

Approximate Density Functional Approaches with Exact Exchange

$$E_{xc}^{HF-LDA} = E_x^{HF} + E_c^{LDA}(X) \text{ inadequate for molecules}$$

Short range correlation - dynamic correlation: covered by E_c^{LDA} and improvements

Second type: near degeneracy correlation: correction to

E_x^{HF} needed; the molecular HF hole function

$\bar{h}_{xHF}^{\sigma\sigma}(\vec{r}_1, s)$ is too diffuse as a function of s

for some positions of \vec{r}_1 , in particular in the limit of bond dissociation; ^{thus} near degeneracy correlation has largely the effect of compacting the total hole correlation function. E_c^{LDA} does not contain near degen. correlation.

Molecular calc. with E_{xc}^{HF-LDA} display deficiencies of the HF method: e.g. bond energies

$\bar{h}_{xNL}^{\sigma\sigma}(\vec{r}_1, s)$ does not suffer from the same deficiencies as $\bar{h}_{xHF}^{\sigma\sigma}(\vec{r}_1, s)$ for large s ; it is thus not necessary to

apply near-degen. corrections to E_x^{LDA} and this is also the case for $E_x^{LDA} + E_x^{NL}$

Thus LDA for exch. and correlation after better bond energies and distances than E_{xc}^{HF-LDA}

to overcome the E_{xc}^{HF+LDA} deficiency:

E_{xc}^{ND} exchange energy and near degeneracy correlation energy - total exchange-corr. energy from a proper dissociation wavefunction; the total E_{xc}^{ND-LDA} is thus:

$$E_{xc}^{ND-LDA} = E_{xc}^{ND} + E_c^{LDA}$$

hybride functionals - 21 -

theoretical justification

Adiabatic connection method $E_{xc} = \int_0^1 E_{ncl}^\lambda d\lambda$ (ACH)

E_{ncl}^λ non-classical: self-interaction correction, exchange (i.e. antisymmetry) and electron correlation effects, suppose E_{ncl}^λ - linear function of λ

$$E_{xc}^{HH} = \frac{1}{2} E_{xc}^{\lambda=0} + \frac{1}{2} E_{xc}^{\lambda=1}$$

half-half (HH) Becke, 1993
JCP, 98, 1372

$E_{xc}^{\lambda=1} \rightarrow E_{xc}^{LPA DFT}$ exch. correl

$E_{xc}^{\lambda=0} \rightarrow$ exact exchange

62 atomization energies: error 6.5 kcal/mol
data base

5.7 kcal/mol BPW91

gradient correct

Next step: Becke 1993, JCP, 98, 5648
semiempirical coefficients

$$E_{xc}^{B3} = E_{xc}^{LSD} + a (E_{xc}^{\lambda=0} - E_x^{LSD}) + b E_x^B + c E_c^{PW91}$$

a - amount of exact exchange ($a = 0.20$)
($b = 0.72$)

b control the contributions of exchange
c control the contributions of correlation gradient

corrections to the local density approximation

E_x^B Becke, 1988

E_c^{PW91} Perdew and Wang's 1991

fit error 2.3 kcal/mol, close to target accuracy

about 2 kcal/mol.

the popular B3LYP functional Stevens et al, 1994,
JCP, 99, 4623

PW91 in Becke's hybrid funct. replaced by LYP

$$E_{xc}^{B3LYP} = (1-a) E_x^{LSD} + a E_{xc}^{\lambda=0} + b E_x^{B88} + c E_c^{LYP} + (1-c) E_c^{LSD}$$

a, b, c adopted from Becke's work: a=0.20, b=0.72, c=0.81

yields unsigned error with respect to the G2 data base
slightly above 2 kcal/mol

Performance and Computational considerations

SCF-DFT; KS-equation:

$$-\frac{1}{2} \nabla^2 + V_N(\vec{r}_1) + V_C(\vec{r}_1) + V_{xc}(\vec{r}_1) \psi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}_1)$$

$$V_N(\vec{r}_1) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}_1|}; V_C(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2; \tilde{V}_{xc}[\rho(\vec{r}_1)] =$$

$$= \delta E_{xc}[\rho(\vec{r}_1)] / (\delta \rho(\vec{r}_1)) \Rightarrow i=1, \dots, N \quad \phi_i(\vec{r})$$

$$\phi_i(\vec{r}_1) = \sum_{k=1}^M c_{ik} \chi_k(\vec{r}_1) \quad \chi_k(\vec{r}_1) \text{ basis functions}$$

c_{ik} , $k=1 \dots M$, $i=1, \dots, N$ eigenfunctions (vectors)

$$\sum_{\mu=1}^M [F_{\nu\mu} - \epsilon_i S_{\nu\mu}] = 0, \quad \nu=1, \dots, M \quad F_{\nu\mu} = \int \chi_\nu(\vec{r}_1) \tilde{h}_{\nu\mu} \chi_\mu(\vec{r}_1) d\vec{r}_1$$

$$S_{\nu\mu} = \int \chi_\nu(\vec{r}_1) \chi_\mu(\vec{r}_1) d\vec{r}_1$$

representation of $V_C(\vec{r}_1)$: fitting the molecular density
to a set of one-center auxiliary functions $f_\gamma(\vec{r}_1)$

$$\tilde{\rho}(\vec{r}_1) \approx \sum_{\gamma} a_{\gamma} f_{\gamma}(\vec{r}_1); \quad \tilde{V}_C(\vec{r}_1) \approx \sum_{\gamma} a_{\gamma} \int \frac{f_{\gamma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2$$

Assessment of Approximate DFT

Calculation of molecular properties and comparison with experimental and ab-initio results.

yields nearly chemical accuracy ± 5 kcal/mol.

Bond Energies : molecular energetics (eV)	exp	HF	HFS	LDA	LDA-NL
B_2	3.1	0.9	3.9	3.9	3.2
C_2	6.3	0.8	6.2	7.3	6.0
N_2	9.9	5.7	9.3	11.6	10.3
O_2	5.2	1.3	7.1	7.6	6.1
F_2	1.7	-1.4	3.2	3.4	2.2

First M-CO Dissociation Energy (kJ/mol)

	HFS	LSD	LSD/NL	expt
$Cr(CO)_6$	278	276	147	162
$Mo(CO)_6$	226	226	119	126
$W(CO)_6$	247	249	142	166
$Ni(CO)_4$	194	192	106	104

largest effect of improvement comes from the NL correction to the exch. effect of E_C^{NL} is modest

HF - underestimates E_{diss} in particular for π -bonds

$\int_{-\infty}^{\infty} \chi_{HF}(\vec{r}_1, s)$ too diffuse with respect to s

HFS : $\int_{-\infty}^{\infty} \chi_{HFS}$ changes little from atoms to molecules overestimates the bond energy slightly

LDA E_C^{LDA} in addition to E_x^{LDA} : even larger bond energies : increases with the number of bonds (electron

$\uparrow p$ pairs), sometimes the overestimate to 100%, important in reactivity studies ; NL exchange and correlation improves the results

Molecular geometries

analytic gradients; HF not able to yield accurate geometries; near degeneracy error, improved by CI

	A-B	HF	HFS	expt
Fe(CO) ₅	Fe-Cax	2.047	1.774	1.807
	Fe-Ceq	1.874	1.798	1.827
Fe(C ₅ H ₅) ₂	Fe-C	1.88	1.60	1.65
HCo(CO) ₄	Co-Ceq	2.02	1.753	1.764
	Co-Cax	1.96	1.779	1.818

	expt	HF	HFS ^{α_{ex}=0.7}	LDA ^{α_{ex}=0.66}	LDA-NL X
B ₂	1.59		1.60	1.60	1.62
C ₂	1.24	1.25	1.24	1.24	1.25
N ₂	1.10	1.06	1.09	1.09	1.10
O ₂	1.21	1.15	1.20	1.20	1.23
F ₂	1.41	1.32	1.38	1.38	1.44

Analytic gradients in DFT (earlier point by point, different to HF)

HFS and LDA in better accord with exp. than HF and very similar; for Li₂, Na₂ LDA better than HFS

HFS and LDA underestimate R by ≈ 0.05 Å

non-local LDA-X tend to elongate the bond

non-local LDA-C -4- to shorten the bond

error in bond lengths in the HFS 1-2°

LDA are about of the same quality as MP2 ab-initio

for organic molecules.

errors on HFS and LDA TM-TM are large 0.05 Å too short but smaller than errors in HF TM-L

Potential energy surfaces, Conformations and Bond energy analysis

Conformation energy differences well reproduced by HF and for LDA; eclipsed vs staggered $\text{Fe}(\text{C}_5\text{H}_5)_2$, C_2H_6

ADF: Morokuma-type energy decomposition



$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} = \Delta E_{\text{prep, geo}} + \Delta E_{\text{prep, el}} + \Delta E_{\text{int}}$$

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta E_{\text{oi}} = \Delta E^{\circ} + \Delta E_{\text{oi}}$$

ΔE_{elstat} - classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments $\int = \int_A + \int_B$

For neutral fragments ΔE_{elstat} is usually attractive.

ΔE_{pauli} arises as the energy change as one goes

from $\int_A + \int_B$ to $\psi^{\circ} = N A [\psi_A \psi_B]$ i.e. antisymmetrized (A) and renormalized (N) of the product of fragment functions.

destabilizing interaction between occupied orbitals - steric (closed shell or noble gas like repulsion) repulsion. For neutral fragments $\Delta E^{\circ} = \Delta E_{\text{elstat}} + \Delta E_{\text{pauli}}$

ΔE° steric interaction;

better to reserve this for ΔE_{pauli}

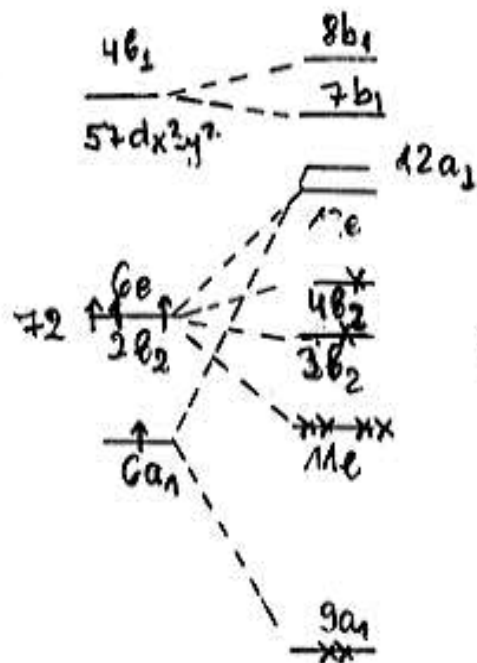
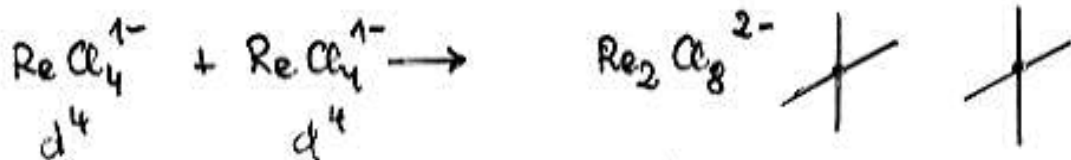
ΔE_{oi} - accounts for the relaxation of the wavefunction

$\psi^{\circ} \rightarrow \psi$ converged wave function; electron pair

bonding, charge transfer (HOMO - LUMO interaction)

$\Delta E_{\text{oi}} = \sum \Delta E_{\text{oi}, \Gamma}$ $\Delta E_{\text{oi}, \Gamma}$ contributions from the distinct, Γ irreducible representations.

The unique bonding in $Re_2Cl_8^{2-}$



ΔE_{Pauli}	ΔV_{Estat}	ΔE_{oi}	ΔE_{int}
25.46	-10.31	-20.79	-5.64

$9a_1^2(\sigma) 11e^4 (3b_2 4b_2)^2$ singlet ground state

ΔE_{oi}	$\Delta E_{oi}(a_1)$	$\Delta E_{oi}(e)$	$\Delta E_{oi}(b_2)$
-20.79	-10.63	-9.29	-0.80

	ΔE_{int}	ΔV_{Estat}	ΔE_{Pauli}	ΔE_{oi}
eclipsed	-5.64	-10.31	25.46	-20.79
staggered	-4.99	-10.08	24.87	-19.77

Scalar, relativistic, ZORA calculation, PW91, TZP

Transition state structures and Reaction Profiles

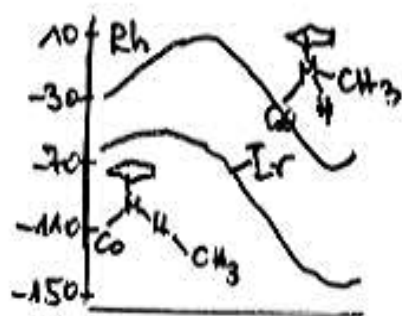
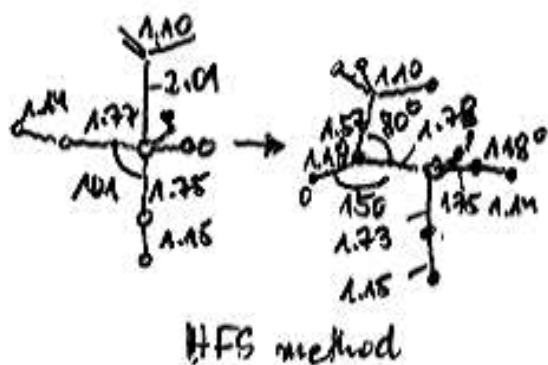
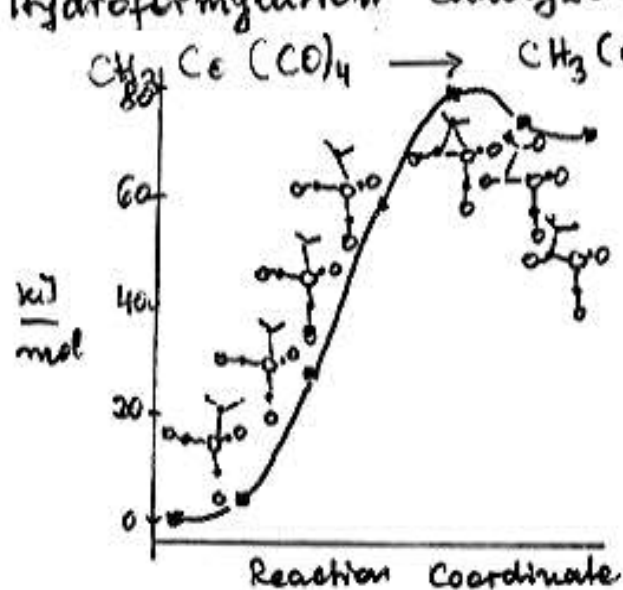
Chemical reaction: determination of the potential energy surface as a function of the nuclear coordinates
 Classical transition state theory

Surface around the reactant(s), product(s), transition state (saddle point), lowest energy pathway connecting them.

$CH_3NC \rightarrow CH_3CN$ barrier 38 kcal/mol (exp.)
 HFS 40.8 kcal/mol, ab-initio SDQ-MBPT(4) 10^7 config.
 barrier 41 kcal/mol.

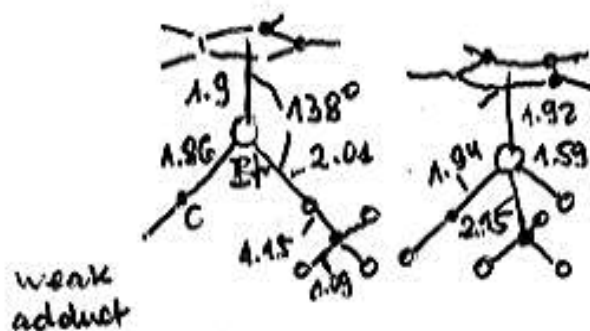
Catalysts using TM complexes

Hydroformylation catalyzed by $HCo(CO)_4$

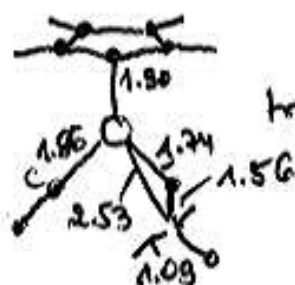


functionalization of methane to more valuable chemicals; low activation for Ir, to activa

Reaction profile for oxidative addition of CH_4 to $Cp(CO)Rh$



hydrido alkyl product.



transition state with elongated C-H bond

Molecular Force Fields

Force field method by Pulay Mol. Phys. 1969, 17, 197
 numerical differentiation of analytical gradients
 routinely

Harmonic frequencies (cm^{-1})

	HF	HFS	LDA	LDA/NL	MP2	exp
C_2	1970	1870	1880	1830	-	1855
N_2	2730	2380	2380	2330	2173	2358
CO	2430	2170	-	-	2113	2170
AuH	1875	2305	-	-	-	2241
Au_2	165	201	-	-	-	191

Failure of HF in particular for π -bonded systems

$\text{C}_2, \text{N}_2, \text{CO}$: inherent near-degeneracy error

eliminated by MP2; HFS good even for AuH, Au_2

going to LDA (dynamical correlation via E_c^{LDA})

no significant change, \rightarrow LDA/NL rather modest

influence

HFS: frequencies somewhat too small compared to exp.

$\text{H}_2\text{C}, \text{H}_2\text{S}, \text{NH}_3, \text{PH}_3, \text{CH}_4, \text{SiH}_4, \text{C}_2\text{H}_2$:

HFS: 1.9% (H_2O) 9.3% (SiH_4) lower percentage deviation
 HF: mean 9% mean 5% & higher than exp.

MP2: mean 4% and thus slightly better than DFT

Salahub: frequencies of organic molecules interacting
 with metal clusters; provides crucial information
 in connection with studies of chemisorption

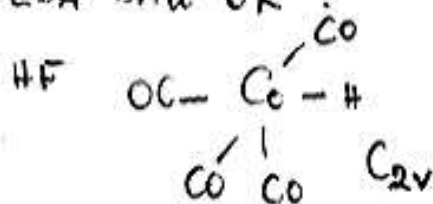
	Sym.	HFS	HF	MP2	expt.
H ₂ O	a ₁	3814 (-18)	4070 (238)	3772 (-60)	3832
	a ₁	1590 (-58)	1826 (178)	1737 (89)	1648
	b ₂	3877 (-66)	4188 (245)	3916 (-27)	3943
H ₂ S	a ₁	2631 (-91)	2918 (186)	2797 (75)	2722
	a ₁	1178 (-37)	1368 (153)	1279 (64)	1215
	b ₂	2644 (-89)	2930 (197)	2824 (91)	2733
NH ₃	a ₁	3314 (-192)	3690 (184)	3504 (-2)	3506
	a ₁	953 (-69)	1207 (185)	1166 (64)	1022
	e	3468 (-109)	3823 (246)	3659 (82)	3577
PH ₃	e	1564 (-127)	1849 (158)	1852 (161)	1691
	a ₁	2313 (-139)	2666 (214)	2510 (58)	2452
	a ₁	950 (-91)	1143 (102)	1079 (38)	1041
CH ₄	e	2329 (-128)	2602 (145)	2526 (69)	2457
	e	1088 (-66)	1278 (124)	1181 (27)	1154
	a ₁	2951 (-186)	3197 (60)	3115 (-22)	3137
SiH ₄	e	1467 (-100)	1703 (136)	1649 (38)	1567
	t ₂	3102 (-56)	3302 (144)	3257 (99)	3158
	t ₂	1236 (-121)	1488 (131)	1418 (61)	1357
SiH ₄	a ₁	2187 (-190)	2233 (-144)	2323 (-14)	2377
	e	905 (-70)	1052 (77)	1005 (30)	975
	t ₂	2217 (-102)	2385 (66)	2337 (18)	2319
	t ₂	777 (-168)	1016 (71)	956 (11)	945

Ionization Potentials

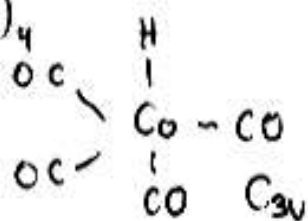
PES testing ground for new theoretical methods including DFT; first applications of HFS → assignment of PES; HFS underestimates IP for closed shell molecules and ions with a single unpaired electron including dynamical correlation (LDA+U) increases IP and thus close the gap between theory and experiment.

Conformers: unsaturated systems (π -bonds) HF fails

but LDA still OK:



$\text{HCo}(\text{CO})_4$



experimental structure, HFS still OK

	IP, Ionization Energies (eV)			first and second IE
	HFS	LDA	LDA/NL	expt
N_2	14.60	15.05	15.24	15.60
	16.60	16.95	16.81	16.98
CO	12.81	13.50	13.85	14.01
	16.74	17.17	17.01	16.53
F_2	14.78	15.02	15.34	15.70
	18.08	18.35	18.58	18.98
H_2O	12.63	12.55	12.59	12.62
	13.85	14.46	14.60	14.75
NH_3	10.66	10.62	10.76	10.88
	15.59	15.98	16.37	16.0
CH_4	13.18	13.61	14.01	14.35
	21.20	21.50	22.0	23.00
C_2H_4	10.14	10.60	10.56	10.51
	11.84	12.22	12.75	12.85

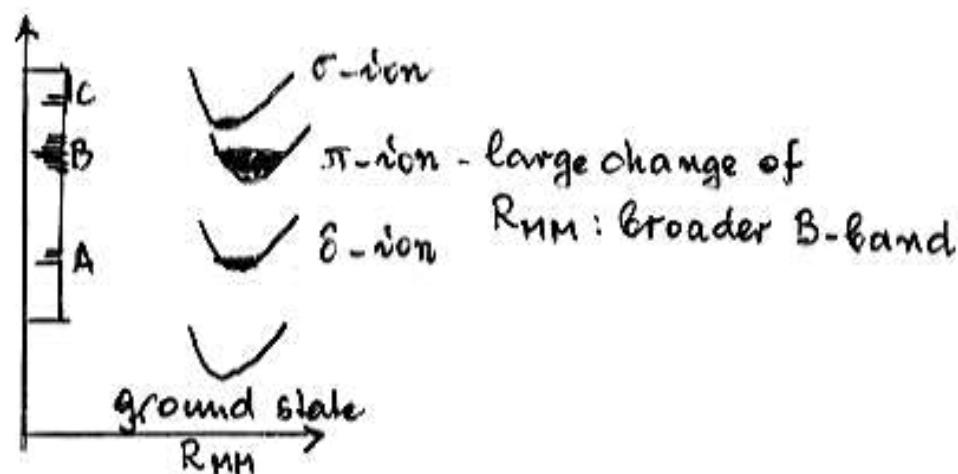
Increase of IE due to E_C^{LSD} : stabilize the molecule relative to the ion; one additional pair with

Restricted (R) - HFS: the ion has a higher energy α spin in R-HFS than U-HFS; from a conceptual point of view use always U-restr.

Non-local corrections: further improve IE

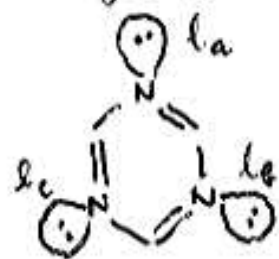
Becke's exchange correction: destabilizes the non, important for s^n -orbitals;

$M_2(L_2CR)_4$, $M_2Cl_4(PR_3)_4$ $M = Cr, Mo, W$ photoelectron spectra (quadruple M-M bonds)



Unphysical features of DFT: ionizations involving non-interacting symmetry-equivalent localized orbitals

symmetrize: ionization localized with electron



hole confined primarily say on l_a

alternatively delocalized D_{3h} $a_1' = \frac{1}{\sqrt{3}}(l_a + l_b + l_c)$

localized state: lower energy $e' = \frac{1}{\sqrt{2}}(l_b - l_c)$

then the delocalized in ab-initio $e' = \frac{1}{\sqrt{6}}(2l_a - l_b - l_c)$

DFT: yields delocalized hole: unphysical result

inadequate description of $\bar{h}_{xx}^{\sigma\sigma}(r_1, s)$ in the delocalized case

spurious self-interaction terms for the electrons

Noodleman Baerends Chem. Phys. 1982, 64, 159

one should apply the localized description in DFT calculation of IE out of localized and non-interacting symmetry equivalent orbitals representing lone pairs or core shells

Multiplets, Excitation Energies, Near Degeneracies

$$E_X^{LDA} = -\left(\frac{9}{4}\right) \alpha_{ex} \left[\frac{3}{4\pi}\right]^{1/3} \left\{ \left[\rho_a^\alpha(\vec{r}_1) \right]^{4/3} + \left[\rho_b^\alpha(\vec{r}_1) \right]^{4/3} \right\} d\vec{r}_1$$

difficulty in evaluating space and spin multiplets in DFT

$a^1 \bar{b}^1$

$$D_1 = |a^+ \bar{b}^+| \quad D_2 = |\bar{a} \bar{b}| \quad D_3 = |a^+ \bar{b}| \quad D_4 = |\bar{a} \bar{b}^+|$$

$${}^3\Psi = D_1 \quad {}^3\Psi = \frac{1}{\sqrt{2}} (D_3 + D_4) \quad {}^{-1}\Psi = D_2 \quad {}^1\Psi = \frac{1}{\sqrt{2}} (D_3 - D_4)$$

$$D_3 = \frac{1}{\sqrt{2}} ({}^3\Psi + {}^1\Psi) = D_4$$

$$f_1^\alpha = \frac{D_1 + D_2}{f_a^\alpha + f_b^\alpha}$$

$$\frac{D_3 + D_4}{\frac{1}{2}(f_a^\alpha + f_b^\alpha)}$$

$$f_a^\alpha = (a^\alpha)^2 \quad f_b^\alpha = (b^\alpha)^2$$

$$f_1^\beta = \frac{D_1 + D_2}{f_a^\beta + f_b^\beta}$$

$$\frac{D_3 + D_4}{\frac{1}{2}(f_a^\beta + f_b^\beta)}$$

$$f_a^\beta = (a^\beta)^2 \quad f_b^\beta = (b^\beta)^2$$

$$E_X^{LDA} ({}^3\Psi) = E_X^{LDA} ({}^{-1}\Psi) \neq E_X^{LDA} ({}^3\Psi) = E_X^{LDA} ({}^1\Psi)$$

E_X^{LDA} is applicable to a single determinant wavefunction

Exchange energies for multiplets represented by linear combinations of determinants must be evaluated indirectly

by Slater's sum rules, Ziegler, Rank, Baerends TCA 1977,

$$E_X^{LDA} (\text{triplet}) = E_X^{LDA} (D_1) = E_X^{LDA} (D_2) \quad 43, 261.$$

$$E_X^{LDA} (D_3) = \frac{1}{2} E_X^{LDA} (\text{triplet}) + \frac{1}{2} E_X^{LDA} (\text{singlet})$$

$$E_X^{LDA} (\text{singlet}) = 2 E_X^{LDA} (D_3) - E_X^{LDA} (D_1)$$

general case: a configuration D_i entering in a number of multiplets: D_i $E_x^{LDA}(D_i)$; known from DFT

M_i multiplets, exchange energy $E_x^{LDA}(M_i)$ unknown

$$E_x^{LDA}(D_i) = \sum_j C_{ij} E_x^{LDA}(M_j); \quad C_{ij} \text{ given by group theory}$$

The procedure in getting $E_x^{LDA}(M_i)$, the multiplet energy using Slater's sum rules is to invert C_{ij} matrix

$$E_x^{LDA}(M_j) = \sum_i A_{ji} E_x^{LDA}(D_i) \quad A_{ji} = [C_{ij}]^{-1}$$

b E_T , E_S in eV HFS method

		E_T	E_T (exp)	E_S	E_S (exp)
H_2CO	$2b_2 \rightarrow 2b_1$	3.18	3.21	3.70	3.50
C_2H_2	$\pi \rightarrow \pi^*$	4.57	4.60	7.45	7.60
C_4H_6	$1b_g \rightarrow 2a_u$	3.31	3.22	5.05	5.9
CO	$5\sigma \rightarrow 2\pi$	5.81	6.3	7.99	8.4
N_2	$3\sigma_g \rightarrow 1\pi_g$	7.83	8.1	9.13	9.3
N_2	$2\sigma_g \rightarrow 1\pi_g$	10.68	11.1	12.34	12.80

von Barth Phys Rev. 1979, A20, 1093, Gunnarsson Physica Sc 1980, 21, 394.

→ atomic multiplets

alternative approach for multiplets: Dunlap, B. Chem. Phys. 1988, 125, 98.

Transition, metals:	MnO ₄ ⁻		HFS Slater CrO ₄ ²⁻		VO ₄ ³⁻	
	E _S	E _S ^{exp}	E _S	E _S ^{exp}	E _S	E _S ^{exp}
t ₂ → 2e.	2.48	2.27	3.30	3.32	4.51	4.58
4t ₂ → 2e	3.96	3.47	4.58	4.53	5.71	5.58
t ₁ → 5t ₂	4.15	3.99	4.90	4.86	6.15	6.15

-5t₂
 → 2e d⁰
 Td-sous
 H-H t₁
 H-H-H t₂

HF and post HF (all-implicit) methods failed to calculate excitation energies of MnO₄⁻ with near quantitative accuracy; source of errors in HF
 J.Chem. Phys. 1990, 93, 4129.

Cases that require more than one determinant even at the lowest level of approximation

- 1) weakly interacting sub units: dissociating bonds (H₂)
- 2) magnetically coupled metal centers
- 3) avoided crossings of potential energy surfaces for states of the same symmetry in which HOMO or SOMO and the LUMO are of nearly the same energy

Dunlap applied to C₂, Si₂, Ni₂
 Chem. Phys. 1988, 125, 98 method of treating avoided crossings
 Adv. Chem. Phys. 1987, 69, 287
 Phys. Rev. 1984, A29, 2902 DFT
 several small cluster systems

Noodleman: method to describe magnetic coupling between weakly interacting metal centers: spin-projection
 → applied to metal dimers and ferredoxin, the method is also potentially applicable to bond dissociations