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GAUSSIAN 09W TUTORIAL. AN INTRODUCTION TO COMPUTATIONAL CHEMISTRY USING G09W AND. AVOGADRO SOFTWARE. Anna Tomberg.

GAUSSIAN 09W TUTORIAL

AN INTRODUCTION TO COMPUTATIONAL CHEMISTRY USING G09W AND

AVOGADRO SOFTWARE

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This is a quick tutorial that will help you to make your way through the first steps of computational chemistry using Gaussian 09W software (G09). The tutorial is oriented to beginners and describes in detail the most used calculations done using G09. However, the theoretical basis of these calculations will not be covered here. If you are interested in understanding the details, please refer to textbooks targeting this subject. I found [1] and [2] very helpful, and strongly recommend to take a look at these wonderful books.

More TERMS

Polarization Basis sets

The previous page was about changing the size of orbitals without change in shape. But when in a molecule, the electron density on an atom is not the same as an isolated atom. This is accomplished by adding orbitals that have d character in the first row, and p character for H.

Examples: 6-31g* = 6-31g(d) adds 6 d-type GTFs for the atoms Li-Ca, and 10 f-type GTFs for Sc-Zn.

6-31g** = 6-31g(d,p) adds p character to H, in addition.

Diffuse Basis Sets

Anions particularly benefit from include large basis functions. e.g, 6-31+g includes extra large s and p functions on heavy atoms, and 6-31++g in addition at a diffuse s orbital to H

Some General Terms

<http://gaussian.com/keywords/>

Names

key words

Route card:

method/basis

for example:

hf/6-31g*

single point

geometry optimization

opt

vibrational frequency (must be opt first)

freq

transition state search

reaction path following

potential energy surface

solvation

Open Shell Calculations (some MOs have only 1 electron)

ROHF (restricted open shell) means electrons with opposite spin in same MO have the same spatial orbital.

UHF (unrestricted HF) means alpha and beta spins may have different spatial functions, thereby giving a slightly lower energy.

(but, will not usually be eigenfunctions of the S^2 operator (i.e., neither singlet or triplet, for example)

Even Larger Basis sets

For example 6-311++G(3df,3pd) is triple zeta set defined for H-Ar, that provides diffuse functions on all atoms, 3 sets of d and 1 set of f functions to non-H atoms, and 3 sets of p functions, 1 set of d functions for H. This also called a VTZ3PD, meaning valence triple zeta with triple polarization and diffuse on all atoms.

The above were developed by Pople.

Dunning and co-workers developed as series of basis functions denoted cc-pVnZ: i.e., cc-pVDZ, cc-pVTZ...,cc-pV6Z, which stand for *correlation-consistent, polarized valence double-zeta*, etc.

These basis sets were specifically designed to be used with methods that introduce electron correlation. Each set increases the orbital types as follows:

cc-pVDZ,	cc-pVTZ	cc-pVQZ,	cc-pV5Z	cc-pV6Z
[3s2p1d]	[4s3p2d1f]	[5s4p3d2f1g]	[6s5p4d3f2g1h]	[7s6p5d4f3g2h1i]

The number and degree of polarization (angular momentum) function increases rapidly from left to right, meaning more nodes, which is what is needed to introduce fine-grained correlation (**better dodging**). Doing a series of calculations with these basis sets on a molecule allow smooth extrapolation to what may be considered a near exact value.

If diffuse functions are added to the cc-pVnZ sets, they are called **aug- cc-pVnZ**.

TABLE 16.1 H₂O Calculations That Include Correlation^a

Reference ^b	Method ^c / Basis Set	Energy / E _h	μ / D	θ	R _{OH}	α
Harrison, Handy	CISD/DZ	-76.150				
Harrison, Handy	FCI/DZ	-76.158				
CCCBDB	MP2(FC)/6-31G*	-76.197	2.24	104.0°	0.969	
CCCBDB	CISD(FC)/6-31G*	-76.198	2.24	104.2°	0.966	
CCCBDB	MP2(full)/6-31G*	-76.199	2.24	104.0°	0.969	
CCCBDB	CCSD(FC)/6-31G*	-76.206	2.25	103.9°	0.969	
CCCBDB	MP4(FC)/6-31G*	-76.207	2.25	103.8°	0.970	
CCCBDB	CCSD(T)(FC)/6-31G*	-76.208	2.25	103.8°	0.971	
CCCBDB	MP2(FC)/6-31G**	-76.220	2.20	103.8°	0.961	
CCCBDB	CISD(FC)/6-31G**	-76.221	2.19	104.2°	0.958	
CCCBDB	MP2(FC)/cc-pVDZ	-76.229	2.10	101.9°	0.965	
CCCBDB	CCSD(T)(FC)/cc-pVDZ	-76.241	2.10	101.9°	0.966	
Scuseria, Schaefer	CISDTQ/DZP	-76.270	2.13	104.5°	0.965	
Schaefer et al.	CISD/TZ2P	-76.312	1.94	104.9°	0.952	
CCCBDB	CISD(FC)/cc-pVTZ	-76.314	2.03	104.2°	0.955	
CCCBDB	MP2(FC)/6-31+G(3df,2p)	-76.318	2.02	104.5°	0.959	
CCCBDB	MP2(FC)/cc-pVTZ	-76.319	2.04	103.5°	0.959	
CCCBDB	CCSD(T)(FC)/cc-pVTZ	-76.332	2.04	103.6°	0.959	
Cortez et al.	CCSD(T)(FC)/cc-pV6Z	-76.372		104.4°	0.958	
Kim et al.	CISD(full)/(13s...2d) ^d	-76.382		104.8°	0.952	
Kim et al.	MP2(full)/(13s...2d)	-76.391		104.2°	0.959	
Kim et al.	CCSD(full)/(13s...2d)	-76.396		104.4°	0.956	
Kim et al.	CCSD(T)(full)/(13s...2d)	-76.406		104.1°	0.959	
Kim et al.	MP4(full)/(13s...2d)	-76.407		104.1°	0.960	
CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969	
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965	
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969	
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e				
Gurtubay, Needs	FN-DQMC	-76.428 ^e				
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	0.961	
<i>Nonrelativistic fixed-nuclei energy</i>		-76.438				
<i>Experimental values</i>		-76.480	1.85	104.5°	0.958	

^aSee footnote a to Table 15.2 in Section 15.6.^bR. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theor. Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.^d(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.^eCalculated at a geometry close to the experimental geometry.

If electron-correlation is added to the wavefunction, all properties converge to experimentally observed values.

CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965
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B3LYP is the most popular DFT method;

B3LYP/cc-pVTZ

99.87% of experiment;

Takes 5 sec on a PC

Electron Correlation

Electrons are particles and dodge each other = electron correlation
(**London dispersion** force and energy = electron correlation between electrons on different molecules)

Two basic types: 1) **dynamic** correlation = dodging because of Coulombic repulsion
2) **static (non-dynamic, strong)** correlation = the ground state not well described by a single Slater determinant. Multi Configurational SCF (MCSCF) needed. The wavefunction “statically” keeps the electrons apart.

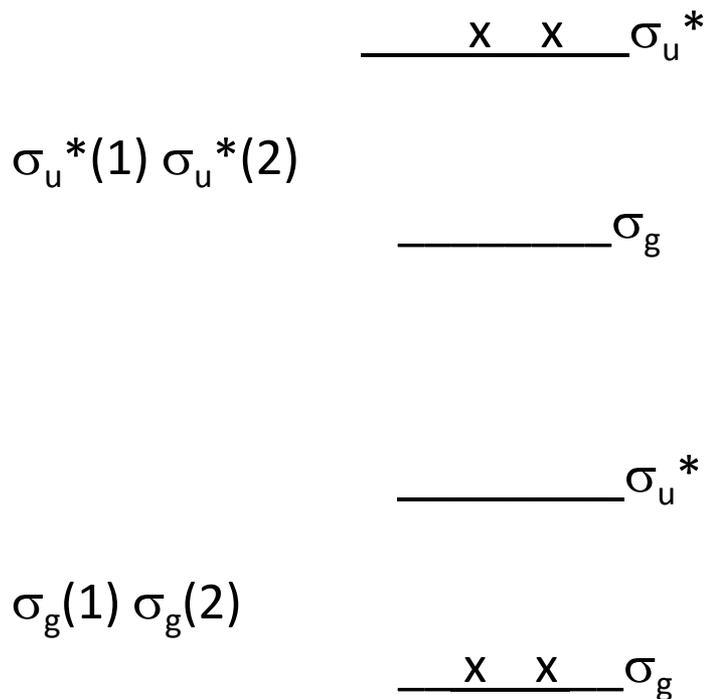
Methods for electron correlation

1. Configuration interaction (**CI**): mixing ground state configuration with excited state configurations (or configuration state functions (**CSFs**)) in **variational** formalism.
2. Moeller-Plesett (**MP**) perturbation theory = **CI** in the **perturbation** formalism
MP2, **MP3**, **MP4** = 2nd, 3rd, 4th, order theory
3. Coupled cluster (**CC**): **CI** by Taylor expansion in a **size-consistent** way
4. **DFT** No CI at all; static correlation built into the electron density functional that minimizes the energy.

How can CI (mixing higher energy state with ground state cause correlation???)

Higher states have **more nodes**. Squaring the linear combination gives cross terms (interference terms), which are negative when 2 electrons are on different sides of a nodal surface. $\Psi^*\Psi$ is thereby **reduced**.

Example: The H₂ molecule (ionic and covalent terms, difference between the MO and Valence Bond (VB) methods



H₂ Molecule Configuration State Functions (CSFs)

A(1) = 1s(1) on Nucleus A B(1) = 1s(1) on Nucleus B

Doubly excited CSF

_____ σ_u^2

Ground CSF

_____ σ_g^2

↑
Energy

$$\sigma_u^2 = [A(1) - B(1)] [A(2) - B(2)] = AA + BB - AB - BA \quad (\text{not normalized})$$

ionic covalent

ionic + covalent = molecular orbital method

$$\sigma_g^2 = [A(1) + B(1)] [A(2) + B(2)] = AA + BB + AB + BA \quad (\text{not normalized})$$

covalent* = AB + BA = valence bond method

*Heitler-London (1927) the **first** wavefunction proposed for H₂ at the dawn of quantum mechanics.