Determination of Atomic Properties by Integration
Atomic Volume, Electron Population, and Atomic Charge

✔ Atoms in molecules are generally not spherical, but rather are irregular shapes defined by their interatomic surfaces in contact with neighboring atoms.

✔ An atom is defined by its nucleus and the surrounding atomic basin, Ω.

☞ Atomic volume is defined by the sum of all volume elements that occupy all space defined by the interatomic surfaces and the ρ = 0.001 au contour of any unbounded regions.

$$v(\Omega) = \int_{\Omega} d\tau$$

✔ The integration is not trivial, owing to the irregular shape, but standard algorithms exist to carry it out on a personal computer.[1]

☞ The electron population of an atom, $N(\Omega)$, is obtained by integrating the electron density of a volume element over the entire basin:

$$N(\Omega) = \int_{\Omega} \rho \, d\tau$$

☞ Atomic charge, $q(\Omega)$, is defined as the nuclear charge minus the electron population within the atomic basin:

$$q(\Omega) = Z_{\Omega} - N(\Omega)$$

☞ AIM defined properties are additive.

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[1]Cf. P. L. A. Popelier, *Molecular Physics* **1996**, *87*, 1169-1187.

Atomic Charge Determinations

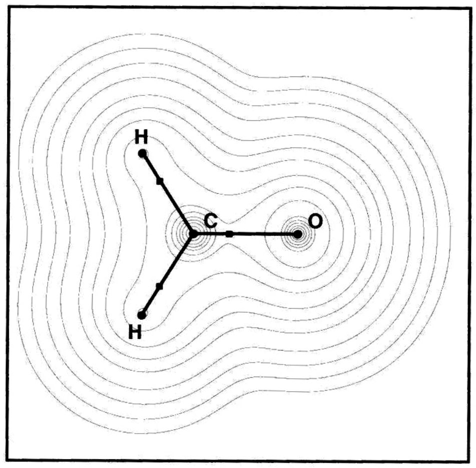
- ✔ Historically, atomic charge calculations have been controversial because all depended on the definition of an atom and how charge should be allotted to each in a molecule.

- ✔ Orbital-based methods suffer from the variety of ways available to define orbitals and difficulties in assessing the contribution of an orbital's electron density about each nucleus.

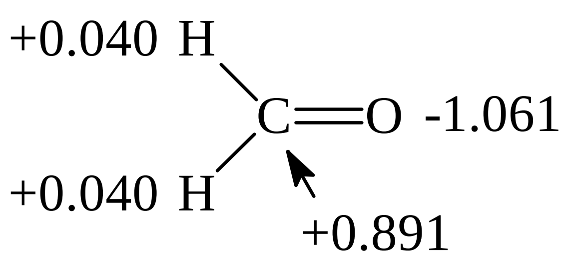
- ✔ AIM values frequently differ significantly from previous calculations.

Atomic Volumes, Populations, and Charges in H_2CO (16 electrons)

Molecular Graph Superimposed on Contour Map of ρ [2]



Atom	$v(\Omega)$ (au)	$N(\Omega)$	$q(\Omega)$ (e)
C	66.39	5.019	+0.891
O	138.36	9.060	–1.061
H	50.48	0.960	+0.040
Total	305.71	16.000	0.000

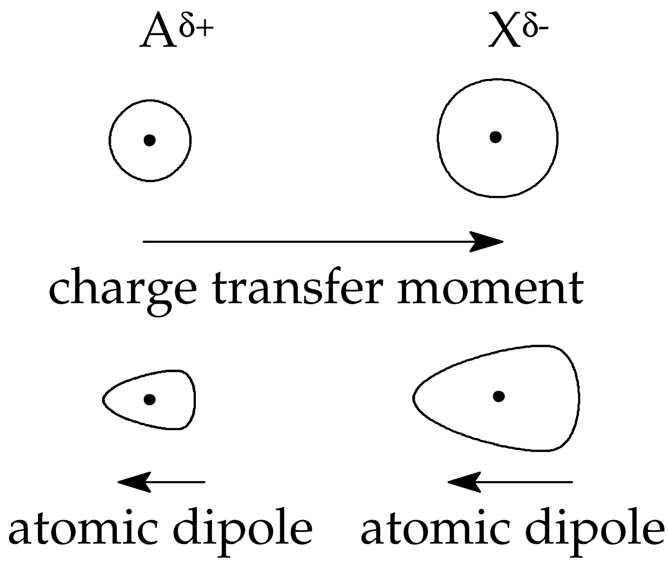


[2]From P. Popelier, *Atoms in Molecules: An Introduction*. New York: Prentice Hall, **2000**, p.60.

Atomic Dipole Moments

✔ The atomic dipole moment, $\mathbf{M}(\Omega)$, measures the extent and shift of an atom's electronic charge relative to the nucleus.

✔ $\mathbf{M}(\Omega)$ is the intra-atomic dipole moment, previously defined as distinct from the charge transfer moment, $\mathbf{M}_{CT}$.



✔ $\mathbf{M}(\Omega)$ is a vector defined by

$$\mathbf{M}(\Omega) = \int_{\Omega} \rho \, \mathbf{r}_{\Omega} \, d\tau$$

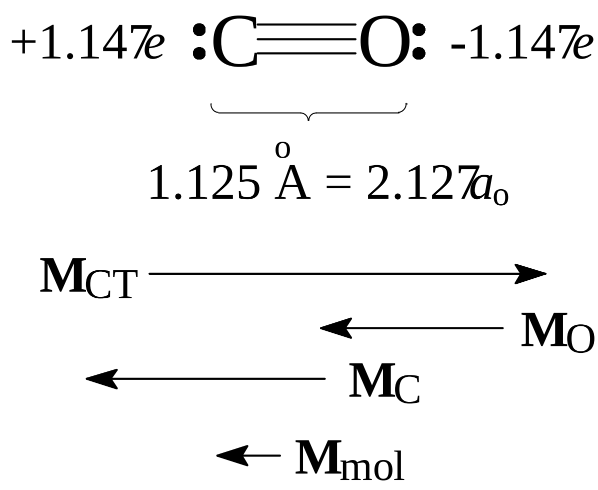
where $\mathbf{r}_{\Omega}$ is a vector centered on the nucleus.

☞ The total molecular dipole moment, $\mathbf{M}_{mol}$, is given by

$$\mathbf{M}_{mol} = \sum_{\Omega} q(\Omega)\mathbf{X}_{\Omega} + \sum_{\Omega} \mathbf{M}(\Omega) = \mathbf{M}_{CT} + \mathbf{M}_{atoms}$$

where $\mathbf{X}_{\Omega}$ are the nuclear positions measured as a vector from a common origin.

Dipole Moment of CO



$\mathbf{M}_{CT} = qr = (1.147\ e)(2.127\ a_o) = 2.440\ ea_o = 2.440$ au

$\mathbf{M}_{C} = –1.64$ au $\quad\quad \mathbf{M}_{O} = –0.84$ au

$\mathbf{M}_{mol} = \mathbf{M}_{CT} + \mathbf{M}_{C} + \mathbf{M}_{O} = (2.440 – 1.64 – 0.84)$ au $= –0.04$ au

☞ The overall dipole moment is very small and in the opposite direction of the charge transfer moment.

✔ This result is mainly due to carbon’s large atomic dipole, resulting from the highly localized and directed lone pair in CO.

Characterizing Bonds in AIM

✔ In terms of electron density, the most characteristic point along the bond line between two atoms is the bond critical point, where one atom ends and another begins.

☞ The following characteristic properties of a bond can be defined at the bond critical point:

① Bond critical point density, ρ_b – value of ρ at the bond critical point.

② Ellipticity, ε – shape of the electron density distribution in a plane passing through the bond critical point, perpendicular to the bond line.

③ Bonding radius, r_b – distance from the nucleus of an atom to the bond critical point.

- Bonding radius indicates the size of the atom in the direction of the bond.
- Atoms bonded to two or more atoms may have different values of r_b for each bond.

Bond Critical Point Density and Covalent Character

✐ Classical concepts: Covalent bonds have a high degree of electron sharing and are less polar; ionic bonds have limited electron sharing and are highly polar.

✔ Values of ρ_b indicate the amount of shared density between two bonded atoms.

✔ High values of ρ_b could be taken as indicating more covalent character, and low values could be taken as indicating ionic character.

ρ_b and q_A for Period 2 Diatomic Hydrides

AH	ρ_b	q_A	Qualitative Description
HH	0.2700	0.0000	pure covalent
HLi	0.0379	+0.8869	most ionic
HBe	0.0952	+0.8323	more covalent, less ionic
HB	0.1916	+0.6679	more covalent, less ionic
HC	0.2807	–0.0235	more covalent, less ionic
HN	0.3360	–0.3036	more covalent, more ionic
HO	0.3717	–0.5427	more covalent, more ionic
HF	0.3801	–0.7073	more covalent, more ionic

☹ If we associate ionic character with bond polarity, these data seem to suggest it is possible to be covalent and ionic at the same time!

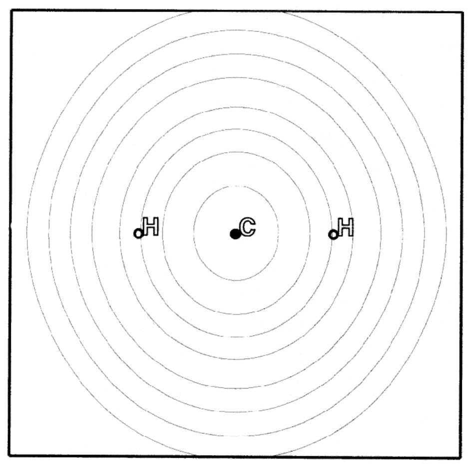
☺ Actually, these data show it is possible to have a high amount of electron sharing in a highly polar bond.

Bond Ellipticity

✔ The ellipticity of a single bond at the bond critical point (BCP) is generally circular ($\varepsilon \approx 0$).

✔ Double bonds and bonds in π-delocalized systems tend to have $\varepsilon > 0$.

✔ Triple bonds have cylindrical electon density distributions along the bond and $\varepsilon \approx 0$.



Contour map in the plane of BCP along C=C bond in ethylene

Ellipticity at BCP for Some C–C bonds[3]

Molecule	Bond	ε
butane	$CH_3CH_2–CH_2CH_3$	0.014
ethylene	$H_2C{=}CH_2$	0.298
acetylene	$HC{\equiv}CH$	0.000
benzene	C_6H_6	0.176[4]
trans-1,3-butadiene	$CH_2CH–CHCH_2$	0.071
	$CH_2{=}CHCHCH_2$	0.289
1,3-cyclobutadiene	$\underbrace{\mathrm{CHCH\text{-}CHCH}}$	0.071
	$\underbrace{\mathrm{CHCH{=}CHCH}}$	0.353
toluene	$C_6H_5–CH_3$	0.187
cyclopropane	C_3H_6	0.417
methylcyclopropane	$C_3H_5–CH_3$	0.020

[3]Data from P. Popelier, *Atoms in Molecules: An Introduction*. New York: Prentice Hall, **2000**, p. 148.

[4]Gillespie & Popelier give ε = 0.23 for benzene (cf. p. 158).

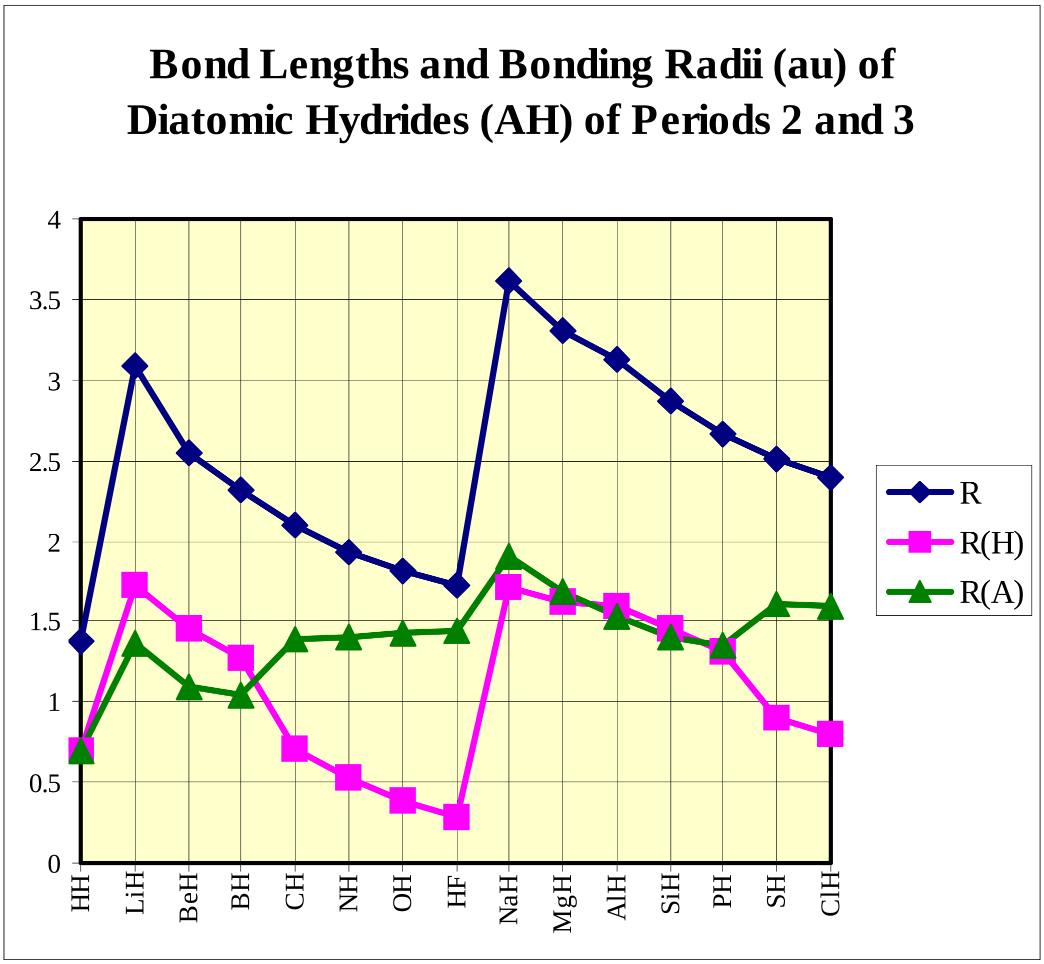
Bonding Radius, r_b

☞ Periodic trends in bonding radii are influenced by two major factors:

① Radii tend to decrease as *Z*, the nuclear charge, increases.

② Radii tend to increase as electronegativity and negative charge increase.

✔ Across a period, radii of a central atom A decrease initially and then increase as a result of these competing trends.



✔ Note decline in r_b(H) as charge changes from negative to positive across each series.

Contour Maps of Period 2 and 3 Diatomic Hydrides

- ✔ Both bonding and nonbonding radii change in the same ways through the series.

- ✔ Nearly spherical profiles indicate strongly ionic character; e.g., LiH, NaH, MgH

- ✔ Charge distribution of anions is polarized toward cations, and charge distribution of cations is polarized away from anions; e.g., BeH, BH, AlH