

Herramientas mecano-cuánticas basadas en DFT para el estudio de moléculas y materiales en Materials Studio 7.0

Javier Ramos

Biophysics of Macromolecular Systems group
(BIOPHYM)

Departamento de Física Macromolecular
Instituto de Estructura de la Materia – CSIC

j.ramos@iem.cfmac.csic.es

Anteriores webinars

Introducción a Materials Studio en la Investigación Química y de Ciencias de los Materiales

Javier Ramos

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Mecánica y Dinámica Molecular con Forcite en Materials Studio

Javier Ramos

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Instituto de Estructura de la Materia – CSIC
j.ramos@iem.cfmac.csic.es

Webinar, 28 de Mayo 2014

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Índice

- *Density Functional Theory (DFT)*
- *The Jacob's ladder*
- *DFT modules in Materials Studio*
- *DMOL3, CASTEP and ONETEP*
 - *XC functionals*
 - *Basis functions*
 - *Interfaces in Materials Studio*
 - *Tasks*
 - *Properties*
- *Example: n-butane conformations*

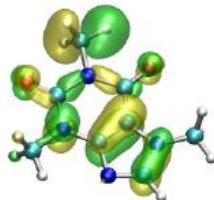
Density Functional Theory (DFT)

DFT is built around the premise that the energy of an electronic system can be defined in terms of its electron probability density (ρ). (Hohenberg-Kohn Theorem)

- wavefunction \leftrightarrow electron density

$$\Psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N)$$

3N dimensional object



$$\rho(\vec{r}) = \sum_i |\varphi_i(\vec{r})|^2$$

Kohn-Sham orbitals



3 dimensional

$$E_0[\rho_0] = T_e[\rho_0] + E_{ne}[\rho_0] + E_{ee}[\rho_0]$$

Kinetic Energy for
noninteracting
electrons(easy)

$$\int \rho(r) v(r) dr$$

(easy)

?????

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(r_1) \rho(r_2) d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho]$$

Classic Term(Coulomb)

Non-classic

Exchange &
Correlation

By minimizing the total energy functional applying the variational principle it is possible to get the SCF equations (Kohn-Sham)

$$\left(-\frac{1}{2} \nabla^2 + v_{Hartree}(r) + v_{ext}(r) + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \right) \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad i = 1, 2, \dots, N$$

The Jacob's Ladder

$E_{XC}[\rho]$



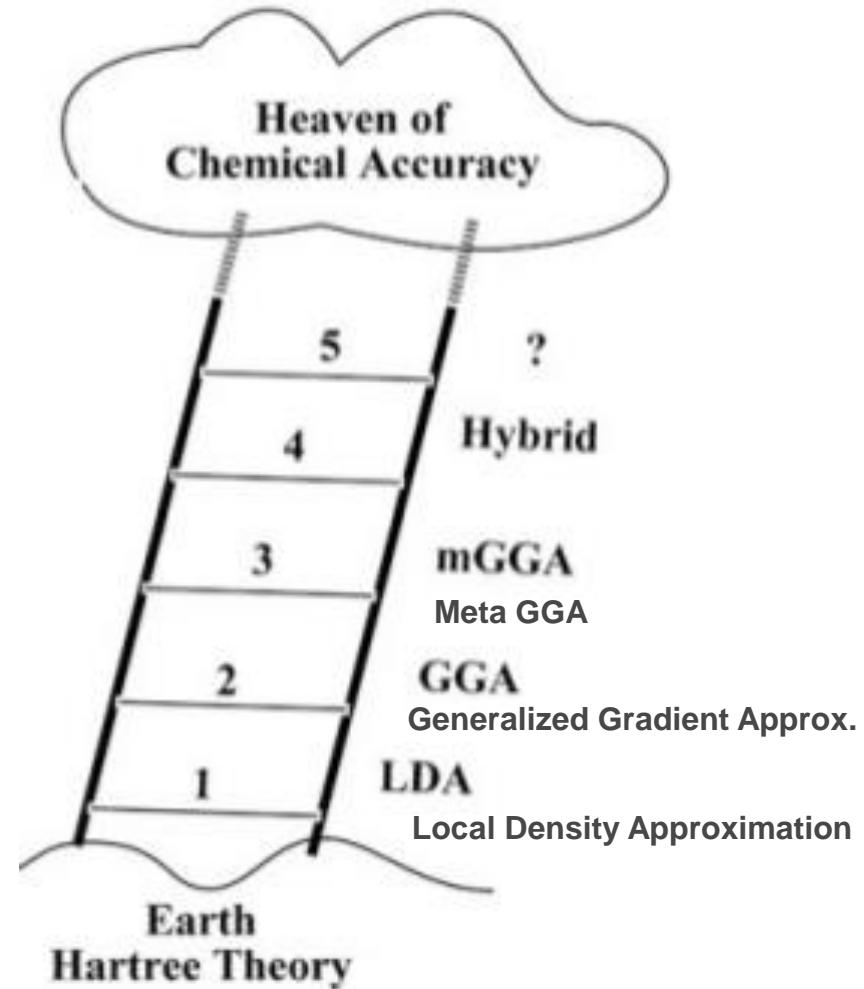
Accurate form of XC potential



Empirical (Fitting to atomic properties)



Non-Empirical
(physics rules)



I. Y. Zhang and X. Xu, *A New-Generation Density Functional*,
SpringerBriefs in Molecular Science, DOI: 10.1007/978-3-642-40421-4_1,

DFT flavor of coordination chemistry

Athanasios C. Tsipis*

[75]
[75]
[75]

Coordination Chemistry Reviews 272 (2014) 1–29

Table 1
Most common density functionals (DFs) in DFT model chemistry.

Density functional	Exchange functional	Correlation functional	
L(S)DA			
S-VWN3	Slater	VWN no 3	
S-VWN5	Slater	VWN no 5	
S-PWL	Slater	PW local	
GGA			
BP86	B88	P86	[76,78]
BPW91	B88	PW91	[78]
BPBE	B88	PBE	[78,99]
BLYP	B88	LYP	[78,100]
XLYP	B88 + PW91	LYP	[78,79,83,101]
OLYP	OptX	LYP	[83,101,102]
PBE	PBE	PBE	[99]
mPWLYP	mPW	LYP	[83,103]
mPW PW91	mPW	PW91	[103]
HCTC	HCTC	HCTC	[104]
meta-GGA			
BB95	B88	B95	[78,81]
mPWB95	mPW	B95	[81,103]
mPW CIS	mPW	Krieger-Chen-Lafrate-Savin	[103,105,106]
M06-L	Truhlar-Zhao	Truhlar-Zhao	[107]
PBEK CIS	PBE	Krieger-Chen-Lafrate-Savin	[99,105,108]
TPSS	TPSS	TPSS	[109]
TPSS CIS	TPSS	Krieger-Chen-Lafrate-Savin	[105,109]
tHCTC	HCTC	HCTC	[102]
VSXC	Van Vourhis-Scuseria	Van Vourhis-Scuseria	[110]
Hybrid- and double hybrid-GGA			
B1B95	B88	B95	[78,81]
B3LYP	B88	Lee-Yang-Parr	[78,81,83]
B3P86	B88	P86	[76,78,83]
B3PW91	B88	PW31	[78,83]
B97-2	B97-2	B97-2	[104]
BB1K	B88	B95	[78,81,111]
BMK	BMK	BMK	[112]
M05	Minnesota	Minnesota (28% HF exchange)	[113]
M05-2X	Minnesota	Minnesota (56% HF exchange)	[114]
M06-2X	Minnesota	Minnesota (54% HF exchange)	[115]
M08-HX	Minnesota	Minnesota (52.23% HF exchange)	[116]
MPW1K	mPW91	PW91	[103]
MN12-SX	Minnesota	Minnesota (screened exchange)	[117]
O3LYP	OptX	Lee-Yang-Parr	[83,102,118]
PBE0	PBE	PBE	[99]
TPSSh	TPSS	TPSS	[109]
X3LYP	B88 + PW91	Lee-Yang-Parr	[78,79,83,119]
Range-separated DFs			
B97XD	Modified B97 exchange DF for short-range interactions		[120]
ω -B97XD	Parametrized DF including 100% long-range exact exchange		[120]
B2PLYP-D	$E_{xc} = (1 - c_x)E_{xc,B88} + c_x E_{xc,HF} + (1 - c_c)E_{xc,LYP} + c_c E_{xc,MP2}$ ($c_x = 0.53$, $c_c = 0.27$)		[121]
CAM-B3LYP	Coulomb-attenuating method-B3LYP		[88]
DFT-D3	Dispersion-corrected conventional DFs		[122]
DSD-BLYP	$E_{xc} = (1 - c_x)E_{xc,B88} + c_x E_{xc,HF} + (1 - c_c)E_{xc,LYP} + c_0 E_{c^0,MP2} + c_s E_{c^s,MP2} + E_D$		[123]
LC- ω PBE	Long-range-corrected hybrid PBE exchange functional		[124]
DFT-dDXDM	Density-dependent dispersion corrected conventional DFs		[125]
DFT-dDS ζ	Density-dependent energy corrected conventional DFs		[126]

DFT modules in Materials Studio

DMol, a Standard Tool for Density Functional Calculations: Review and Advances

J.M. Seminario and P. Politzer (Editors)
Modern Density Functional Theory: A Tool for Chemistry
Theoretical and Computational Chemistry, Vol. 2
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B. Delley

First-principles simulation: ideas, illustrations and the CASTEP code

J. Phys.: Condens. Matter 14 (2002) 2717–2744

M D Segall^{1,2}, Philip J D Lindan^{3,7}, M J Probert⁴, C J Pickard¹, P J Hasnip⁵, S J Clark⁶ and M C Payne¹

THE JOURNAL OF CHEMICAL PHYSICS 122, 084119 (2005)

Introducing ONETEP: Linear-scaling density functional simulations on parallel computers

Chris-Kriton Skylaris,^{a)} Peter D. Haynes, Arash A. Mostofi, and Mike C. Payne
Theory of Condensed Matter, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

DMol³: Combine computational speed with the accuracy of quantum mechanical methods to predict materials properties reliably and quickly

CASTEP: CASTEP offers simulation capabilities not found elsewhere, such as accurate prediction of phonon spectra, dielectric constants, and optical properties. Simulate the properties of solids, interfaces, and surfaces for a wide range of materials classes, including ceramics, semiconductors, and metals.

ONETEP: Accurately treat systems such as protein-ligand complexes, grain boundaries, and nanoclusters with this revolutionary quantum mechanics-based program designed specifically for calculations on large systems (>500 atoms)

DMOL3, CASTEP and ONETEP. XC Functionals

Functional	DMOL3	CASTEP	ONETEP
LDA (Local Density Approximation)			
1980 VWN (Vosko-Wilk-Nusair)	X		X
1981 CA-PZ (Ceperley-Alder-Perdew-Zunger)		X	X
1992 PWC (Perdew-Wang)	X		
GGA (Generalized Gradient Approximation)			
1988 BP (Becke-Perdew)	X		
1988 BLYP (Becke, Lee-Yang-Parr)	X		X
1992 PW91 (Perdew and Wang)	X	X	X
1992 VWN-BP (Vosko-Wilk-Nusair, Becke-Perdew)	X		
1996 PBE (Perdew-Burke-Ernzerhof)	X	X	X
1998 REV-PBE			X
1999 BOP	X		
1999 RPBE (Revised Perdew-Burke-Ernzerhof)	X	X	X
2001 HCTH	X		
2004 XLYP			X
2006 WC		X	X
2008 PBESOL	X		
Hybrids			
B3LYP (Becke 3, Lee-Yang-Par)	X	X	
PBE0 (Perdew-Burke-Ernzerhof)		X	
Van der Waals Functionals			
2004 VDW-DF			X
2010 VDW-DF2			X
2010 optPBE			X
2010 optB88			X
2010 VDW-DK			X

DMOL3, CASTEP and ONETEP. Basis Function

$$\rho_i(x,y,z) = \sum_i |\phi_i^{KS}(x,y,z)|^2 \quad \phi_i^{KS}(x,y,z) = \sum_{\mu=1}^K c_{\mu i} f_{\mu}(x,y,z)$$

- **Gaussian:** Gaussian and Slater Type Orbitals (GTO and STO), i.e. 6-311G*
- **DMOL3:** Numerical Basis Set.
 - ✓ Small BSSE and best performance than GTO
 - ✗ No systematic way to improve basis set quality and careful tests required to construct a basis set
- **CASTEP:** Plane wave basis set.
 - ✓ Good description of periodic systems, no BSSE, mathematically simple. A single parameter controls convergence of the basis (Energy cutoff)
 - ✗ Need many functions to converge result. They provide the same accuracy at all points in space even if there is no electronic density there (pseudopotential approach addresses these issues). The periodicity is mandatory (supercell for isolated molecules).
- **ONETEP:** non-orthogonal generalized Wannier functions (NGWFs).
 - ✓ Linear scaling
 - ✗ It is still under development

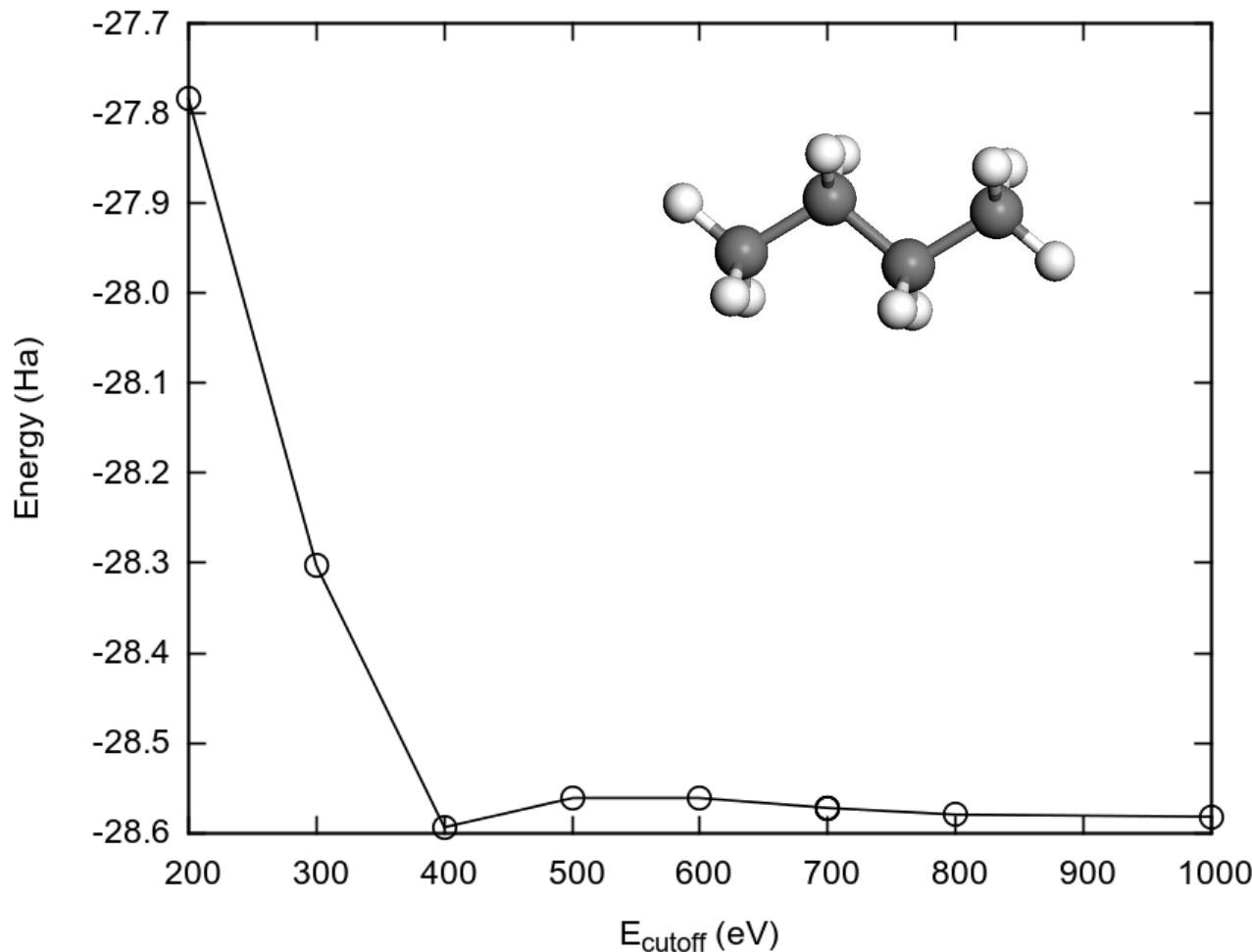
DMOL3. Basis Function

NUMERICAL BASIS FUNCTION

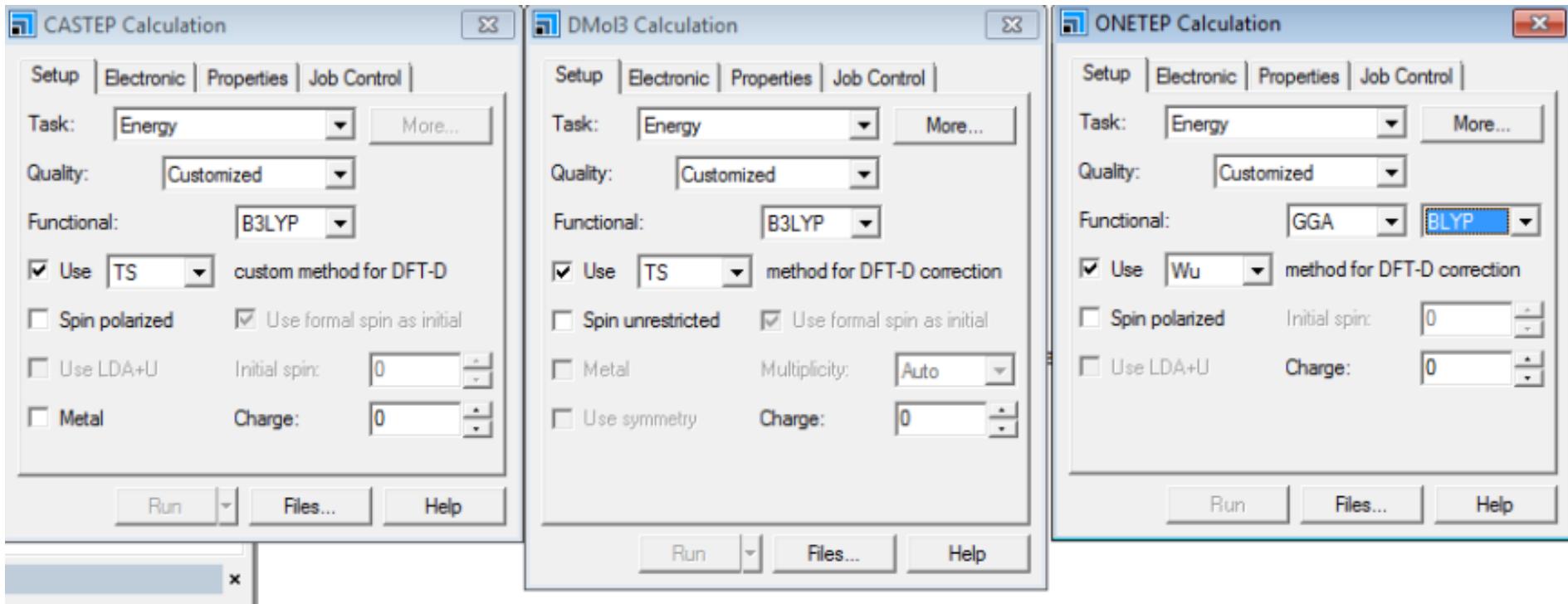
Basis Name	Description	Examples
MIN	Minimal basis. One AO for each occupied atomic orbital. Yields low accuracy but fast computation.	H: 1s C: 1s 2s 2p Si: 1s 2s 2p 3s 3p
DN	Double Numerical. MIN + a second set of valence AOs. Improved accuracy over MIN.	H: 1s 1s' C: 1s 2s 2p 2s' 2p' Si: 1s 2s 2p 3s 3p 3s' 3p'
DND	Double Numerical plus d-functions. Like DN with a polarization d-function on all non-hydrogen atoms. The default basis set, providing reasonable accuracy for modest computational cost.	H: 1s 1s' C: 1s 2s 2p 2s' 2p' 3d Si: 1s 2s 2p 3s 3p 3s' 3p' 3d
DNP	Double Numerical plus polarization. Like DND including a polarization p-function on all hydrogen atoms. Best accuracy, highest cost. Important for hydrogen bonding.	H: 1s 1s' 2p C: 1s 2s 2p 2s' 2p' 3d Si: 1s 2s 2p 3s 3p 3s' 3p' 3d
TNP	Triple Numerical plus polarization. Like DNP including additional polarization functions on all atoms. Available only for H to Cl except He and Ne. Best accuracy, highest cost.	H: 1s 1s' 2p 1s" 2p' 3d O: 1s 2s 2p 2s' 2p' 3d 2s" 2p" 3p 4d S: 1s 2s 2p 2s' 2p' 3s 3p 3s' 3p' 3d 3s" 3p" 3d' 4d
DNP+	Double Numerical plus polarization, with addition of diffuse functions. Good accuracy for cases requiring diffuse functions, very high cost coming mostly from very large atomic cutoffs required for this set. Important for anions, excited state calculations and for cases where long-range effects are non-negligible. The bold components are the additional diffuse functions.	H: 1s 1s' 2p 1s" 2p' C: 1s 2s 2p 2s' 2p' 3d 1s' 2p" 3d' Si: 1s 2s 2p 3s 3p 3s' 3p' 3d 1s' 2p' 3d'

CASTEP and ONETEP. Plane waves

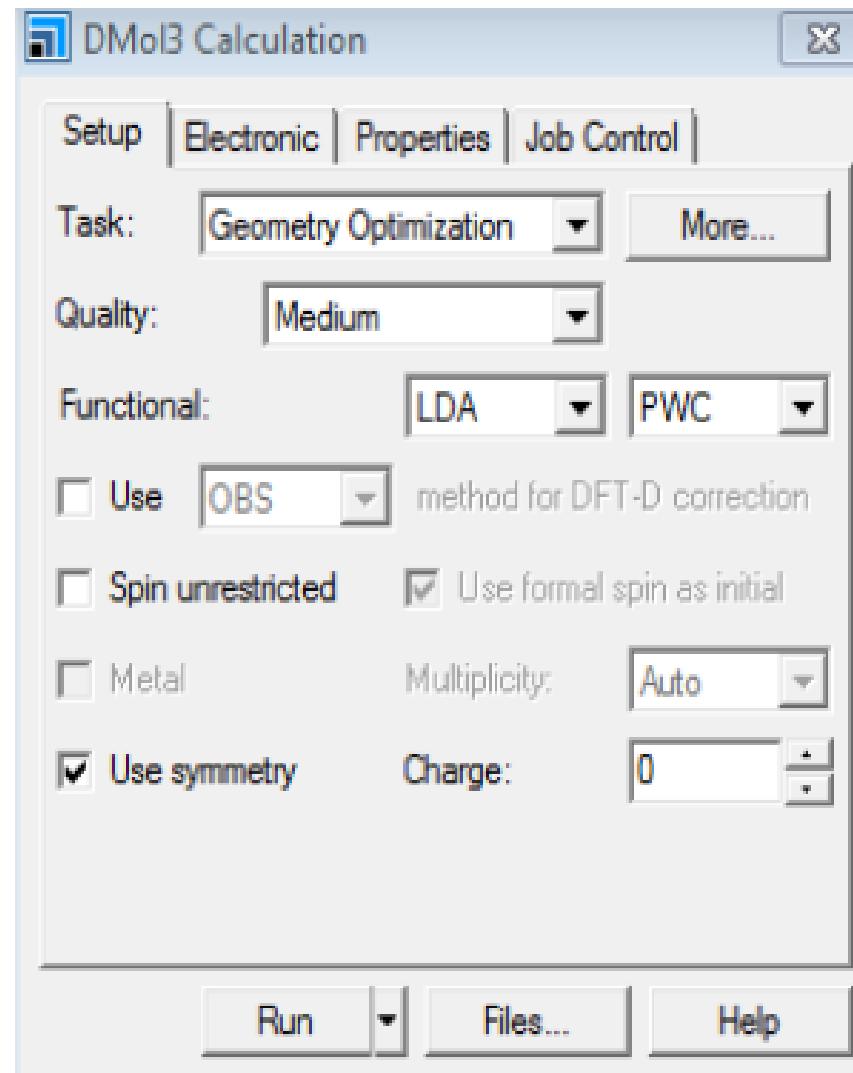
Ecut-off ~ Number of plane waves



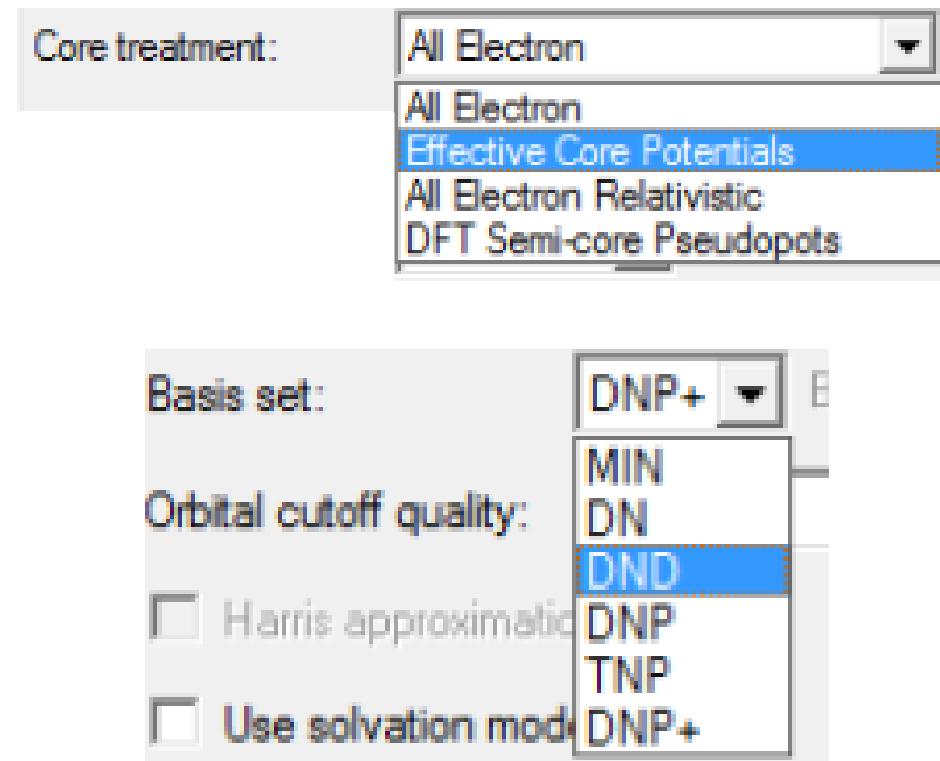
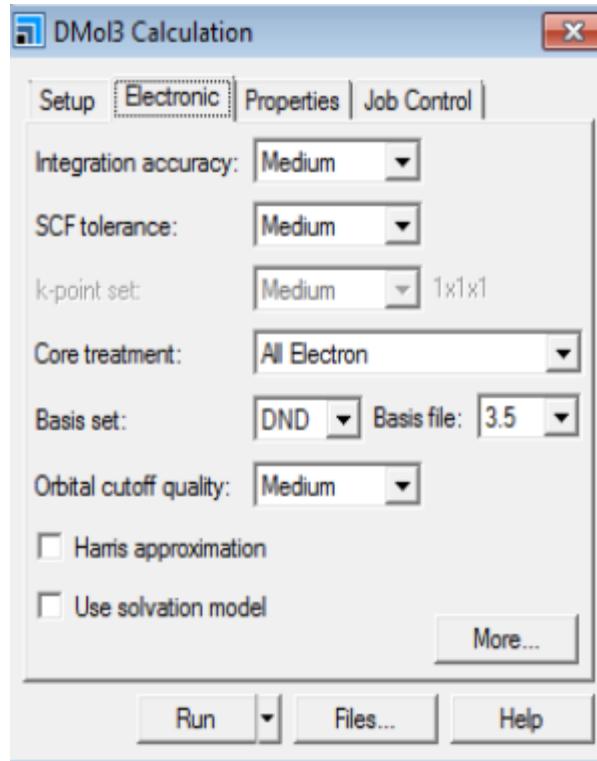
DMOL3, CASTEP and ONETEP. Interface in Materials Studio.



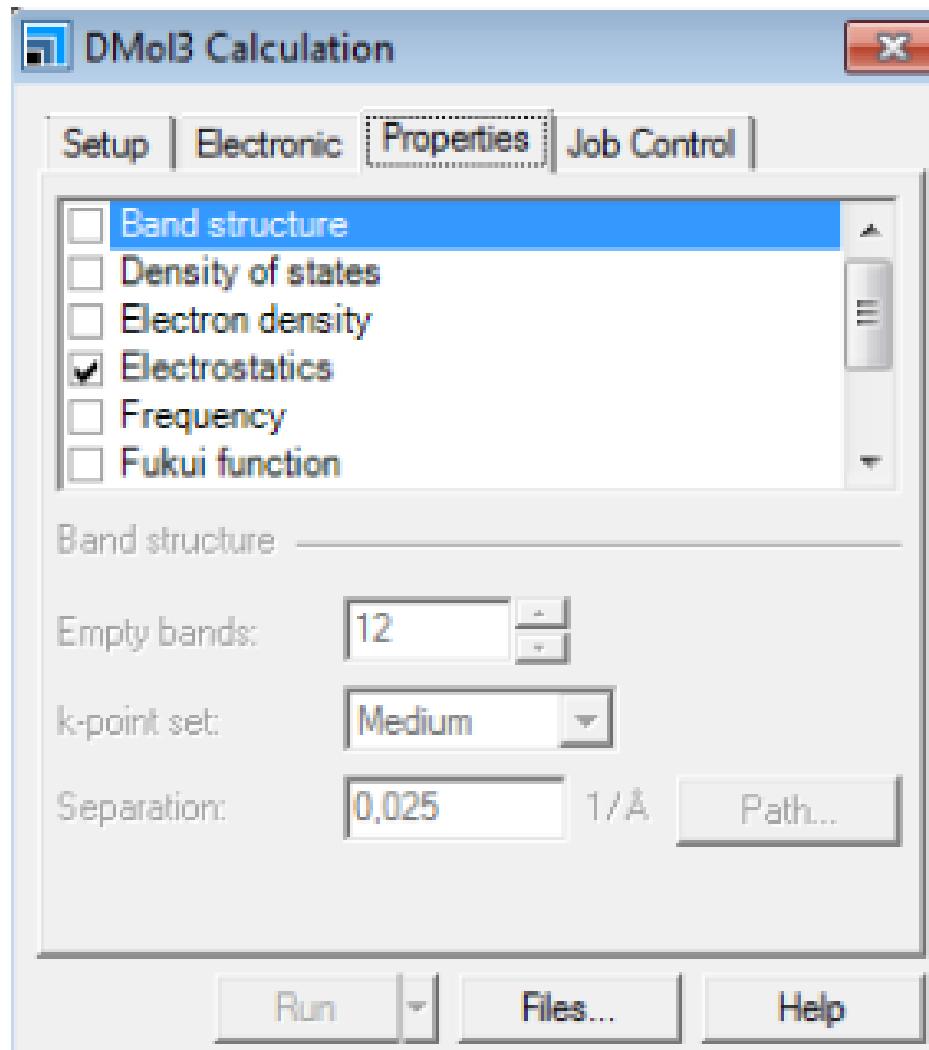
DMOL3 - Calculation



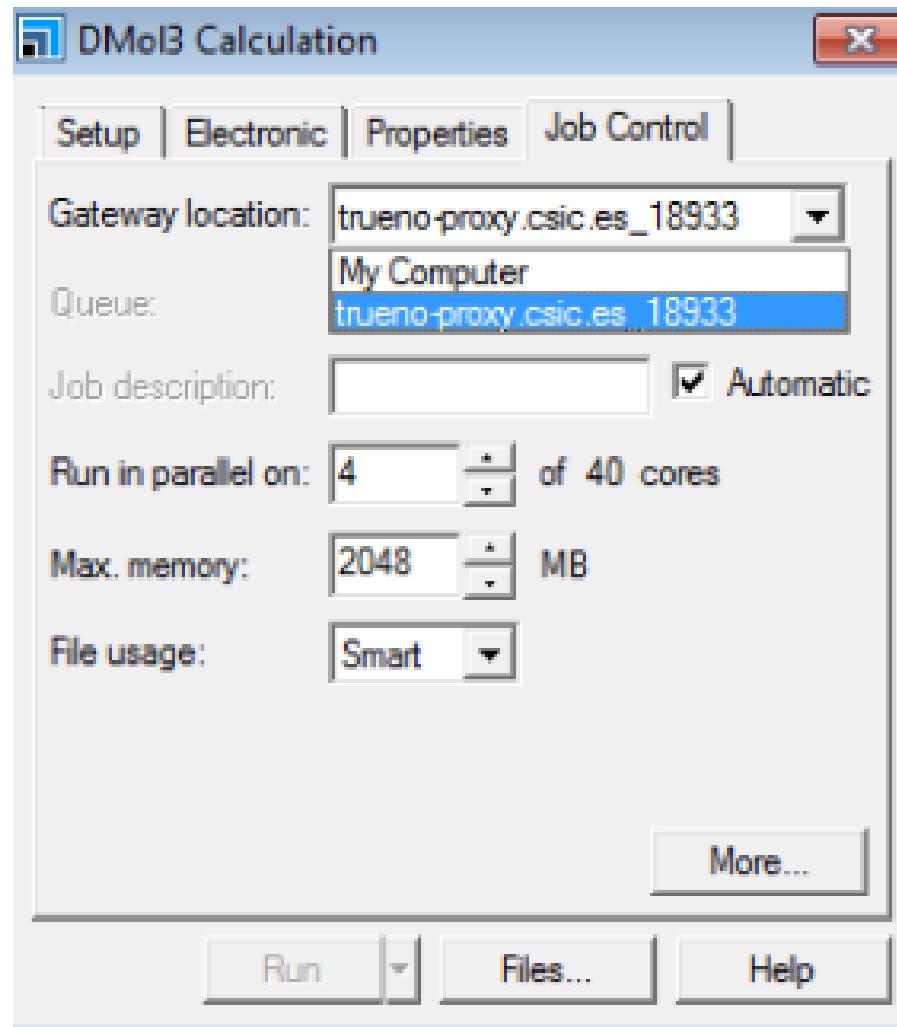
DMOL3 - Electronic



DMOL3 - Properties



DMOL3 – Job Control



DMOL3, CASTEP and ONETEP. Tasks

Task	DMOL3	CASTEP	ONETEP
Energy Single Point	X	X	X
Geometry Optimization	X	X	X
Dynamics	X	X	
TS Search	X	X	X
TS Optimization	X		
TS Confirmation	X	X	
Elastic Constant	X	X	

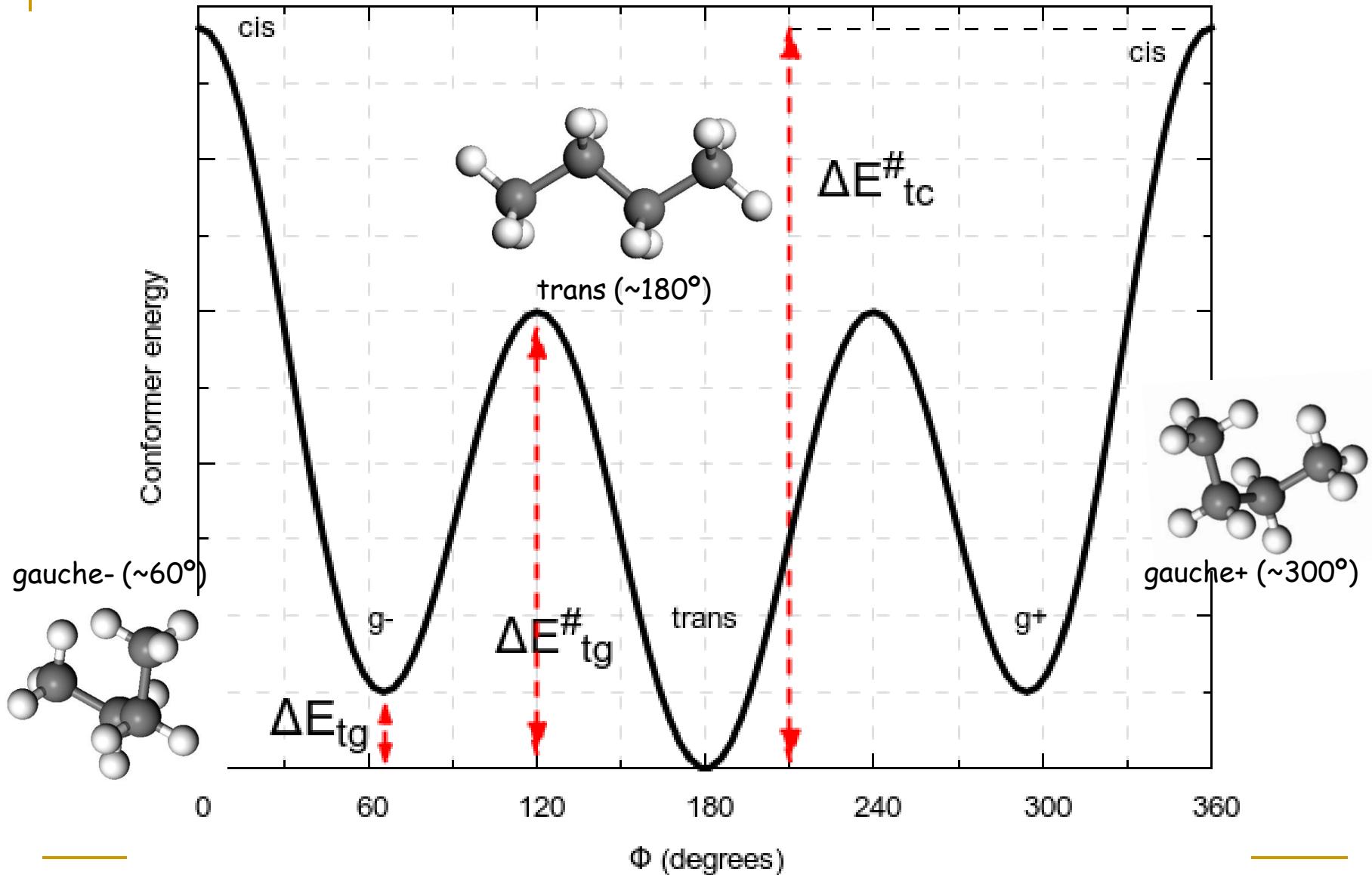
DMOL3, CASTEP and ONETEP. Properties

Properties	Description	DMOL3	CASTEP	ONETEP
Band Structure	It provides a useful tool for qualitative analysis of the electronic structure of a material. It is also instructive to look for directions with relatively flat, dispersionless bands, as these directions are likely to contribute strongly to optical absorption (anisotropy of optical properties). The energy band gap is also easily deduced from the band.	X	X	
Density of States	Density of states (DOS) and partial density of states (PDOS) charts give a quick qualitative picture of the electronic structure of a material and sometimes they can be related directly to experimental spectroscopic result	X	X	
Electron Density	It computes several different types of charge density	X	X	
Electrostatics	It computes several different properties related to the electrostatics of the input structure	X		
Frequency	It computes a Hessian and vibrational spectrum. You can visualize the vibrational spectrum and the results of the calculation by using the Vibrational Analysis dialog. The frequencies and corresponding intensities are also given	X		
Fukui Function	It computes the Fukui index for chemical reactivity. $f(+)$ reflects susceptibility to nucleophilic attack. $f(-)$ reflects susceptibility to electrophilic attack. $f(0)$ reflects susceptibility to attack by radicals.	X		
Optics	It computes optical properties for the structure using time-dependent density functional theory (TD-DFT)	X	X	X
Orbitals	It computes molecular orbitals for volumetric rendering	X	X	X

DMOL3, CASTEP and ONETEP. Properties

Properties	Description	DMOL3	CASTEP	ONETEP
Population Analysis	Several types of atomic population analysis: Mulliken analysis- produces charges based on the density matrix and atomic overlap matrix Hirshfeld analysis - produces partitioned charges that are defined relative to the deformation density ESP charges -- produces atomic-centered charges that best reproduce the DFT Coulomb potential	X	X	X
Core level spectroscopy	It produces electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transition		X	
Elastic constants	The elastic constants of a material describe its response to an applied stress or, conversely, the stress required to maintain a given deformation		X	
Electron Density Difference	It provides the option of generating the electron density difference in two different ways: <ul style="list-style-type: none">• Electron density difference with respect to a linear combination of the atomic densities.• Electron density difference with respect to a linear combination of the densities of sets of atoms contained in the model.		X	
Energy Evolution	Evolution of the energy along a trajectory		X	
IR & Raman Spectrum	CASTEP can be used to calculate the electric field response of isolated molecules as well as of solids. It is recommended that only the Γ -point is used for electronic calculations on molecular systems		X	
NMR	NMR calculations can generate the shielding tensor and/or electric field gradients for all of the atoms in the selected system		X	
Phonon Dispersion	Setup calculations that provide vibrational frequencies and eigenvectors at a selected set of q-vectors in the Brillouin zone. Two approaches: i) Linear response formalism and ii) Finite displacement method		X	

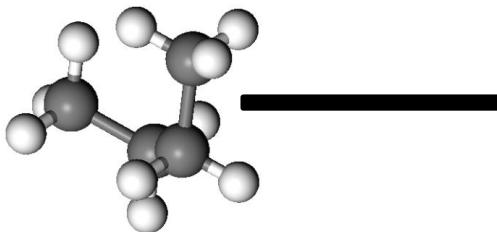
Example: n-butane conformations



Example: n-butane conformations

Energy trans-gauche conformations

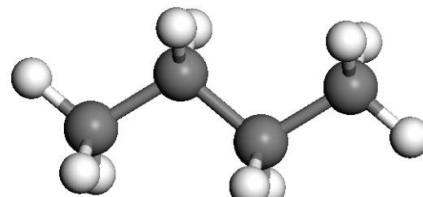
gauche- ($\sim 60^\circ$)



Experimental (gas phase) = 0.660 ± 0.022 kcal/mol
High-level ab-initio QM = $0.59 - 0.68$ kcal/mol
(MP2, CCSD(T), ...)

DMOL3 (LDA/DND)	=	0.18 kcal/mol
DMOL3 (BLYP/DND)	=	0.76 kcal/mol
DMOL3 (BLYP/TNP)	=	0.91 kcal/mol
DMOL3 (BLYP/TNP, ZPE)	=	1.10 kcal/mol
DMOL3(B3LYP/TNP)	=	1.18 kcal/mol
DMOL3(B3LYP/DNP+)	=	0.73 kcal/mol
CASTEP (B3LYP,680eV)	=	0.78 kcal/mol
CASTEP (PW81,680eV)	=	0.86 kcal/mol
ONETEP (PW81,700eV)	=	0.72 kcal/mol
ONETEP (BLYP,700eV)	=	0.74 kcal/mol

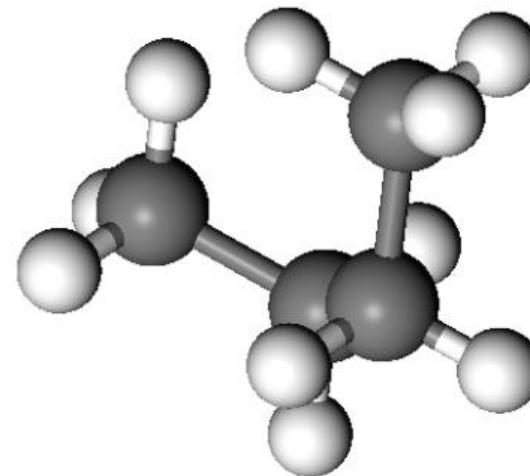
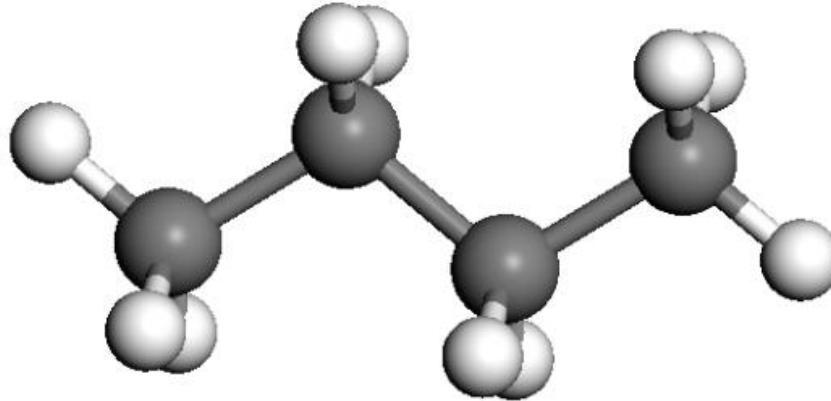
trans ($\sim 180^\circ$)



- a) M.J. Hafezi, F. Sharif Journal of Molecular Structure: THEOCHEM 814 (2007) 43–49
b) D. Gruzman, A. Karton, and J.M. L. Martin, J. Phys. Chem. A 113 (2009) 11974–11983

Example: n-butane conformations

Geometry trans and gauche conformations

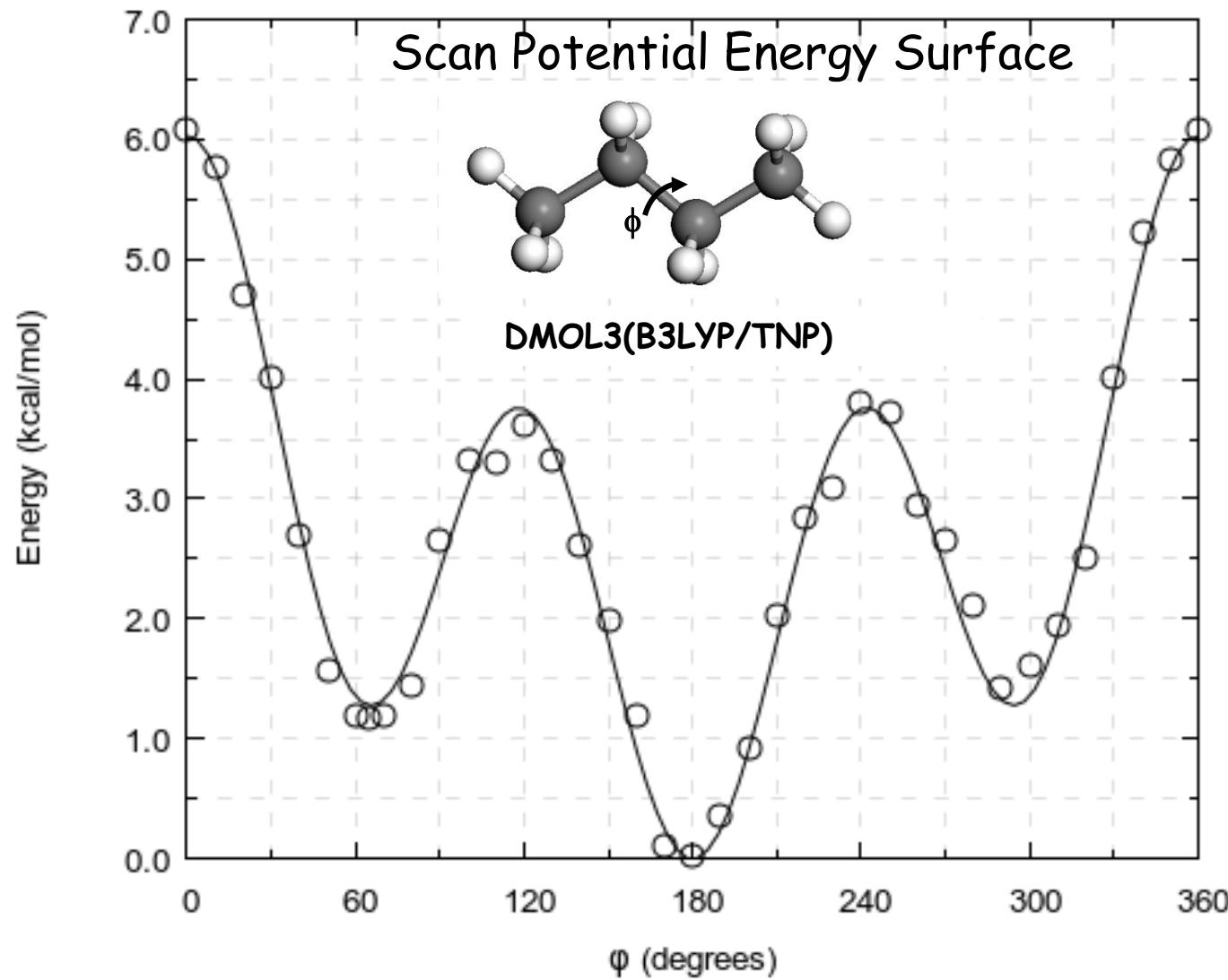


	MP2/ 6-311G(2df-p) ^{a)}	LDA/ DND	BLYP/ TNP	BLYP/ DNP+	Exp (gauche) ^{b)}
C1-C2 (A)	1.522 (1.524)	1.508 (1.510)	1.539 (1.540)	1.538 (1.540)	1.530
C2-C3 (A)	1.522 (1.526)	1.510 (1.514)	1.539 (1.544)	1.540 (1.544)	1.532
C1-C2-C3 (°)	112.6 (113.5)	112.8 (113.1)	113.4 (114.7)	113.3 (114.2)	113.3
C1-C2-C3-C4 (°)	180.0 (62.7)	180.0 (62.5)	180.0 (65.4)	180.0 (66.4)	62.8

a) M.J. Hafezi, F. Sharif Journal of Molecular Structure: THEOCHEM 814 (2007) 43–49

b) W.F. Bradford, S. Fitzwater, L.S. Bartell, J. Mol. Struct. 38 (1977) 185.

Example: n-butane conformations



$$\begin{aligned}\Delta E_{gt} \text{ (kcal/mol)} &= 1.16 \\ \Delta E_{gt}^{\#} \text{ (kcal/mol)} &= 3.70 \\ \Delta E_{ct}^{\#} \text{ (kcal/mol)} &= 6.07\end{aligned}$$

$$\begin{aligned}CCSD(T)-CB: 0.628^b \\ CCSD(T)-CB: 3.303^b \\ CCSD(T)-CB: 5.400^a\end{aligned}$$

a N.L. Allinger, J.T. Fermann, W.D. Allen, H.F. Schaefer, J. Chem. Phys. 106 (1997) 5143.

b R.W. Pastor, R.M. Venable, J.B. Klauda, B.R. Brooks Jr., A.D. MacKerell, J. Phys. Chem. B 109 (2005) 5300.

Example: n-butane conformations

Infrared Spectra DMOL3(BLYP/DNP+)

