(MP2)$

$= E_\beta(HF) - E_\alpha(HF) + \Delta E_{disp}$

$= E_\beta(BLW) - E_\alpha(BLW) + \Delta E_{del} + \Delta e_{disp}$

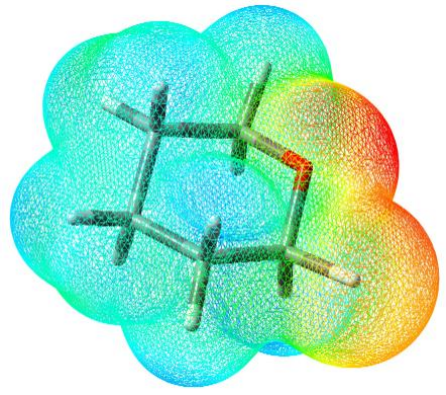
$= \Delta E_s + \Delta E_{del} + \Delta E_{disp}$

Y	$\Delta E_{\alpha\rightarrow\beta}$	ΔE_s	ΔE_{del}	ΔE_{disp}
	Substituted tetrahydropyran			
F	3.41	3.46	-0.66	0.61
OH	1.32	2.19	-1.42	0.55
Cl	2.69	1.76	0.70	0.33
NH_2	-2.73	-2.45	-0.61	0.34
CH_3	-3.30	-2.31	-1.18	0.18
	Substituted cyclohexane			
F	0.09	-0.07	-0.01	0.17
OH	-0.40	-0.60	-0.09	0.29
Cl	-0.96	-1.00	-0.17	0.21
NH_2	-1.71	-2.02	-0.03	0.33
CH_3	-2.19	-2.23	-0.16	0.19

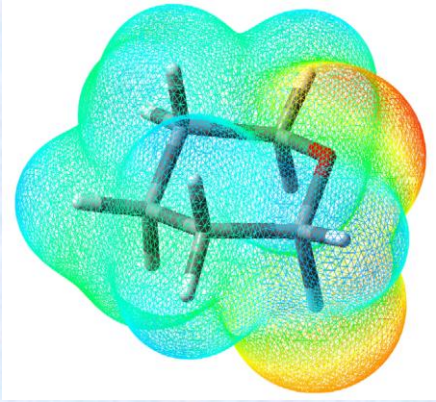
Mo, *Nat. Chem.* 2, 666 (2010).

Applications of BLW: Anomeric Effect

Electrostatic potential surface

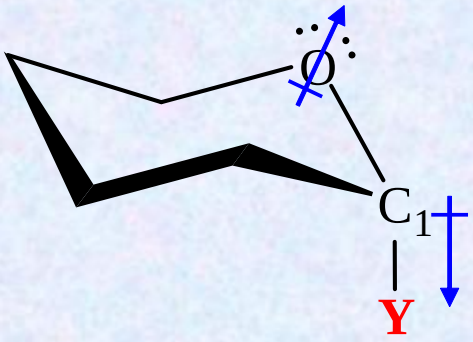


β-$C_5OH_{10}F$



α-$C_5OH_{10}F$

Relative orientations (degree) of local dipoles in $C_6H_{11}Y$:



Y	α	β
F	119.2	46.3
OH	169.3	92.1
Cl	116.5	48.4
NH_2	112.3	127.5

Mo, *Nat. Chem.*, 2, 666 (2010).

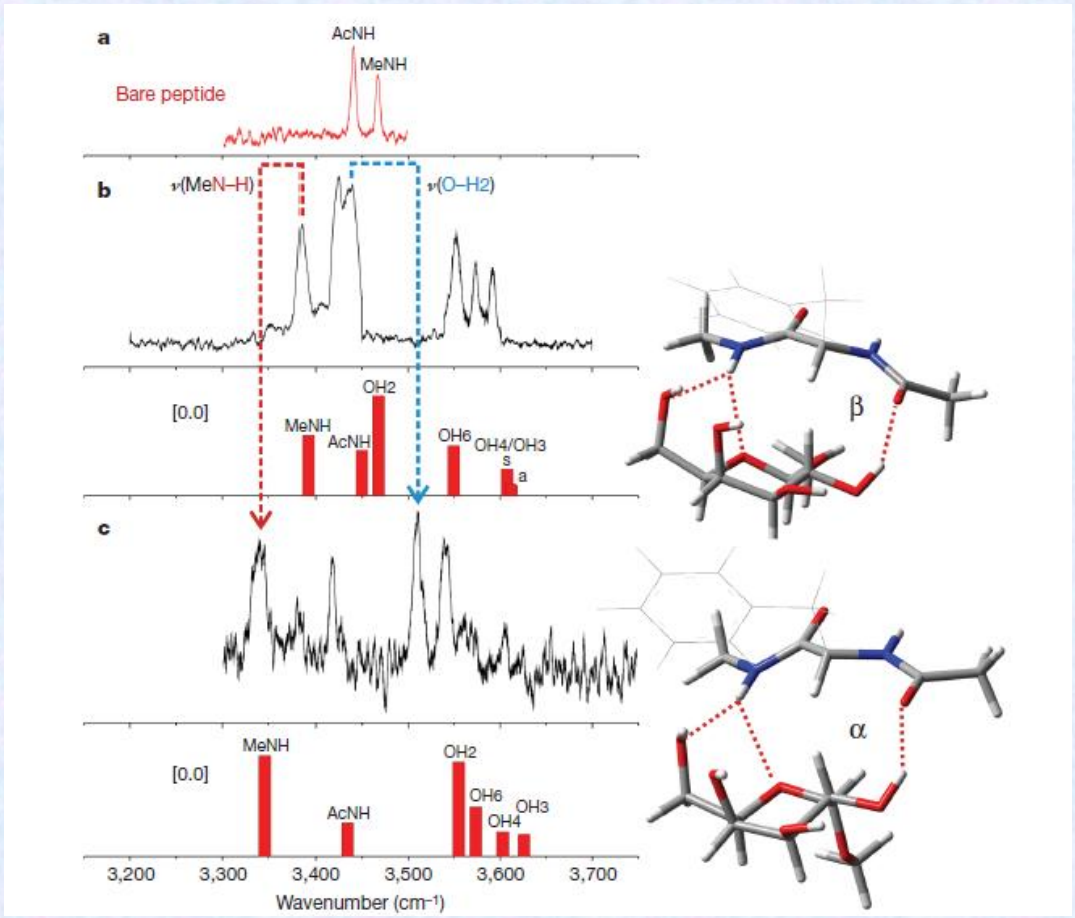
Applications of BLW: Anomeric Effect

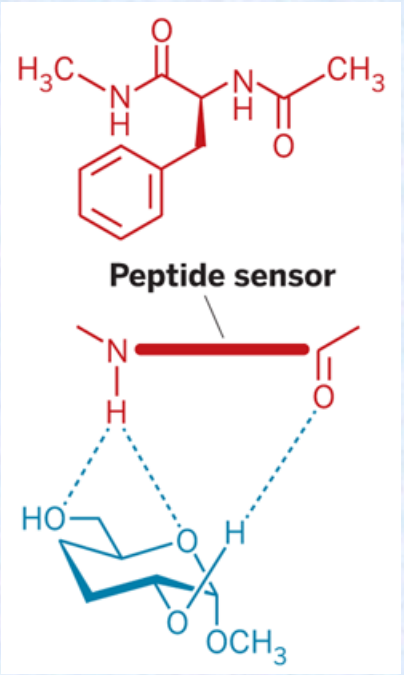
LETTER

doi:10.1038/nature09693

Sensing the anomeric effect in a solvent-free environment

Emilio J. Cocinero[1]†, Pierre Çarçabal[1]†, Timothy D. Vaden[1]†, John P. Simons[1] & Benjamin G. Davis[2]



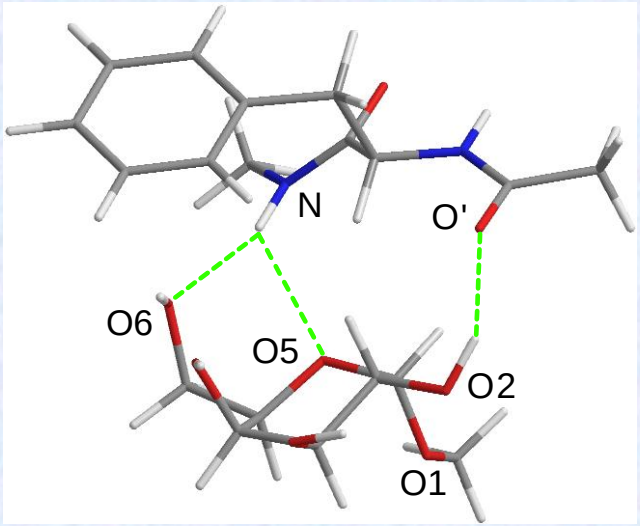


Chem. Eng. News
January 10, 2011
Volume 89, Number 2
p. 5
Probing The Anomeric Effect

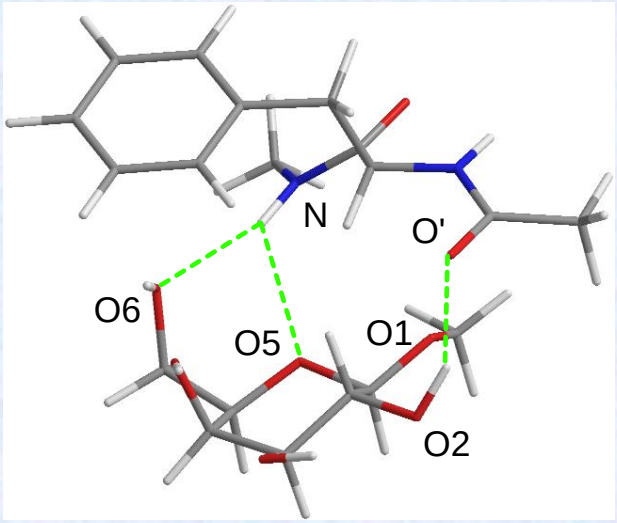
Carbohydrate Chemistry: Peptide sensor provides clues to phenomenon that stabilizes sugars

Applications of BLW: Anomeric Effect

Can a sensing molecule probe the anomeric effect?



(**a**) α-anomer



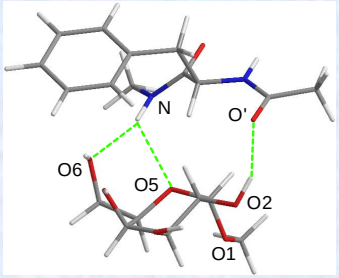
(**b**) β-anomer

Strategy: Mutating the involved functional groups individually.

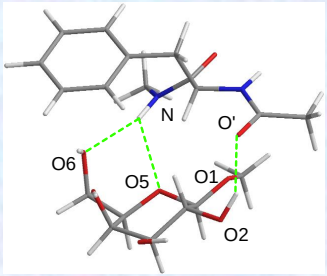
Applications of BLW: Anomeric Effect

Key H-bond distances and vibrational frequencies:

Complex		R(O6···H)	R(O5···H)	R(H···O')	ν(N-H)	ν(O2-H)
1	α	1.997	2.610	1.954	3328 -45	3569 +91
	β	2.098	2.444	1.900	3373	3478
2	α	2.018	2.546	1.935	3335 -60	3544 +5
	β	2.106	2.463	1.946	3395	3539
3	α	2.052	/	2.023	3365 -67	3568 +53
	β	2.192	/	1.956	3432	3515
4	α	/	2.038	1.949	3379 -41	3566 +87
	β	/	2.181	1.873	3420	3479



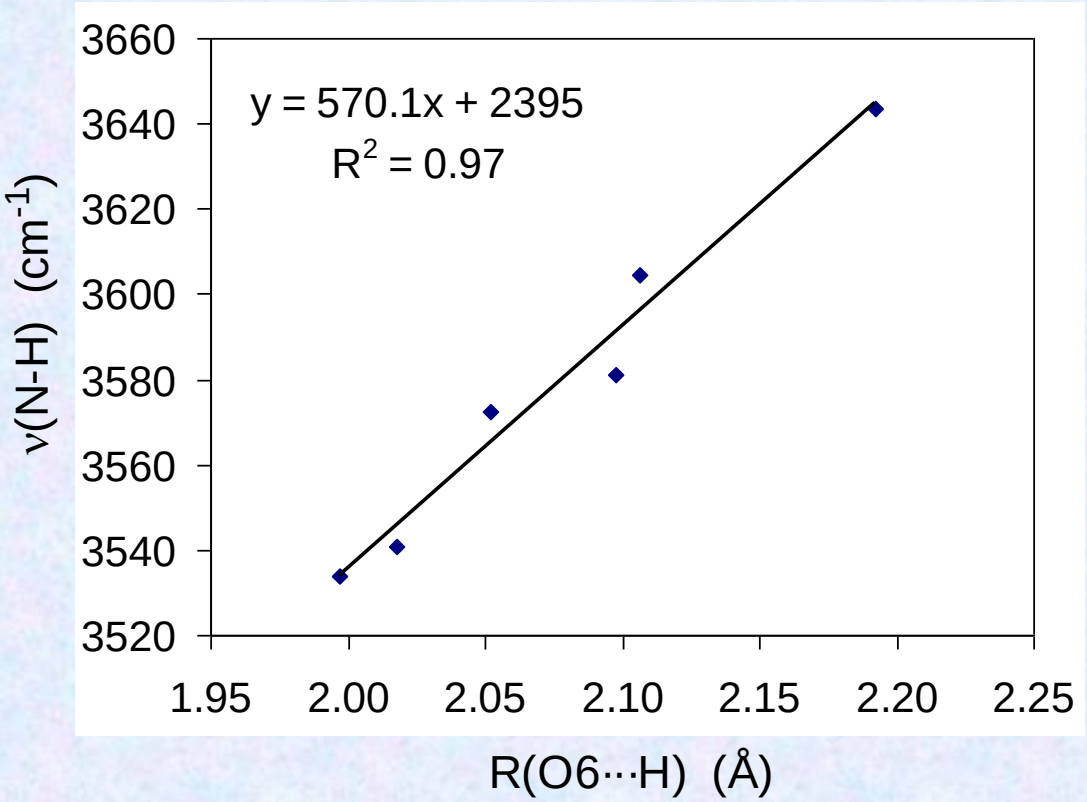
(**a**) α-anomer

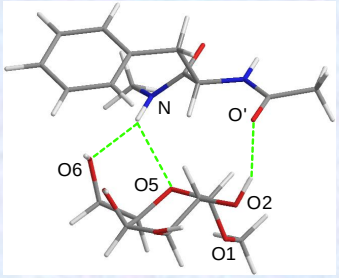


(**b**) β-anomer

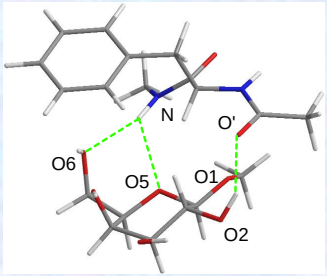
Applications of BLW: Anomeric Effect

Correlation between the n(N-H) and the O6···HN distance:





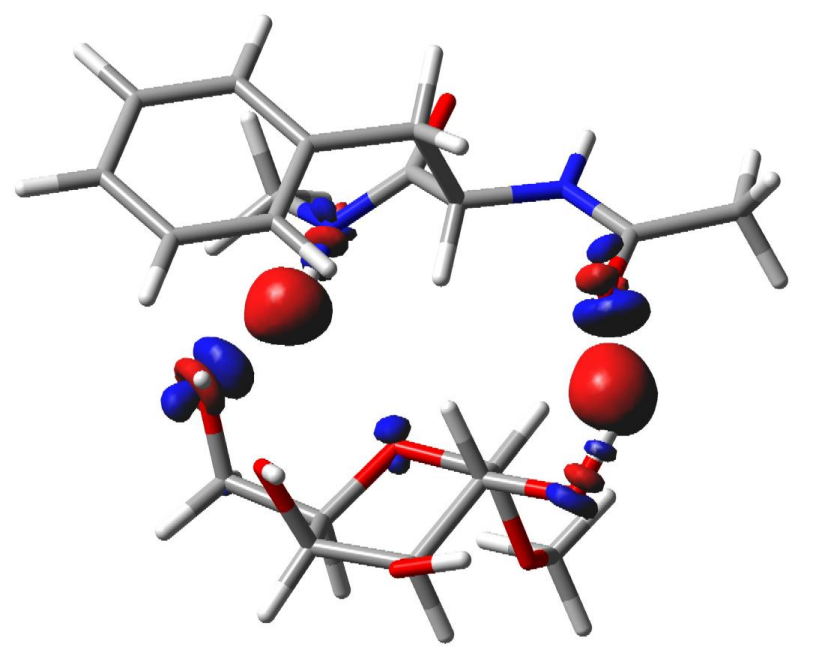
(**a**) α-anomer

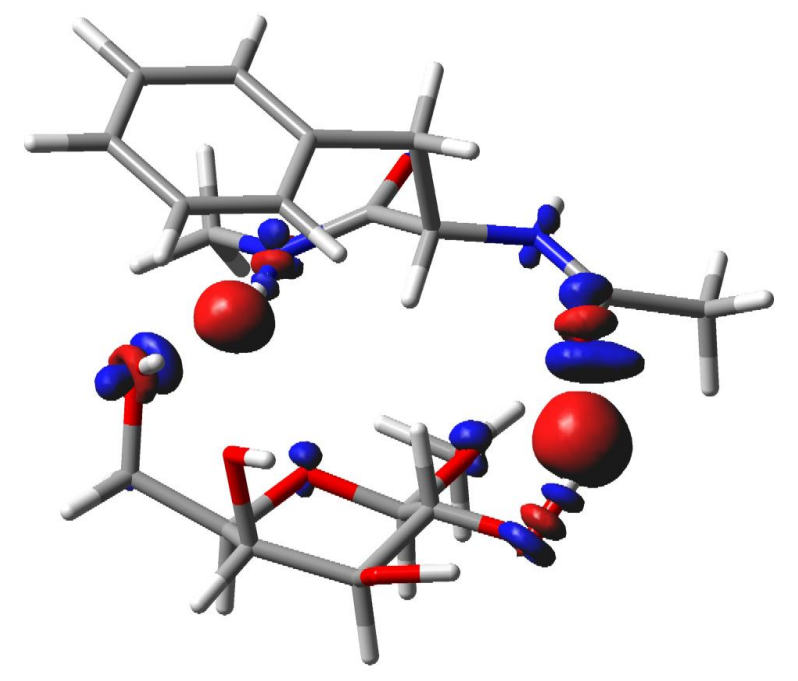


(**b**) β-anomer

Applications of BLW: Anomeric Effect

Electron density difference (EDD) maps:





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Sensing or No Sensing: Can the Anomeric Effect Be Probed by a Sensing Molecule?

Changwei Wang,[†,‡] Fuming Ying,[†] Wei Wu,[*,†] and Yirong Mo[*,‡]

Wang et al., J. Am. Chem. Soc. 133, 13731 (2011).

Methodology: Two-State Model Based on BLW

Approach I:

$$\Psi = \sum_I C_I \Psi_I^{BLW}$$

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0 \rightarrow V_{AB} = H_{AA} - E_1 = \frac{H_{AB} - S_{AB} H_{AA}}{(1 - S_{AB})}$$

Approach II (reverse CI):

$$\Psi_{GS} = a\psi_A + b\psi_B$$

Assuming $\langle \psi_a | \psi_b \rangle = 0 \rightarrow E_{GS} = a^2 E_a + b^2 E_b + 2abV_{ab}$

Since $\frac{\partial E_{GS}}{\partial a} = \frac{\partial E_{GS}}{\partial b} = 0 \rightarrow a^2 = \frac{E_{GS} - E_b}{2E_{GS} - E_a - E_b}; \; b^2 = \frac{E_{GS} - E_a}{2E_{GS} - E_a - E_b}$

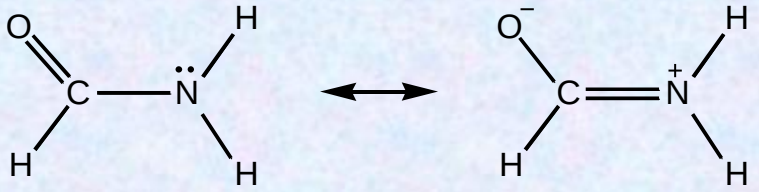
$$V_{ab} = \sqrt{(E_{GS} - E_a)(E_{GS} - E_b)}$$

$$E_{ES} = E_a + E_b - E_{GS}$$

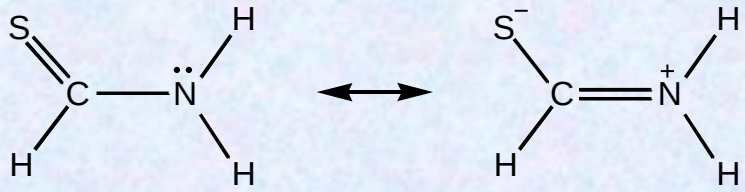
Mo, Y. *J. Chem. Phys.*, 126, 224104 (2007).

Application: Intramolecular ET Systems

Formamide and thioformamide in the gas phase (B3LYP):



6-31G(d)	a^2 = 71.7%	b^2 = 28.3%	$\Delta E_{\pi\rightarrow\pi^*} = 4.82$
6-311+G(d,p)	a^2 = 71.5%	b^2 = 28.5%	4.86 eV



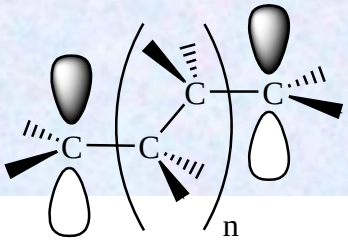
6-31G(d)	a^2 = 57.4%	b^2 = 42.6%	$\Delta E_{\pi\rightarrow\pi^*} = 4.04$
6-311+G(d,p)	a^2 = 57.9%	b^2 = 42.1%	4.10 eV

Application: Intramolecular ET Systems

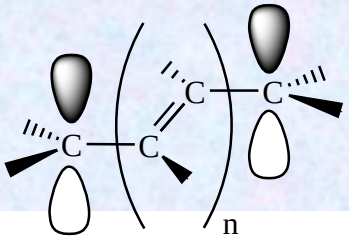
A

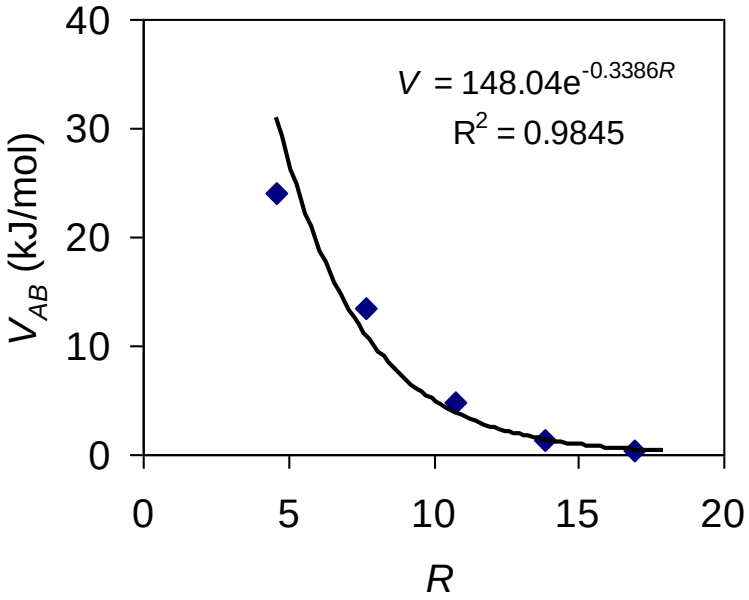
B

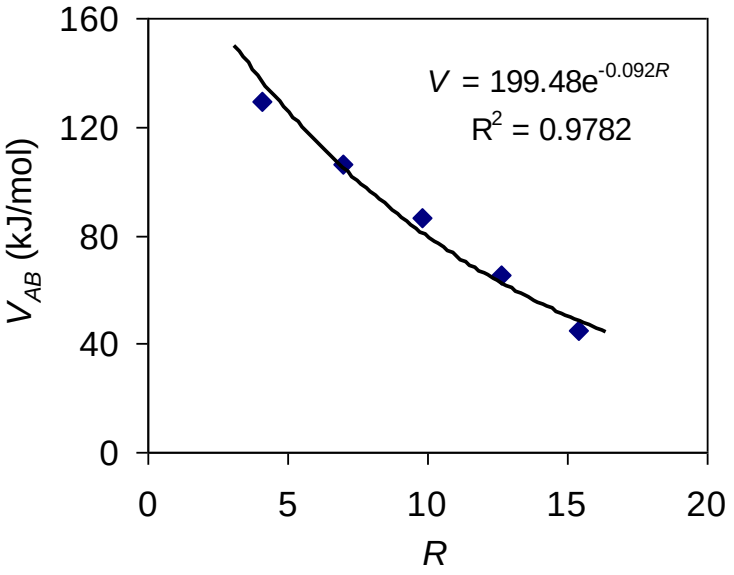
$CH_2(CH_2CH_2)_nCH_2^+$



$CH_2(CH{=}CH)_nCH_2^+$







Correlation between the electronic coupling energy and the electron-transfer distance.

Mo, Wu, Zhang, *J. Chem. Phys.* 119(13), 6448-6456 (2003).

Application: Intramolecular ET Systems

$$k_{ET} = Ae^{-\beta R_{AB}} \rightarrow V_{AB} \propto e^{-\beta R_{AB}/2}$$

$CH_2(CH_2CH_2)_nCH_2^+$

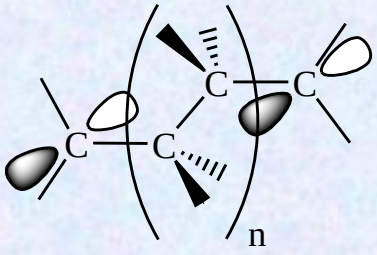
$\beta_{comp} = 0.68$ Å^{-1}

$\beta_{expt} = 1.0$ Å^{-1}

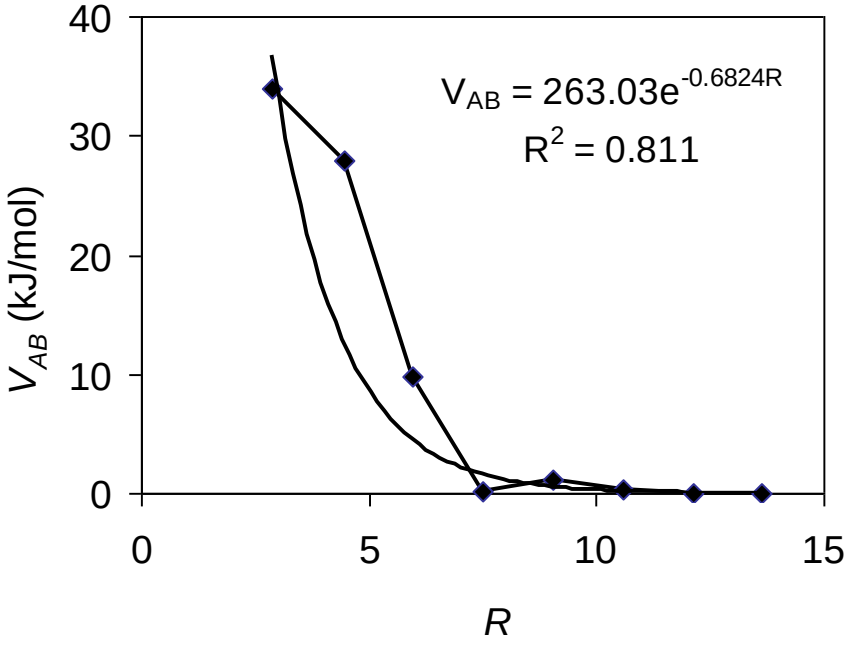
$CH_2(CH{=}CH)_nCH_2^+$

$\beta_{comp} = 0.18$ Å^{-1}

$\beta_{expt} = 0.2$ Å^{-1}



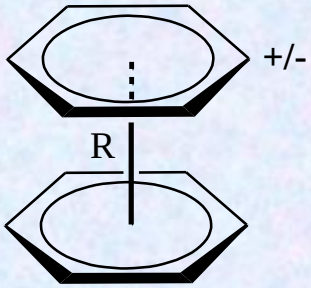
$\beta_{comp} = 1.36$ Å^{-1}

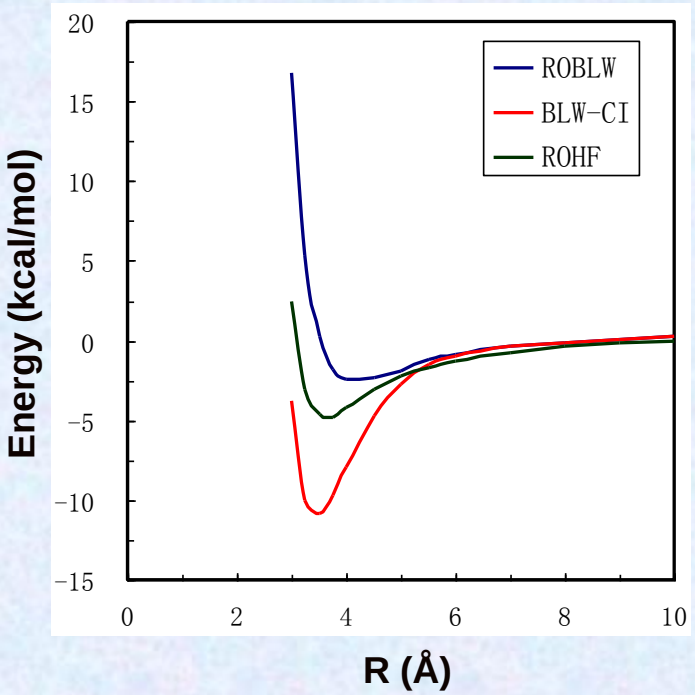


Correlation between the electronic coupling energy and the electron-transfer distance.

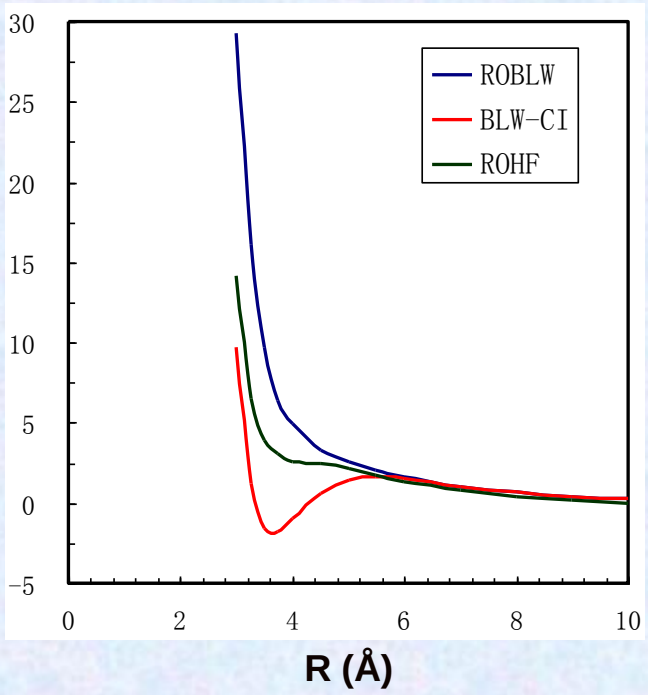
Application: Intermolecular ET Systems

Electron transfer between phenyl rings:





(**a**) Cation

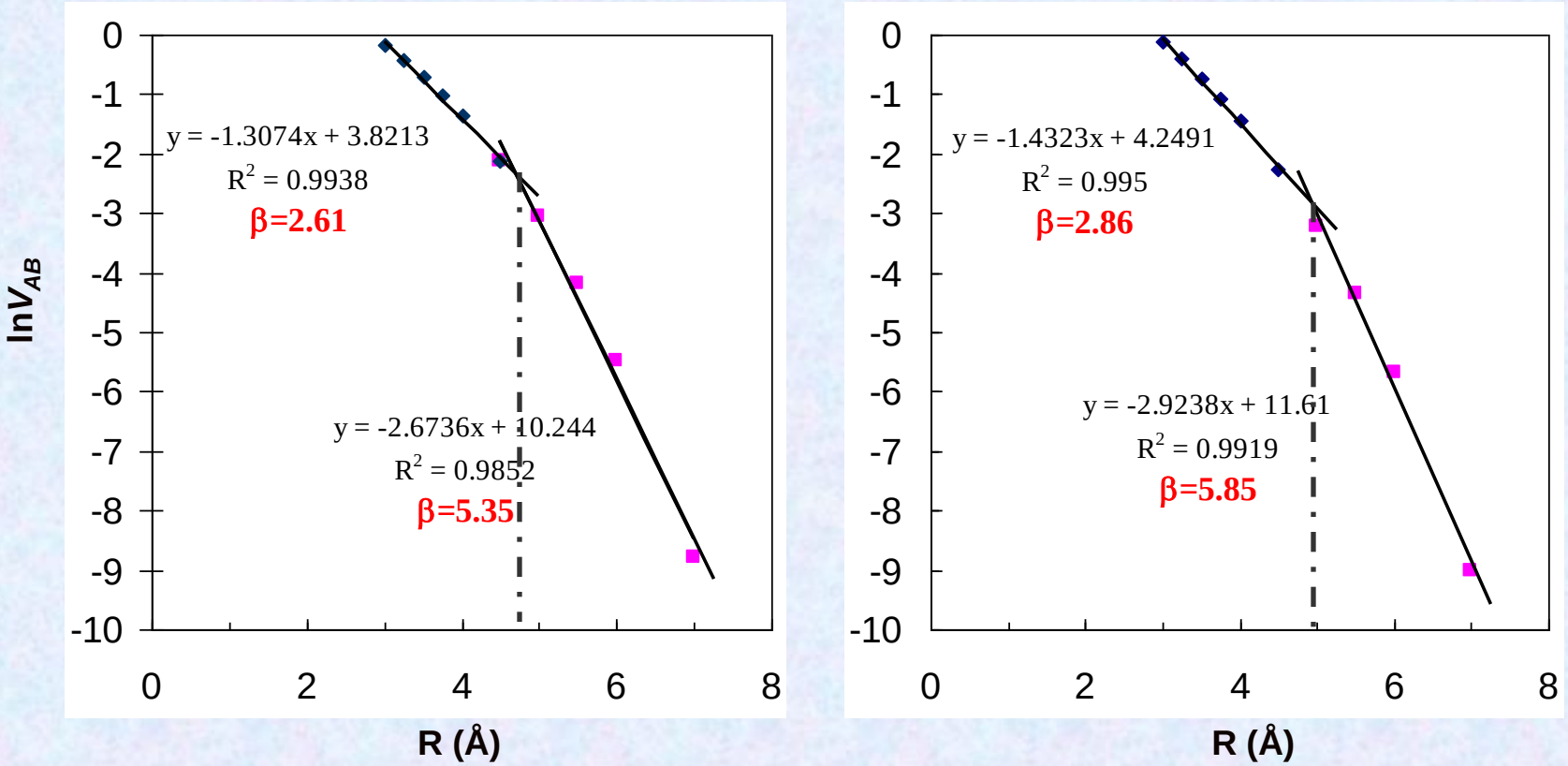


(**b**) Anion

Interaction energy between a benzene ion and a neutral benzene.

Mo, *et al*., *J. Chem. Theory Comput.*, 8(3), 800-805 (2012).

Application: Intermolecular ET Systems



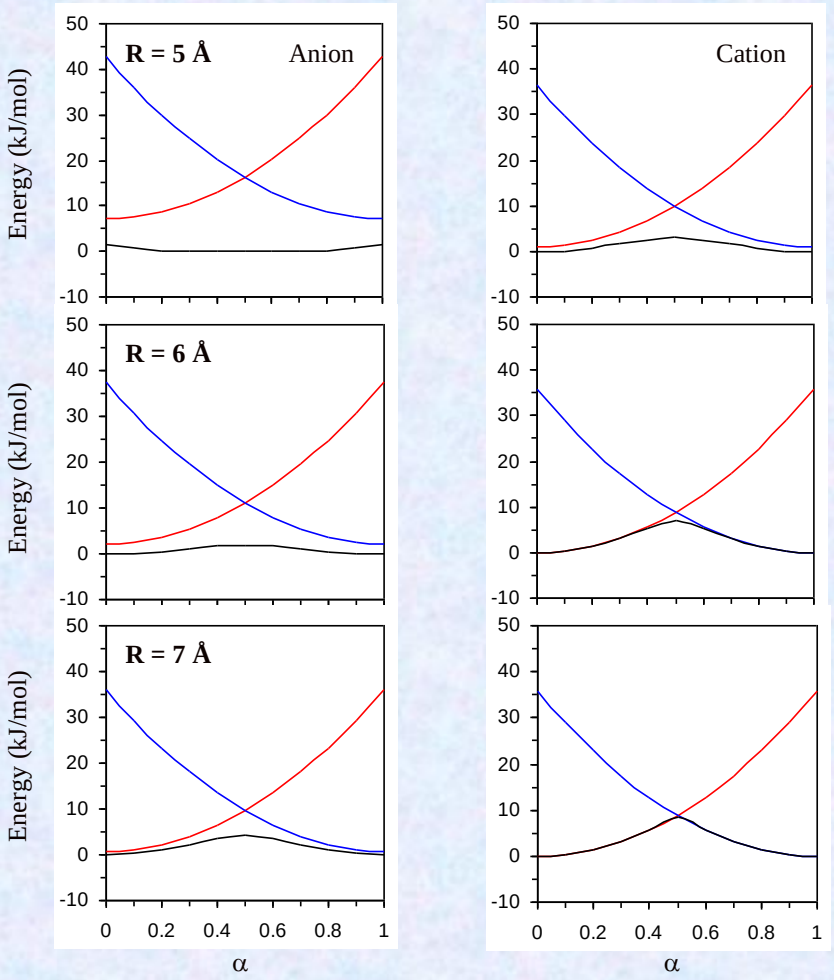
(**a**) Cation (**b**) Anion

Correlation between the electronic coupling energy and the electron-transfer distance between an ionic benzene and a neutral benzene.

Application: Intermolecular ET Systems

The ET reactions accompanied by nuclear rearrangements. Define a reaction coordinate Q_i

$$Q_i = \alpha Q_B + (1-\alpha) Q_A$$



Application: Intermolecular ET Systems

Marcus hypothesized:

$$\Delta G^{*} = \Delta E_a + V_{AB} \approx \lambda / 4$$

Coupling energy V_{AB}, charge transfer barrier DE_a, and reorganization energy l (in eV) at several distances when the donor and acceptor groups are weakly coupled.

R (Å)	Anion			Cation		
	V_{AB}	ΔE_a	λ	V_{AB}	ΔE_a	λ
6.0	/	/	/	0.018	0.074	0.369
7.0	0.053	0.046	0.366	4.7×10^{-3}	0.087	0.371
8.0	0.028	0.066	0.365	1.0×10^{-3}	0.091	0.371
9.0	0.013	0.079	0.365	2.0×10^{-4}	0.093	0.372
10.0	5.0×10^{-3}	0.087	0.365	5.7×10^{-5}	0.093	0.372

Summary

- BLW-ED can quantify the conjugation effect and explore its geometric and energetic impacts;
- BLW can uniquely define both the non-CT and CT states;
- The BLW-based two-state model can provides a quantitative means to derive the quantities in the Marcus-Hush theory;
- BLW results support the conventional view that the ethane rotation barrier comes from the steric repulsion;
- BLW computations disapproved the popular hyperconjugation explanation for the anomeric effect. Instead, alternative explanation such as the electrostatic model must be called.

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