

Información Suplementaria

1) Costos computacionales

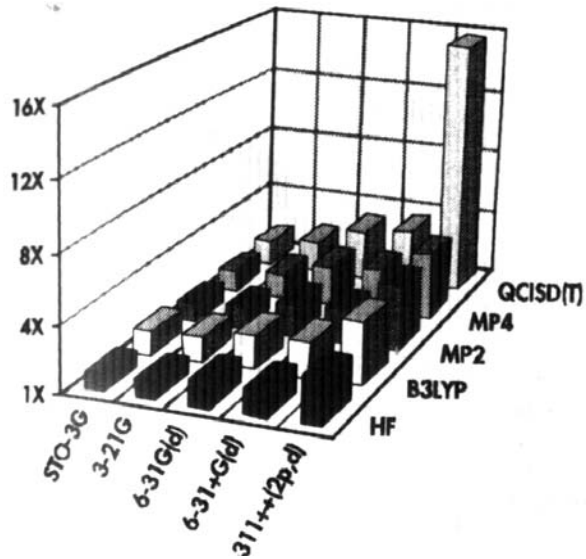
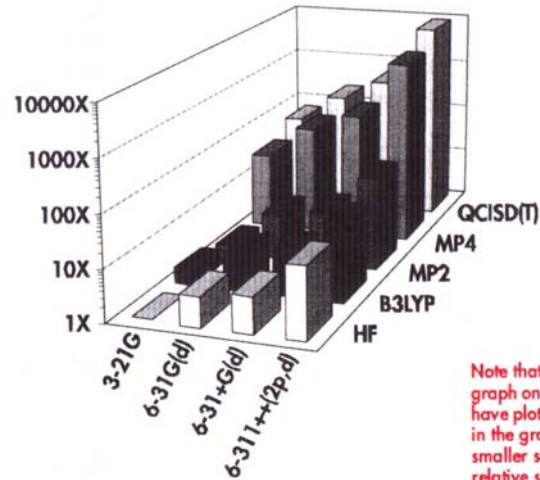
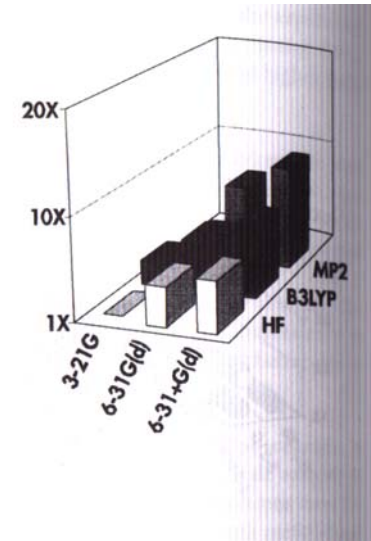


Gráfico de los recursos computacionales requeridos (en tiempo) para realizar cálculos Single-point a los niveles mencionados sobre la molécula de metano.

A continuación se grafica la misma información pero para el pentano. El gráfico de la izquierda tiene el eje z en escala logarítmica:



Note that the vertical scale in the graph on the left is logarithmic! We have plotted the smaller jobs again in the graph at the right, using a smaller scale, so you can see their relative sizes more clearly.



2) Métodos compuestos

optimization may be more cost effective than computing the B3LYP/6-31G(d) frequencies.

- ◆ When the B3LYP/6-31G(d) model chemistry is too expensive for the geometry optimization and frequency calculation, often the best tradeoff is using HF/3-21G(d) geometries and zero-point corrections, saving CPU cycles for the final B3LYP energy calculation.
- ◆ When AM1 geometries are all that are practical for a molecular system, using the B3LYP functional for a single point energy calculation will still often significantly improve the accuracy of the final energy.

For a much more detailed discussion of this study, consult the paper listed in the references.

Compound Methods

A variety of compound methods have been developed in an attempt to accurately model the thermochemical quantities we have been considering. These methods attempt to achieve high accuracy by combining the results of several different calculations as an approximation to a single, very high level computation which is much too expensive to be practical. We will consider two families of methods: the Gaussian-*n* methods and the Complete Basis Set (CBS) methods.

Gaussian-1 and Gaussian-2 Theories

The Gaussian-1 and Gaussian-2 theories are general procedures for computing the total energies of molecules at their equilibrium geometries (they are known as G1 and G2 for short). Both consist of several component calculations whose results are then combined in a pre-defined way.

We'll examine the steps involved in computing an energy with the G1 procedure in some detail in order to give you a feel for these types of methods. We will describe each component calculation in turn, including the values to be computed from the results. Note that for all calculations, either restricted or unrestricted methods are used, as appropriate for the system of interest.

- Step 1. Produce an initial equilibrium structure at the Hartree-Fock level using the 6-31G(d) basis set. Verify that it is a minimum with a frequency calculation and predict the zero-point energy (ZPE). This quantity is scaled by 0.8929.

- Step 2. Beginning with the final optimized structure from step 1, obtain the final equilibrium geometry using the full MP2 method—requested with the **MP2(Full)** keyword in the route section—which includes inner shell electrons.[†] The 6-31G(d) basis set is again used. This geometry is used for all subsequent calculations.
- Step 3. Compute a base level energy, which we will denote E^{base} , using MP4/6-311G(d,p) at the optimized geometry from step 2. Various corrections will be made to this energy in subsequent steps. Note that this energy is obtained from the job run for Step 6.
- Step 4. Correct the base energy by including diffuse functions on a second energy calculation by computing the MP4/6-311G+(d,p) energy. Subtract the base energy E^{base} from this energy to obtain ΔE^+ .
- Step 5. Correct the base energy with higher polarization functions on heavy atoms by computing the MP4/6-311G(2df,p) energy. Subtract E^{base} from this energy to obtain ΔE^{2df} . If ΔE^{2df} is positive (meaning the additional polarization functions produced a higher energy than resulted without them), set this term to zero.
- Step 6. Correct the base energy for residual correlation effects (to counteract known deficiencies of truncating perturbation theory at fourth order) by computing the QCISD(T)/6-311G(d,p) energy. Subtract E^{base} from this energy to produce ΔE^{QCI} .
- Step 7. Correct the energy from step 6 for remaining basis set deficiencies by empirically estimating the remaining correlation energy between spin-paired electrons with the formula:

$$\Delta E^{\text{HLC}} = -0.00019n_{\alpha} + -0.00595n_{\beta}$$

where n_{α} is the number of alpha electrons, and n_{β} is the number of beta electrons in the molecule. This term is known as the higher level correlation.

By convention, n_{α} must be greater than n_{β} for a system with an odd number of electrons. Also, this counting should ignore the core electrons in the molecule (these are treated in step 6). *Gaussian* will indicate the number of electrons of each type. Look for the line containing NOB in the output from the single point energy calculation in step 3:

```
NROrb= 19 NOA= 5 NOB= 4 NVA= 14 NVB= 15
```

The number of alpha electrons is NOA, and the number of beta electrons is

NOB. The energy corrected in this way is the G1 value for the electronic energy, denoted E_e .

We can now compute the G1 energy:

$$E^{G1} = E^{\text{base}} + \Delta E^+ + \Delta E^{2df} + \Delta E^{\text{QCI}} + \Delta E^{\text{HLC}} + \text{ZPE}$$

The quantity E^{G1} is essentially an approximation to an energy calculated directly at QCISD(T)/6-311+G(2df,p).[†] Replacing this one very large calculation with four smaller ones is much faster. The components of a G1 calculation are summarized in steps 1 through 7 of the following table:

Components of G1 and G2 Total Energies

Step	Job	Result	Notes
1	HF/6-31G(d) Opt Freq	ZPE	Scale by 0.8929.
2	MP2(Full)/6-31G(d) Opt	geometry	Start from HF results; use this geometry for all later jobs.
3	MP4/6-311G(d,p) [†]	E^{base}	Base level energy.
4	MP4/6-311+G(d,p)	ΔE^+	= Energy - E^{base}
5	MP4/6-311G(2df,p)	ΔE^{2df}	= Energy - E^{base} (set to 0 if > 0).
6	QCISD(T)/6-311G(d,p) [†]	ΔE^{QCI}	= Energy - E^{base}
7	Any job	ΔE^{HLC}	= $-0.00019n_\alpha + -0.00595n_\beta$
8	MP2/6-311+G(3df,2p)	Δ^{G2}	= Energy - $E^{\text{Step5(MP2)}} - E^{\text{Step4(MP2)}} + E^{\text{Step3(MP2)}}$
9	Any job	Δ^{HLC}	= $+0.00114n_\beta$

[†] These quantities are computed in a single job.

G2 Theory

Gaussian-2 theory adds some additional corrections to the G1 final result. The major term is a correction at the MP2 level, described in the next step:

Step 8. Perform an MP2/6-311+G(3df,2p) energy calculation. Use this energy to correct the G1 energy according to the formula:

$$\Delta^{G2} = (\Delta^{+2df} - \Delta^+ - \Delta^{2df}) + \Delta^{3d2p}$$

The parenthesized term corrects for the assumption in G1 theory that the 2df and diffuse function corrections were additive. It is formed by

[†] This additivity assumption has been tested by Carpenter and coworkers, who computed the quantities in the entire G2 set at the QCISD(T)/6-311+G(3df,2p) level. They obtained a MAD of 1.17 kcal·mol⁻¹ from experiment (vs. 1.21 for G2), and an average absolute difference from the G2 values of 0.3 kcal·mol⁻¹. See the paper listed in the references for full details.

computing the MP2-level +2df correction and then subtracting the separate MP2-level diffuse function and 2df corrections from it.[†]

The final term computes the correction for a third set of f functions on heavy atoms and a second set of p functions on the hydrogen atoms.[‡]

Note that all of the required MP2 energies can be extracted from the previously-run MP4 jobs in steps 3 through 5. Thus, after algebraic manipulation,[§] the final formula is:

$$\Delta^{G2} = E^{\text{Step8}} - E^{\text{Step5(MP2)}} - E^{\text{Step4(MP2)}} + E^{\text{Step3(MP2)}}$$

Step 9. G2 theory makes a modification to the higher-level correction of G1 theory by adding 0.00114 n_β into the final energy calculation (which we denote Δ^{HLC}).^{*}

The G2 energy can now be computed as $E^{G2} = E^{G1} + \Delta^{G2} + \Delta^{\text{HLC}}$.

Example 7.5: G2 Proton Affinity of PH₃ file: e7_05

We'll compute the proton affinity of PH₃ at the G2 level. G2 energies can be computed automatically in Gaussian via the G2 keyword. Here is the output from a G2 calculation (which appears at the conclusion of the final component job step):

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.034647	E(Thermal)=	0.037639
E(QCISD(T))=	-342.959149	E(Empiric)=	-0.024560
DE(Plus)=	-0.000757	DE(2DF)=	-0.023352
G1(0 K)=	-342.973171	G1 Energy=	-342.970179
G1 Enthalpy=	-342.969234	G1 Free Energy=	-342.992286
E(Delta-G2)=	-0.007122	E(G2-Empiric)=	0.004560
G2(0 K)=	-342.975733	G2 Energy=	
G2 Enthalpy=	-342.971796	G2 Free Energy=	-342.994849
DE(MP2)=	-0.027479		
G2MP2(0 K)=	-342.971982	G2MP2 Energy=	-342.968989
G2MP2 Enthalpy=	-342.968045	G2MP2 Free Energy=	-342.991097

[†] The relevant formulas are: $\Delta^{+2df} = E(\text{MP2/6-311+G(2df,p)}) - E(\text{MP2/6-311G(d,p)})$;
 $\Delta^+ = E(\text{MP2/6-311+G(d,p)}) - E(\text{MP2/6-311G(d,p)})$;
 $\Delta^{2df} = E(\text{MP2/6-311G(2df,p)}) - E(\text{MP2/6-311G(d,p)})$.

[‡] $\Delta^{3d2p} = E(\text{MP2/6-311+G(3df,2p)}) - E(\text{MP2/6-311+G(2df,p)})$

[§] Note that the $E(\text{MP2/6-311+G(2df,p)})$ energies cancel when we add Δ^{G2} and Δ^{3d2p} , so this job never needs to be run. How's that for sleight of hand?

^{*} Alternatively, one can modify the ΔE^{HLC} formula to be: $-0.00019n_\alpha + -0.00481n_\beta$.

The components of the final G2 energy are listed as well as the computed value (in red). Note that the G1 energy is also given, as well as the value predicted by the G2(MP2) method, a related procedure to G2 designed to be less expensive.[†]

Here are the results we obtained for the proton affinity of PH₃:

	G1	G2	G2(MP2)	Exp.
PH ₃	-342.67362	-342.67611	-342.67131	
PH ₄ ⁺	-342.97018	-342.97274	-342.96899	
PA (kcal-mol ⁻¹)	186.10	186.14	186.80	187.1
Δ(Exp)	1.00	0.96	0.30	
CPU seconds	682.4	829.1	607.5	

The values are in excellent agreement with experiment, well under the desired 2 kcal-mol⁻¹ limit. This table also lists the CPU requirements for this problem.

The following table summarizes the accuracy of the various methods we have considered for the G2 molecule set:

Model	MAD	Max. Error
G1	1.53	7.4
G2	1.21	4.4
G2(MP2)	1.58	6.3

G2 theory is the most accurate and also the most expensive. G2(MP2) probably represents the best compromise between cost and accuracy among these three methods. Note that the performance differences between G2 and the other methods become more pronounced as molecule size increases. At the conclusion of the next section, we will compare these model chemistries with the CBS family of methods.

Complete Basis Set Methods

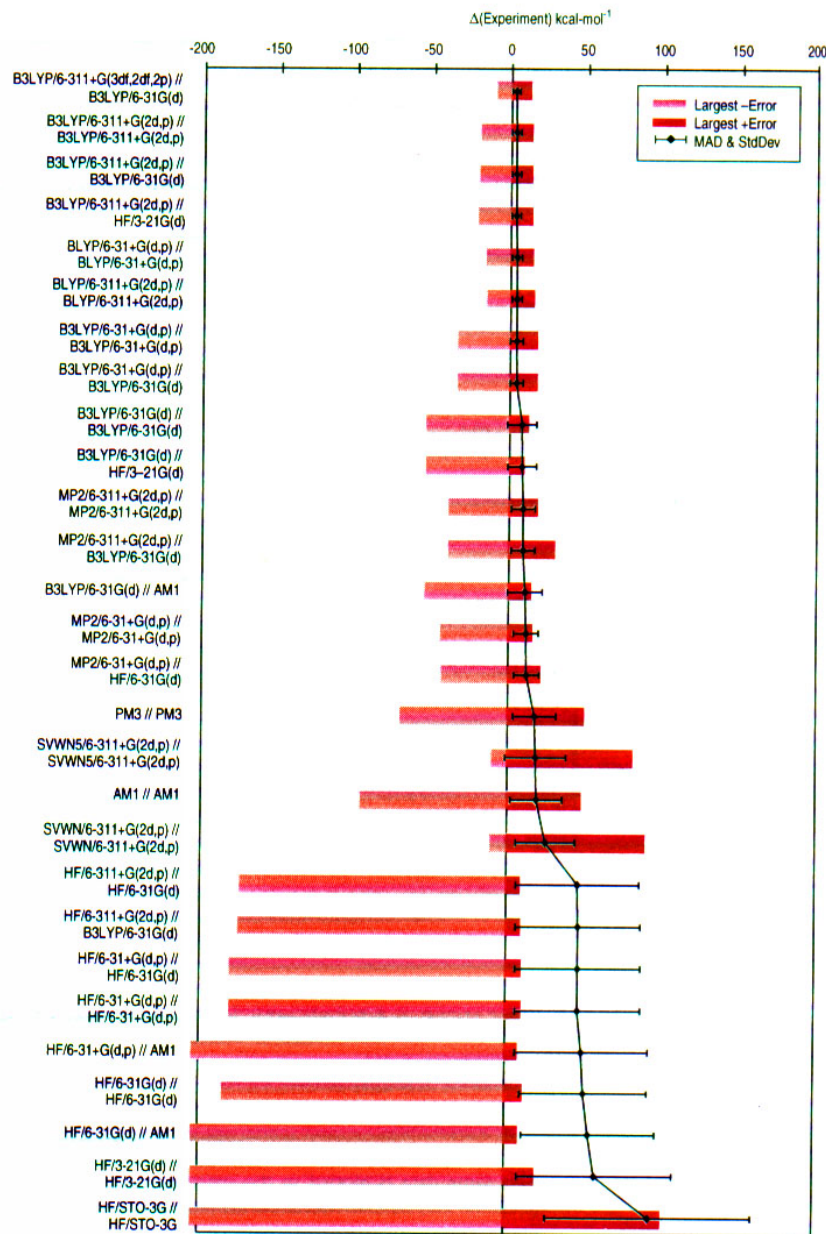
The Complete Basis Set (CBS) methods were developed by George Petersson and several collaborators. The family name reflects the fundamental observation underlying these methods: the largest errors in ab initio thermochemical calculations result from basis set truncation.

[†] In the G2(MP2) method, the several basis set extension corrections added to G1 are replaced by a single MP2-level correction: $\Delta^{MP2} = E(MP2/6-311+G(3df,2p)) - E(MP2/6-311G(d,p))$.

Exactitud relativa en las determinaciones termoquímicas de varios métodos. MAD= Desviación media absoluta entre los valores calculados y los valores experimental (no importa el signo).

Model Chemistry	MAD	StdDev	Largest Errors	
			Positive	Negative
B3LYP/6-311+G(2d,p) // B3LYP/6-311+G(2d,p)	3.1	3.0	13.6	-19.7
BLYP/6-311+G(2d,p) // BLYP/6-311+G(2d,p)	3.9	3.2	14.3	-15.9
BLYP/6-31+G(d,p) // BLYP/6-31+G(d,p)	3.9	3.2	15.2	-15.2
B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p)	3.9	4.2	17.6	-33.8
B3LYP/6-31G(d) // B3LYP/6-31G(d)	7.9	9.5	12.2	-54.2
MP2/6-311+G(2d,p) // MP2/6-311+G(2d,p)	8.9	7.8	18.3	-39.2
MP2/6-31+G(d,p) // MP2/6-31+G(d,p)	11.4	8.1	15.6	-44.0
PM3 // PM3	17.2	14.0	49.6	-69.9
SVWN5/6-311+G(2d,p) // SVWN5/6-311+G(2d,p)	18.1	19.8	81.0	-10.1
AM1 // AM1	18.8	16.9	47.8	-95.5
SVWN/6-311+G(2d,p) // SVWN/6-311+G(2d,p)	24.9	19.2	89.3	-10.4
HF/6-31+G(d,p) // HF/6-31+G(d,p)	46.7	40.6	10.1	-179.8
HF/6-31G(d) // HF/6-31G(d)	51.0	41.2	11.5	-184.2
HF/3-21G(d) // HF/3-21G(d)	58.4	50.1	19.5	-215.2
HF/STO-3G // HF/STO-3G	93.3	66.3	101.3	-313.9
B3LYP/6-311+G(3df,2df,2p) // B3LYP/6-31G(d)	2.7	2.6	12.5	-9.3
B3LYP/6-311+G(2d,p) // B3LYP/6-31G(d)	3.2	3.0	13.6	-20.1
B3LYP/6-31+G(d,p) // B3LYP/6-31G(d)	4.0	4.2	17.6	-33.9
MP2/6-311+G(2d,p) // B3LYP/6-31G(d)	8.9	7.8	29.7	-39.2
HF/6-311+G(2d,p) // B3LYP/6-31G(d)	46.6	40.5	9.1	-174.6
MP2/6-31+G(d,p) // HF/6-31G(d)	11.8	8.2	20.9	-43.2
HF/6-311+G(2d,p) // HF/6-31G(d)	46.1	40.0	8.8	-173.8
HF/6-31+G(d,p) // HF/6-31G(d)	46.6	40.7	10.0	-179.9
B3LYP/6-311+G(2d,p) // HF/3-21G(d)	3.2	3.0	13.8	-21.2
B3LYP/6-31G(d) // HF/3-21G(d)	8.0	9.4	9.4	-54.2
B3LYP/6-31G(d) // AM1	10.5	11.3	14.7	-54.2
HF/6-31+G(d,p) // AM1	49.4	43.1	8.0	-206.1
HF/6-31G(d) // AM1	54.2	43.1	8.6	-207.2

En la próxima página están graficados los valores de la tabla.



3) Factores para escalar las frecuencias

Method	Scale Factor	
	Frequency	ZPE/Thermal
HF/3-21G	0.9085	0.9409
HF/6-31G(d)	0.8929	0.9135
MP2(Full)/6-31G(d)	0.9427	0.9646
MP2(FC)/6-31G(d)	0.9434	0.9676
SVWN/6-31G(d)	0.9833	1.0079
BLYP/6-31G(d)	0.9940	1.0119
B3LYP/6-31G(d)	0.9613	0.9804

4) Propiedades moleculares

Table 10.1 Properties which may be calculated from derivatives of the energy

n_F	n_B	n_I	n_R	Property
0	0	0	0	Energy
1	0	0	0	Electric dipole moment
0	1	0	0	Magnetic dipole moment
0	0	1	0	Hyperfine coupling constant
0	0	0	1	Energy gradient
2	0	0	0	Electric polarizability
0	2	0	0	Magnetizability
0	0	2	0	Spin-spin coupling (for different nuclei)
0	0	0	2	Harmonic vibrational frequencies
1	0	0	1	Infra-red absorption intensities
1	1	0	0	Circular dichroism
0	1	1	0	Nuclear magnetic shielding
3	0	0	0	(first) Electric hyperpolarizability
0	3	0	0	(first) Hypermagnetizability
0	0	0	3	(cubic) Anharmonic corrections to vibrational frequencies
2	0	0	1	Raman intensities
2	1	0	0	Magnetic circular dichroism (Faraday effect)
1	0	0	2	Infra-red intensities for overtone and combination bands
4	0	0	0	(second) Electric hyperpolarizability
0	4	0	0	(second) Hypermagnetizability
0	0	0	4	(quartic) Anharmonic corrections to vibrational frequencies
2	0	0	2	Raman intensities for overtone and combination bands
2	2	0	0	Cotton-Mutton effect

Exercise 8.4: Atomic Charge Analysis

file: 8_04

This exercise will examine other ways of computing charges other than Mulliken population analysis. Since atomic charge is not a quantum mechanical observable, all methods for computing it are necessarily arbitrary. We'll explore the relative merits of various schemes for partitioning the electron density among the atoms in a molecular system.

Compute the charge distributions for allyl cation using the following methods:

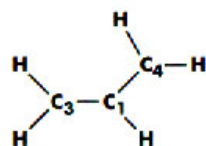
- ✦ Mulliken population analysis (the default procedure)
- ✦ Natural population analysis (keyword: **Pop=NPA**)
- ✦ Electrostatic potential-derived charges using the CHelpG scheme of Breneman (keyword: **Pop=CHelpG**)
- ✦ Electrostatic potential-derived charges using the Merz-Kollman-Singh scheme (keyword: **Pop=MK**)

Run the jobs at the MP2/6-31G(d) level. You should be aware that this is the practice adopted by researchers who include charge distribution analysis in publications.

In order to save computation time, set up the second and subsequent jobs to extract the electron density from the checkpoint file by using the **Geom=Checkpoint** and **Density=(Checkpoint,MP2)** keywords in the route section. You will also need to include **Density=MP2** for the first job, which specifies that the population analysis should be performed using the electron density computed at the MP2 level (the default is to use the Hartree-Fock density).

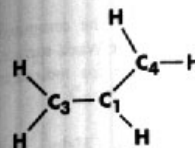
Solution

Here are the Mulliken charges for this system:



```
Total atomic charges:
1
1 C -0.117948
2 H 0.301526
3 C -0.184767
4 C -0.184767
5 H 0.304392
6 H 0.288586
7 H 0.304392
8 H 0.288586
Sum of Mulliken charges= 1.00000
```

The Mulliken scheme places the negative charge more or less evenly on the three carbons, and splits the positive charge among the hydrogens. Mulliken population analysis computes charges by dividing orbital overlap evenly between the two atoms involved.



NBO Population Analysis

Natural population analysis is carried out in terms of localized electron-pair "bonding" units. Here are the charges computed by natural population analysis (the essential output is extracted):

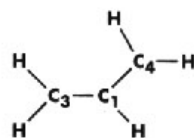
```
*****Gaussian NBO Version 3.1*****
  NATURAL ATOMIC ORBITAL AND
  NATURAL BOND ORBITAL ANALYSIS
*****Gaussian NBO Version 3.1*****
Analyzing the MP2 density
...
Summary of Natural Population Analysis:
      Natural Population
Atom No  Natural Charge  Core  Valence  Rydberg  Total
-----
C 1      -0.34614      1.99903  4.30125  0.04585  6.34614
H 2       0.29596      0.00000  0.70181  0.00223  0.70404
C 3       0.01453      1.99914  3.94980  0.03653  5.98547
C 4       0.01453      1.99914  3.94980  0.03653  5.98547
H 5       0.25378      0.00000  0.73427  0.00195  0.73622
H 6       0.24678      0.00000  0.75073  0.00249  0.75322
H 7       0.25378      0.00000  0.73427  0.00195  0.73622
H 8       0.24678      0.00000  0.75073  0.00249  0.75322
=====
* Total * 1.00000      5.9973  15.87267  0.13001  22.00000
...
Natural Population
-----
Core                5.99732 ( 99.9553% of 6)
Valence             15.87267 ( 99.2042% of 16)
Natural Minimal Basis 21.86999 ( 99.4090% of 22)
Natural Rydberg Basis  0.13001 ( 0.5910% of 22)
-----
...
Atom No  Natural Electron Configuration
-----
C 1      [core]2s( 1.03)2p( 3.27)3s( 0.01)3p( 0.02)3d( 0.02)
H 2              1s( 0.70)
C 3      [core]2s( 1.12)2p( 2.83)3p( 0.02)3d( 0.02)
C 4      [core]2s( 1.12)2p( 2.83)3p( 0.02)3d( 0.02)
H 5              1s( 0.73)
H 6              1s( 0.75)
H 7              1s( 0.73)
H 8              1s( 0.75)
```

The scheme assigns charges very differently, placing most of the negative charge on one carbon atom. Its more detailed analysis also includes the number of core electrons, valence electrons, and Rydberg electrons, located in diffuse orbitals. It also partitions the charge on each atom among the atomic orbitals.[†]

CHelpG Electrostatic Potential-Derived Charges

Electrostatic potential-derived charges assign point charges to fit the computed electrostatic potential at a number of points on or near the van der Waals surface. This sort of analysis is commonly used to create input charges for molecular mechanics calculation.

There are three major schemes for selecting the points: CHelp, CHelpG, and Merz-Kollman-Singh. The CHelpG scheme of Breneman produces these charges:

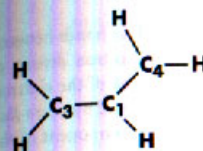


```

*****
Electrostatic Properties Using The MP2 Density
*****
...
Charge= 1.00000 Dipole= 0.0000 0.0000 -0.5753 Tot= 0.5753
      1
  1 C  -0.103415
  2 H   0.169957
  3 C   0.166042
  4 C   0.166042
  5 H   0.161798
  6 H   0.138884
  7 H   0.161798
  8 H   0.138884
  
```

This scheme also assigns the negative charge to the middle carbon atom.

[†] If the NBO program (Gaussian Link 607) is used to produce published results, then it should be cited as well. The reference is: NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.



MKS Electrostatic Potential-Derived Charges

Here are the results using the Merz-Kollman-Singh scheme, which fits the electrostatic potential to points selected on a set of concentric spheres around each atom:

```

*****
Electrostatic Properties Using The MP2 Density
*****
...
Charge= 1.00000 Dipole= 0.0000 0.0000 -0.5841 Tot= 0.5841
      1
  1 C  -0.091216
  2 H   0.183731
  3 C   0.101199
  4 C   0.101199
  5 H   0.186162
  6 H   0.166382
  7 H   0.186162
  8 H   0.166382
  
```

This scheme also places the negative charge on the middle carbon. However, its partitioning of the positive charge is more uniform than that of CHelpG. ■

Exercise 8.5: Group Charges file: 8_04

Compute the group charges for the CH and CH₂ groups with each method for allyl cation using each of the methods from the previous exercise.

Solution

Here are the results:

	Mulliken	NPA	CHelpG	MKS
CH	+18	-05	-10	+09
CH ₂	+41	+52	+47	+45

There is much greater agreement among the methods when it comes to the group charges than there was for the charges on each individual atom. The methods agree that the CH₂ has the majority of the positive charge. NPA and CHelpG assign a very small negative charge to the CH group while MKS and Mulliken analysis assign a small positive charge to this group. ■