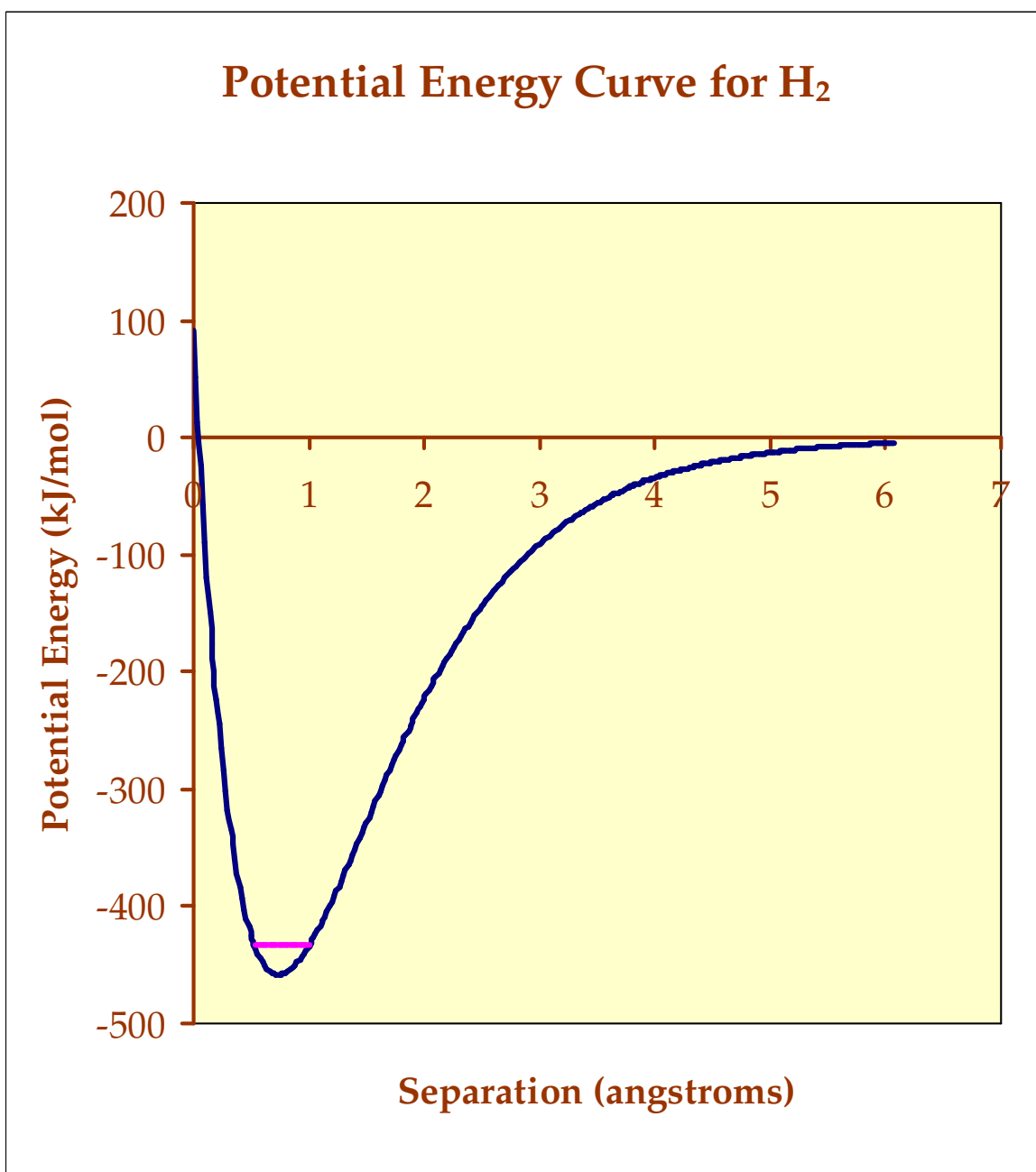


## Bond Length and Potential Energy (Morse Curve)



$$\Delta U_{\text{el}} = -458 \text{ kJ/mol}$$

$$\begin{aligned} \Delta U_{298} &= \Delta U_{\text{el}} - \Delta U_{\text{vib,rot,trans}} = -(458 - 25) \text{ kJ/mol} \\ &= -433 \text{ kJ/mol} \end{aligned}$$

## Bond Parameters

- Equilibrium bond length,  $r_e$  — internuclear separation at the minimum potential energy
- $-U_{el}$  is the theoretical bond dissociation energy for a quiescent molecule at 0K.
- Bond dissociation energy (bond energy),  $D$ , is usually taken as a measured quantity.
- $U_{298}$  is the energy difference from the lowest vibration, rotation, translation state to the zero point of the system, where  $r = \infty$ . (Slightly less than the energy from the potential well minimum for a quiescent molecule.)
- $-U_{298}$  is the measured bond dissociation energy under constant volume conditions.
- Zero point energy — Difference between  $\Delta U_{el}$  and  $\Delta U_{298}$ .

## Measured Bond Lengths

- Measured bond lengths are slightly longer than  $r_e$ , because real molecules have motion above 0 K.
- Electron diffraction and neutron diffraction measure internuclear distances.
- X-ray diffraction measures distances between maxima of electron density, which may not always coincide with the nuclei.
- Historically, bond lengths have been quoted in ångströms (Å), but current discussions of structural chemistry tend to use picometers (pm)

$$1 \text{ Å} = 100 \text{ pm}$$

## Covalent Radii

- The term “atomic radius” in the context of molecules usually refers to what more properly should be called the covalent radius.
- Most covalent radii have been obtained by taking half of the distance between identical atoms having a single bond. For example, from diamond and S<sub>8</sub>

$$r_{\text{C}} = \frac{1}{2}d_{\text{C-C}} = \frac{1}{2}(154 \text{ pm}) = 77 \text{ pm}$$

$$r_{\text{S}} = \frac{1}{2}d_{\text{S-S}} = \frac{1}{2}(208 \text{ pm}) = 104 \text{ pm}$$

- For many molecules covalent radii can be added to predict bond length in heteronuclear cases with an accuracy of approximately  $\pm 2$  pm.

$$d_{\text{C-S}} \approx r_{\text{C}} + r_{\text{S}} = 77 \text{ pm} + 104 \text{ pm} = 181 \text{ pm}$$

In S(CH<sub>3</sub>)<sub>2</sub>  $d_{\text{C-S}} = 180.7$  pm and in HSCH<sub>3</sub>  $d_{\text{C-S}} = 181.4$  pm

- Covalent radii are only semi-quantitative, because the underlying assumption that atoms in bonds have spherical distributions that are the same from case to case is at best an approximation.

## Problems with N, O, F, H Covalent Radii

- X—X bonds from H<sub>2</sub>N—NH<sub>2</sub>, HO—OH, and F—F are longer and weaker than expected, probably from nuclear repulsions between such small atoms.
- Values in Gillespie & Popelier's Table 2.1 (p. 28) are extrapolated from the trend of the preceding period 2 elements.

Atom	Schomaker & Stevenson (1941)	Pauling (1960)	Table 2.1
N	74	70	70
O	74	66	65
F	72	64	60

- Covalent radii of N, O, and F are of little use, because virtually all bonds with these elements are very ionic, except O—O, O—F, and F—F.
- With no inner core electrons, the covalent radius of H is highly variable from 37 pm in H<sub>2</sub> to approximately 30 pm in most heteronuclear bonds.

## Bond Order and Bond Length

- From classic Lewis modeling, bond order is defined as the number of shared pairs between two atoms.
- Because bond lengths contract with greater bond order, covalent radii for multiply bonded atoms are smaller. (Pauling values shown below.)

Bond Order	C	N	O	P	S
X—X	77	70	66	110	104
X=X	67	61	57	100	94
X≡X	60	55	52		

## Resonance

- Resonance does not exist!
- The need to use two or more resonance structures to describe the bonding in a molecule is a reflection of the inadequacy of Lewis structures for describing bonding in molecules in which some of the electrons are not as localized as the Lewis structure implies.<sup>1</sup>
- Resonance or delocalization energy is not a real energy inasmuch as it is not something that can be measured. It is simply the difference between the actual energy of the molecule and the energy of two or more hypothetical resonance structures.<sup>1</sup>

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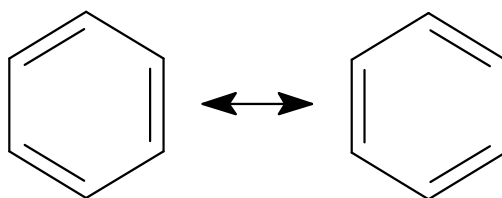
<sup>1</sup>Gillespie and Poplier, p. 32.

## Bond Order of Resonance Hybrids

- For resonance hybrids for which all forms contribute equally

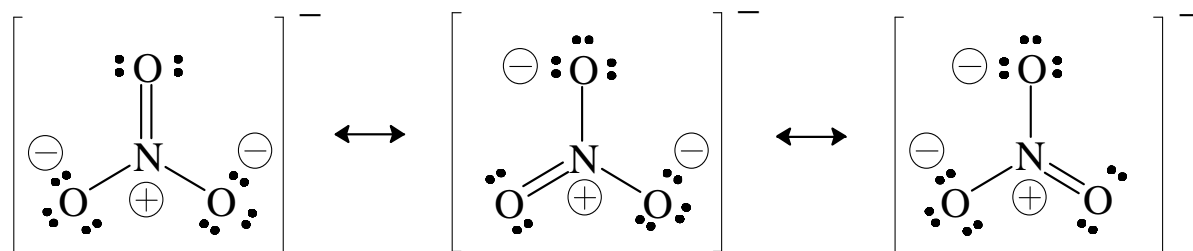
$$\text{B.O.} = \frac{x \text{ bond pairs}}{y \text{ equivalent bonds}}$$

- The benzene ring has 9 pairs over 6 equivalent bonds, so  $\text{B.O.} = 9/6 = 1.5$



$d_{\text{C-C}} = 140 \text{ pm}$  (cf. 154 pm for C—C and 134 pm for C=C)

- Nitrate ion has 4 pairs over 3 equivalent bonds, so  $\text{B.O.} = 4/3 = 1\frac{1}{3}$

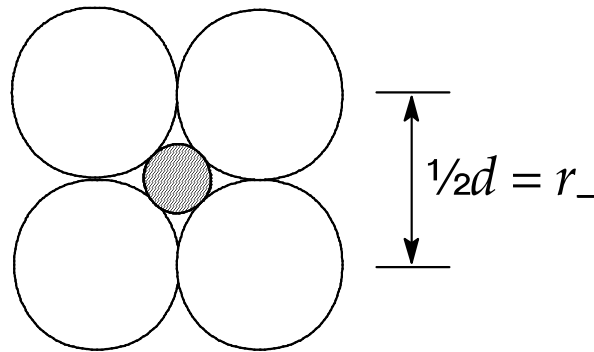


- Numerical estimates of bond order are not appropriate for cases in which all forms do not contribute equally (e.g.,  $\text{OCN}^-$ ).



## Ionic Radii

- Ionic radii are estimates, generally based on best fit for a commonly occurring ion, such as  $O^{2-}$  (e.g., Pauling).
- Ionic radii for some large anions in the presence of small cations can be obtained directly if it can be assumed that the anions are touching.



- Assuming the cation touches the anions in close-packed structures, the cation radius increases as the size of the hole increases.
- The cation hole, and hence the cation radius, increases as the coordination number increases.
- Conversely, the coordination number (CN) increases as the size of the cation increases.
- Shannon<sup>2</sup> tabulated ionic radii for several CN values.

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<sup>2</sup>R. D. Shannon, *Acta Crystallogr.*, A32, 751-767 (1976).

## Comparison of Some Pauling and Shannon Ionic Radii

Ion	Pauling	Shannon		
		CN4	CN6	CN8
Li <sup>+</sup>	60	59	76	
Na <sup>+</sup>	95	99	102	116
K <sup>+</sup>	133	137	138	151
Rb <sup>+</sup>	148		152	161
Cs <sup>+</sup>	169		167	174
F <sup>-</sup>	136	131	133	
Cl <sup>-</sup>	181		181	
Br <sup>-</sup>	195		194	
I <sup>-</sup>	216		220	

- Shannon CN6 values are most often used as a set when exact coordinations are not known.
- Shannon CN6 values tend to be a little larger for cations and about the same or smaller for anions, relative to Pauling values.
- The set used is less important than using one set for comparisons (i.e., don't "mix and match")

## Radius Ratio

- Most often cations are smaller than anions (except cases like KF, CsF, etc.)
- CN about a cation, to a first approximation, can be predicted on the basis of the radius ratio,  $r_+/r_-$ .

$r_+/r_-$	Predicted CN	Predicted Geometry
<0.15	2	linear
0.15-0.22	3	trigonal planar
0.22-0.41	4	tetrahedral
0.41-0.73	6	octahedral
>0.73	8	cubic

- Many exceptions occur, because ions are not hard spheres.

## Radius Ratio Calculation Examples

### Data (Shannon CN6 values)

Cation	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
$r_+$	76	102	138	152	167
Anion	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	
$r_-$	133	181	194	220	

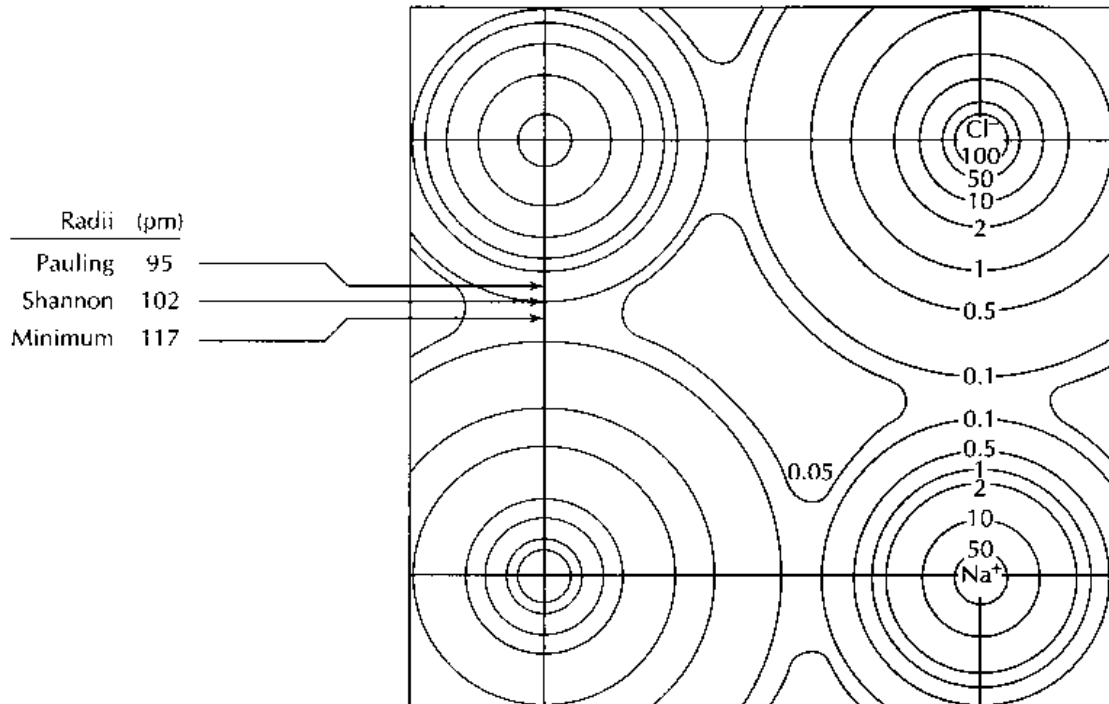
### Examples

Salt	$r_+/r_-$	Predicted CN	Observed CN
NaCl	102/181 = 0.56	6	6
KBr	138/194 = 0.71	6	6
CsI	167/220 = 0.76	8	8
LiF	76/133 = 0.57	6	6
LiCl	76/181 = 0.94	8	6
LiI	76/220 = 0.34	4	6
CsF	167/133 = 1.26	8	6

- ☞ All alkali halides at room temperature have the NaCl (CN6) structure, except CsCl, CsBr, and CsI.

## Electron Density Mapping

- It is now possible to map electron density or calculate it for simple cases.
- The minimum of electron density on a line between a cation-anion pair can be taken as the “end” of one ion and the “beginning” of the other ion.



- ☞ From the electron density map of NaCl, the radius of Na<sup>+</sup> is larger and the radius of Cl<sup>-</sup> is smaller than either the Pauling or Shannon values.

## Lengths of Polar Bonds

- Polar bonds are shorter than the lengths calculated from their covalent radii.
- Polar bonds are shorter and stronger than the average of the two corresponding homonuclear bonds because of the electrostatic attraction between the charges on the atoms.
- Schomaker and Stevenson<sup>3</sup> proposed the following equation to correct for bond polarity, but it is of limited use:

$$d_{AB} = r_A + r_B - k|\chi_A - \chi_B|$$

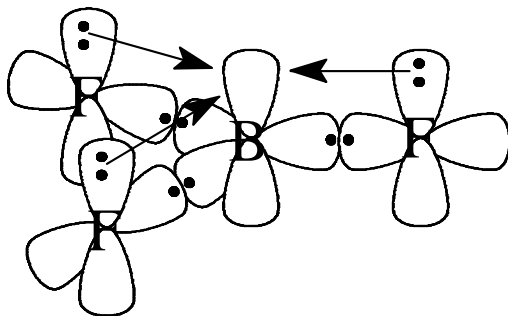
Compound	Bond	$r_A + r_B$	SS calc.	Obs.
SiO <sub>2</sub>	SiO	182	171	163
SiF <sub>4</sub>	SiF	177	169	155
BF <sub>3</sub>	BF	148	137	131
PF <sub>3</sub>	PF	170	169	154
SiCl <sub>4</sub>	SiCl	216	205	200

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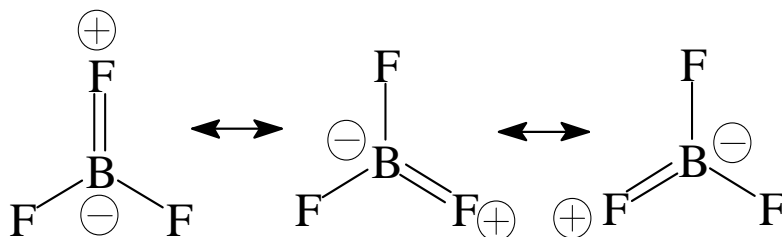
<sup>3</sup>V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, 63, 37 (1941).

## Back Bonding

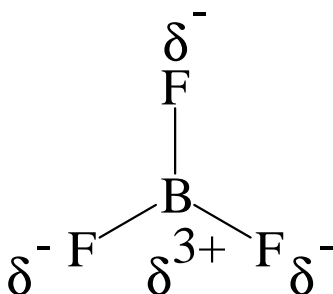
- Back bonding is sometimes invoked to account for the shorter length of polar bonds; e.g.,  $\text{BF}_3$ .



- This is equivalent to the following resonance forms:



- Back bonding is not necessary to account for the short BF bond.
- Partial charges on the atoms draw them together, resulting in shorter bonds.



## Bond Dissociation Energies and Bond Enthalpies

- For a diatomic molecule, the bond dissociation energy is  $\Delta U_{\text{el}}$ , the energy from the bottom of the Morse curve well to the reference zero of energy ( $d = \infty$ ).
- This can be obtained from an ab initio calculation and refers to the hypothetical quiescent molecule at 0 K.
- $U_{298}$  is the measured bond dissociation energy *under constant volume conditions*.
- It is more common to make such measurements under *constant pressure* conditions, thereby obtaining  $\Delta H_{298}$ , which includes  $P\Delta V$  work. For  $\text{H}_2$ ,

$$\Delta H_{298} = U_{298} + P\Delta V = (233 + 2.5) \text{ kJ/mol} = 236 \text{ kJ/mol}$$

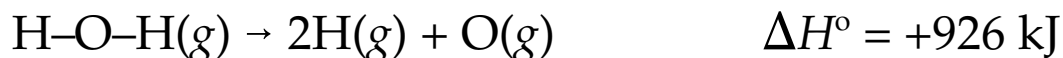
- $\Delta H_{298}$  is commonly referred to as the bond energy and refers to a thermochemical equation of the type





## Bond Energies of Polyatomic Molecules

- For molecules consisting of one kind of bond, average bond energy can be calculated from the enthalpy of atomization divided by the number of bonds.



$$D(\text{O—H}) = 926 \text{ kJ}\cdot\text{mol}^{-1} / 2 = 463 \text{ kJ}\cdot\text{mol}^{-1}$$

- Individual bond energies in more complicated cases can be approximated if some bond energies are assumed to be transferrable from cases where they can be determined exactly.



$$\Delta H^\circ = D(\text{C—C}) + 6D(\text{C—H})$$

Assuming  $D(\text{C—H}) = 415.8 \text{ kJ}$ , the value in  $\text{CH}_4$

$$\begin{aligned} D(\text{C—C}) &= \Delta H^\circ - 6D(\text{C—H}) \\ &= [2826 - (6)(415.8)] \text{ kJ} = 331 \text{ kJ} \end{aligned}$$

- The strongest single bonds are B—F (613 kJ) and C—F (485 kJ)

## Selected Single, Double, and Triple Bond Energies kJ·mol<sup>-1</sup>

- Bond energies increase with bond order for a given atom pair.

B.O.	CC	NN	OO	CN	CO
1	348	159	138	293	335
2	619	418	497	616	707
3	812	946		879	1070

- Double bond and triple bond energies are typically less than 2X and 3X the single bond value.
- O—O and N—N single bonds are unusually weak, so double and triple bonds are more than 2X and 3X the single bond value.
- Heteronuclear bond values *tend* to be greater than the average of the corresponding homonuclear cases, particularly if electronegativities are very different.

$$D(\text{C}=\text{O}) = 707 \text{ kJ}$$

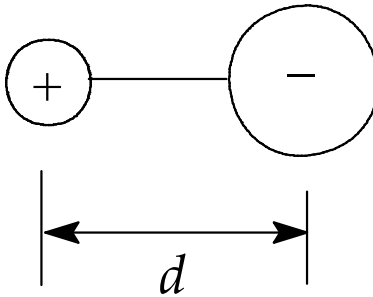
$$[D(\text{C}=\text{C}) + D(\text{O}=\text{O})] = [619 \text{ kJ} + 497 \text{ kJ}]/2 = 558 \text{ kJ}$$

## Force Constants

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- Force constant measures the “stiffness” of the bond, but not necessarily its strength.
- For given masses, higher  $k$  means higher  $\nu$ .
- Vibrations of molecules with more massive atoms tend to occur at lower  $\nu$ .
- Force constant is a measure of the curvature of the potential energy well about the minimum.
- The sharper the potential energy well the higher  $k$  will be.
- Deep potential wells tend to have steep sides, so strong bonds with large dissociation energies tend to have higher  $k$  values.
- However, there is no general relationship between  $k$  and  $D$ .

## Dipole Moments



- $\mu = qd = \text{C}\cdot\text{m}$       1 debye (D) =  $3.34 \times 10^{-30} \text{ C}\cdot\text{m}$
- If atoms are assumed to behave as point charges, knowing  $d$  and  $\mu$  would seem to allow calculation of the charge on each atom.

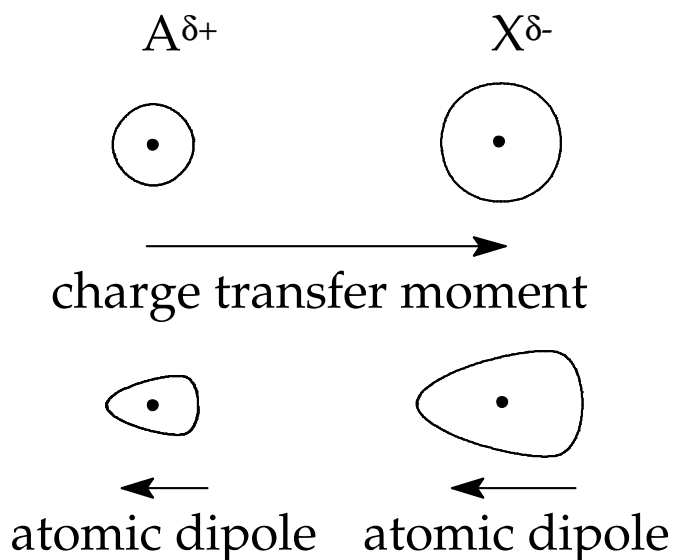
For HCl,  $\mu = 3.44 \times 10^{-30} \text{ C}\cdot\text{m}$  and  $d = 127 \text{ pm}$ :

$$\begin{aligned} q &= \mu/d = \pm(3.44 \times 10^{-30} \text{ C}\cdot\text{m}) / (127 \times 10^{-12} \text{ m}) \\ &= \pm(2.70_{87} \times 10^{-20} \text{ C}) \text{ (electron} / (1.6 \times 10^{-19} \text{ C}) \\ &= \pm 0.17 \text{ electron} \end{aligned}$$

⇒ H—Cl bond is 17% ionic

- Such calculations are too simplistic, because atoms are not point charges, and the electron distribution around atoms in covalently bonded molecules is not always spherical.
- Electron clouds about the two atoms are distorted by each other's charges.

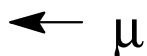
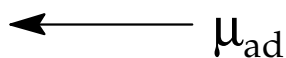
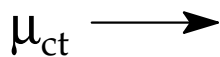
## Atomic Dipole Moment



- Bond dipole moment is the sum of charge transfer moment and atomic dipole moments,  $\mu = \mu_{ct} + \mu_{ad}$ .
- Atomic dipoles can be quite large and may be larger than the bond's charge transfer moment.

Example: CO       $d_{CO} = 133 \text{ pm}$        $\chi_C = 2.5$      $\chi_O = 3.5$

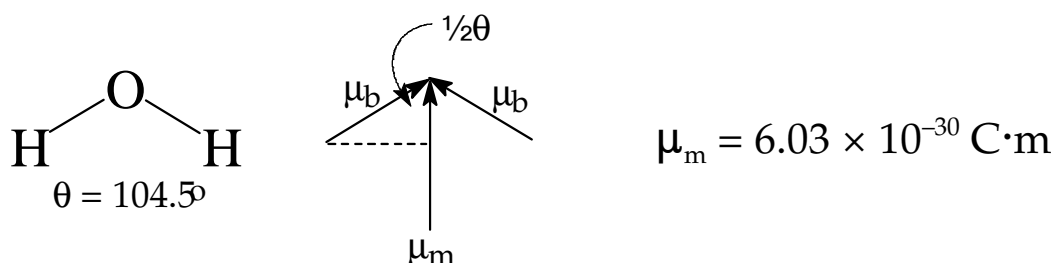
Observed dipole moment is only  $0.37 \times 10^{-30} \text{ C}\cdot\text{m} = 0.11 \text{ D}$  and in the opposite direction suggested by electronegativities.



Formal charges have it correct!

## Dipole Moments of Polyatomic Molecules

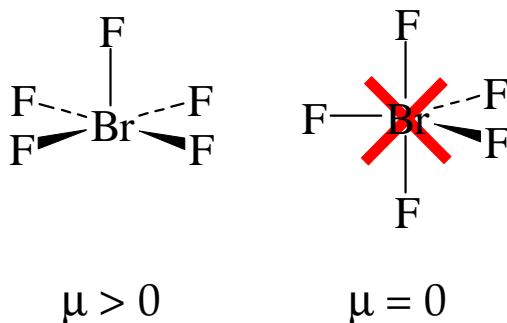
- Bond moments are estimated from observed moments of simple molecules with known geometries.



$$\mu_b = \frac{1/2\mu_m}{\cos(1/2\theta)} = \frac{(1/2)(6.03 \times 10^{-30})}{\cos 54.25^\circ} = \frac{3.015 \times 10^{-30}}{0.6122} = 4.92 \times 10^{-30}$$

- Bond moments are only approximately transferrable, because they include atomic moments that may not be the same in other molecules.
- Concept of bond moment is more useful qualitatively than quantitatively.

Example:  $\text{BrF}_5$ ,  $\mu = 4.92 \times 10^{-30} \text{ C}\cdot\text{m} \Rightarrow$  Not *tbp*



## Effect of Lone Pairs on Molecular Dipole Moments

- Lone pairs on an atom can produce a significant atomic dipole, called a lone pair dipole, which may reinforce or oppose bond polarities, thereby strongly influencing the overall molecular dipole moment.

