# Types of Chemical Bonds and Electronegativity

## *Why?*

One of the goals of chemistry has been to explain why atoms associate with each other to form molecules. We now understand the key role that electrons play in this process: that the distribution of electrons around the nuclei (i.e. the orbital shapes) change when atoms come together to form molecules (i.e. $CO_2$) or solid materials (i.e. NaCl), in such a way that the energy of the "system" is lowered when the atoms are together. Covalent and ionic bonding models provide alternative explanations for why the energy is lowered when the atoms come together. Electronegativity (a concept introduced by American chemist and peace activist Linus Pauling) is related to ionization energies and electron affinity, and is used to predict the relative importance of covalent and ionic contributions to chemical bonding.

## *Learning Objectives*

- Understand the covalent and ionic models of bonding, and know that each model is only an approximation of the "truth" about why atoms group together as molecules.
- Learn the meaning of electronegativity and be able to use it to predict properties of chemical substances.

## *Success Criteria*

## *Resources and Prerequisites*

Zumdahl and Zumdahl, *Chemistry* (6th ed.), sections 8.1 – 8.4 (pp. 46-48).

## *Vocabulary and New Concepts*

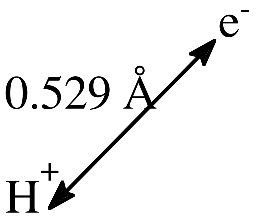
Covalent bond, Ionic bond, Bond Energy, Electronegativity

### *Focus 1 – Coulomb's Law*

A "chemists' version" of this law is as follows:

$$\text{Electrical Potential Energy} = E_{potential} = \left(1390\frac{kJ\cdot \mathring{A}}{mol}\right)\left(\frac{(Q_1)(Q_2)}{r}\right)$$

Example:



$$E_{potential} = \left(1390\frac{kJ\cdot \mathring{A}}{mol}\right)\left(\frac{(+1)(-1)}{0.529\mathring{A}}\right) = -2630kJ$$

### *Focus 2 – Tendency toward low Energy states*

Based on observations, we can detect a "tendency" for atoms to adopt arrangements that minimize the potential energy. This tendency is most pronounced at low temperatures.

Room temperature is considered low temperature (flames and the sun are high temperature).

### *Key Questions*

1. What do the symbols $Q_1$, $Q_2$ and r represent in the chemists' version of Coulomb's Law

2. What are the meanings of each of the units in the constant of Coulomb's Law?

3. Zumdahl and Zumdahl give the following expression for Coulomb's Law (p. 349): $E = (2.31\times 10^{-19} J\cdot nm)\left(\frac{Q_1Q_2}{r}\right)$. Is this the same Law?

4. Are intact molecules more likely to be found on the surface of the earth or inside the sum? Why?

## *Exercises*

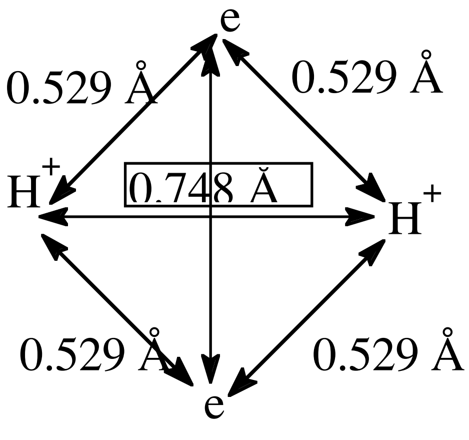
1. The electrical potential energy of the H atom is calculated in Focus 1. Compare this to the total energy of the hydrogen atom. The total energy of the H atom is ΔE for $H^+ + e^- \rightarrow H$, which can be calculated from information in chapter 7 of Zumdahl and Zumdahl.

2. To a "good first approximation",[1] the total energy of H atom = (kinetic energy of electron) + (electric potential energy). Use this approximation to calculate the kinetic energy of the electron in the hydrogen atom.

3. Are the signs (+ or -) of the potential energy and kinetic energy the same, or are they opposite? Will the potential energy and kinetic energy of any atom have the same signs as do those in hydrogen?

For the next few exercise we will forget about the kinetic energy and imagine that the electrons are at fixed positions. The purpose is to show how the potential energy of two H atoms can decrease by moving the atoms close to each other.

4. Calculate the potential energy for the following arrangement of two electrons and two protons (nuclei of H atoms). To do this, you need to add up the pairwise interaction energies (i.e. add up the Coulomb's Law energies for all six double-headed arrows).



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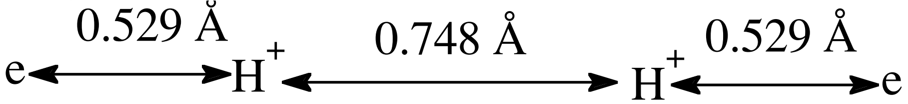
[1] This "good first approximation" neglects magnetic interactions. The energy contribution from magnetic interactions is a form of potential energy, but is much smaller in magnitude than the electric potential energy.

5. Now calculate the potential energy change going from two isolated H atoms (exercise 1) to the configuration in exercise 4. Does bringing the atoms together in this way reduce the potential energy of the system?

6. Of course, the electrons are moving around, and at any given moment could be in different configurations from that shown in exercise 4. Calculate the potential energy for the following configuration, again being sure to take into account all six pairwise interactions (three of these are not shown). Would bringing the atoms together in this way result in reduction of potential energy?



7. Using the results of the previous exercises, and given that H atoms **do** form into $H_2$ molecules, make a prediction on the correct answer to this multiple choice question. Which statement best describes the positions of electrons in diatomic molecules such as $H_2$?

   a. The electrons spend more of their time in the region between the nuclei (as in the figure of exercise 4) than at the outer ends of the molecule.

   b. The electrons spend more of their time at the outer ends of the molecule in order to stay as far away from each other as possible.

   c. The two electrons will be at exactly the same position, halfway between the two nuclei, in order to minimize the potential energy.

## *Focus 2 – Quantum Mechanical Calculations – Molecular Orbitals*

The calculations of the previous section show that it is **plausible** that Coulombic attractions between electrons and nuclei hold molecules together. But these calculations have neglected the necessary movements of the electrons (the kinetic energy). It turns out that kinetic energy can also be lessened (made less positive) when atoms come together. To show this requires quantum mechanics, using the Shroedinger equation $H\psi = E\psi$.

Computer programs such as “Spartan Plus” are able to find approximate solutions to this equation for molecules. The solutions are molecular orbitals (probability distributions for the electrons) and energies of the orbitals. As in atoms, only two electrons can occupy each orbital, and the total energy of the molecule is calculated by adding up the orbital energies for each electron.

We will use Spartan Plus to calculate an energy curve similar to Figure 8.1 of Zumdahl and Zumdahl for $H_2$ (and if time permits for other molecules such as $F_2$ and HF). The points below give you an overview; you will need to get instruction on specific steps from your instructor

1. Start up Spartan Plus (not Spartan Pro).

2. Choose a “New” molecule from the File menu, and build an $H_2$ molecule.

3. Click on the “measure distance” icon and select the H-H bond. Then set the distance to a very large value (say 100 Å) to correspond to separated H atoms.

4. Setup … Calculations:

   - Calculate: Single Point Calculation with Hartree-Fock (STO-G) approximations
   - Start from: Initial Geometry
   - Total charge: neutral.
   - Multiplicity: singlet (this means there are no unpaired electrons)
   - Check boxes for: Compute **Elect. Charges**, Print **Orbitals & Energies**, and **Symmetry**

5. Setup … Submit (the calculations). The calculations will take several seconds, and give you an alert message when the calculations are started, and when they are finished.

6. After the calculation is done, Display … Properties to show the energy. The energy is in units of a.u. (The potential energy of an H atom – i.e. exercise 1 – is equal by definition to -1 a.u.) Write down this number. Subtract this value from that of future calculations to give the “bond energy” (the vertical axis for Figure 8.1).

7. Now set the distance to other values between 3Å and 0.1 Å and recalculate the energy. Give the results (distance + energy) to the instructor, who will create a graph of energy vs. bond distance.

8. Finally, change the calculation type to Equilibrium Geometry and let the program determine the distance between H atoms that minimizes the total energy of the system. Compare this to the experimental H-H distance of 0.714 Å. Increasing the level of sophistication of the quantum chemical calculations (i.e. choosing one of the options below STO-G in the calculation setup dialog) results in better agreement with experiment (but takes more computer time).

9. The instructor will show you how to create an electron density surface for the $H_2$ molecule. Is the electron density concentrated between the nuclei, or on the outsides? (cf. your answer to exercise 7 on the previous page).

## *Focus 3 –Electronegativity*

Electronegativity is related to the partial charges that are generated on atoms in molecules. These partial charges are generated because electrons spend more time near one nucleus than the other when the atoms have different nuclear charges.

1. Use Spartan Pro to calculate partial charges on the atoms in the diatomic molecules formed from the following elements: H, Li, B, N, F, Na, Cl. Different groups can calculate for different combinations – share results with the class.

2. Which elements have the greatest tendency to have partial positive charges? Which have the greatest tendency to have partial negative charges?

3. Compare your answer to the previous question to Pauling's Electronegativity Scale (Figure 8.3).

4. The Mulliken electronegativity scale is based on the average of the IE of the neutral atom and the $X^{\neq}$ ion (the IE of $X^-$ = - EA of X). Use data from chapter 7 to calculate Mulliken electronegativities for the following selection of elements, and compare to the Pauling Scale:

| Element | H | B | C | N | O | F | Si | P | S |
|---|---|---|---|---|---|---|---|---|---|
| IE | | | | | | | | | |
| -EA | | | | | | | | | |
| avg | | | | | | | | | |
| ÷ 250 | | | | | | | | | |