

where Ψ_{3s} , Ψ_{3p} , Ψ_{1s} are the atomic orbitals on chlorine (3s and 3p) and hydrogen (1s). Now a and b can be varied relative to each other in such a way that any amount of p character can be involved in the molecular orbital. For example, if $a = 0$, the chlorine uses a pure p orbital, but if $a = \frac{1}{3}b$, the p character will be 75% (an " sp^3 hybrid" in VB terminology). And, of course, the relative weighting of a and b vs. c indicates relative contribution of chlorine vs. hydrogen to the bonding molecular orbital.

Electronegativity and molecular orbital theory

As we have seen, the "distortion" that takes place as one progresses from Figs. 4.58 and 4.59 results from differences in electronegativity between the bonding atoms. In general, MO language does not speak of the "electronegativity difference" but of the magnitude of the *coulomb integrals* of the constituent atoms. These may be taken as the *valence state ionization energies* (VSIE), *i.e.*, the energy necessary to remove an electron from an atom *under the conditions that exist in the molecule*. The VSIE will therefore not be identical to the usual ionization energy of an atom though related to it. A discussion of the various methods of estimating coulomb integrals would be beyond the scope of this text but it may be mentioned that the VB methods of evaluating electronegativity are related to this problem. Inasmuch as more work has probably been done in the valence bond context, this aspect of electronegativity will be discussed at greater length with the reminder that the results can be transferred qualitatively to MO theory.

Pauling's electronegativity and valence bond theory

Pauling first defined electronegativity and suggested methods for its estimation. Pauling's definition⁶⁰ has not been improved upon: *The power of an atom in a molecule to attract electrons to itself*. It is evident from this definition that electronegativity is not a property of the isolated atom (although it may be related to such properties) but rather a property of an atom in a molecule, in the environment of and under the influence of surrounding atoms.

Pauling based his electronegativity scale on thermochemical data. It had been observed that bonds between dissimilar atoms were almost always stronger than might have been expected from the strength of bonds of the same elements when bonded in homonuclear bonds. For example, the bond energy of chlorine monofluoride, ClF, is about 255 kJ/mole, greater than either Cl₂ (242 kJ/mole) or F₂ (153 kJ/mole).⁶¹ Pauling suggested that molecules formed from atoms of different electronegativity would be stabilized by *ionic resonance energy* resulting from resonance of the sort:

$$\Psi_{AB} = a\Psi_{A-B} + b\Psi_{A^+B^-} + c\Psi_{A^-B^+} \quad (4.54)$$

For molecules in which atoms A and B are identical, $b = c \ll a$ (see page 96 for the H₂ molecule), and the contribution of the ionic structures is small. If B is more electronegative than A, then the energy of the contributing structure A⁺B⁻ approaches more nearly to that of the purely covalent structure A—B and resonance is enhanced. On the other hand, the energy of B⁺A⁻ is so prohibitively high that this structure may be dismissed from further consideration. For a predominantly covalent, but polar,

⁶⁰ L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 88.

⁶¹ See Appendix F.

bond, $a > b \gg c$. The greater the contribution of the ionic structure (*i.e.*, the closer it comes to being equivalent in energy to the covalent structure) the greater the resonance between the contributing structures and the greater the stabilizing resonance energy. Pauling suggested that electronegativity could be estimated from calculations involving this *ionic resonance* energy. The method is briefly outlined as follows.

An estimate of the ionic resonance energy may be obtained from subtracting an average "nonpolar" bond energy for atoms A and B from the real, experimentally obtained bond energy. The "nonpolar" energy is supposed to be that resulting if a purely covalent bond (corresponding to contributing structure (I)) could be formed between A and B. Pauling first suggested that the arithmetic mean of the bond energies AA and BB would provide a suitable estimate of this quantity, but because of difficulties with this method, later suggested the geometric mean as more reliable. For the ClF bond mentioned above, the two methods yield:

	Arithmetic mean	Geometric mean
Bond energy, Cl ₂	$E_{\text{ClCl}} = 240$	$E_{\text{ClCl}} = 240$
Bond energy, F ₂	$E_{\text{FF}} = 155$	$E_{\text{FF}} = 155$
Average energy, ClF	$E_{\text{ClCl}} + E_{\text{FF}}/2 = 198$	$(E_{\text{ClCl}} \times E_{\text{FF}})^{\frac{1}{2}} = 194$
Experimental energy, ClF	$E_{\text{ClF}} = 249$	$E_{\text{ClF}} = 249$
Ionic res. energy	$\Delta = 249 - 198 = 51$	$\Delta' = 249 - 194 = 55$

The two methods do not differ appreciably, but geometric means are always smaller than arithmetic means, so the ionic energy calculated by the geometric mean method (Δ') will be slightly larger than when using the arithmetic mean (Δ). Table 4.8 lists estimates of ionic resonance energy obtained by both methods. The values of Δ and Δ' parallel our intuitive feelings about electronegativity: Bonds between elements expected to have large differences in electronegativity (*e.g.*, H—F) have large ionic resonance energies, but with elements having small electronegativity differences

Table 4.8 Ionic Resonance Energy of Some Common Bonds (kJ/mole)

	H	C	S	Cl	F
	Arithmetic mean method, ^a Δ				
H	0	22.6	35.1	92.0	272
C	25.1	0	-13.0	34.3	235
S	51.5	-7.5	0	22.6	94.1
Cl	106	39.3	22.6	0	51.5
F	306	254	97.5	56.5	0
	Geometric mean method, ^b Δ'				

^a Values to the right of the "step rule" were derived by the arithmetic mean method.

^b Values to the left of the "step rule" were derived by the geometric mean method.

(H—C, C—S), small ionic resonance energies are found.⁶² The elements may thus be arranged in the order of their electronegativities as has been done in Table 4.8. However, in order to obtain quantitative estimates of electronegativity, it is necessary to replace Δ (or Δ') by an additive function.⁶³ For this purpose, Pauling suggested that the *square root* of the ionic resonance energy was more nearly additive and should be used as an estimate of the difference in electronegativity between two elements. He first used the arithmetic mean method of calculation and bond energies in electron volts (1 eV = 96.49 kJ/mole). The difference in electronegativity between two elements, A and B, then becomes⁶⁴

$$\Delta\chi = \frac{\Delta_{AB(\text{kJ})}}{96.49}$$

Later, when the advantages of the geometric mean method became apparent, Pauling suggested the arbitrary conversion factor of 125 to make the values obtained from Δ' compatible:

$$\Delta\chi = \frac{\Delta'_{AB(\text{kJ})}}{125}$$

Values for electronegativity differences, using both methods, are listed in Table 4.9.

Table 4.9 Differences in Electronegativity Obtained from Ionic Resonance Energies

	H	C	S	Cl	F
	Arithmetic mean method ^a				
H	0	0.48	0.60	0.98	1.68
C	0.44	0	"0"	0.60	1.56
S	0.64	"0"	0	0.48	0.99
Cl	0.92	0.56	0.42	0	0.73
F	1.56	1.43	0.88	0.67	0
	Geometric mean method ^b				

^a Values to the right of the "step rule" were derived by the arithmetic mean method.

^b Values to the left of the "step rule" were derived by the geometric mean method.

The values are roughly additive, especially when the electronegativity differences are not too great:

$$\Delta\chi_{\text{HC}} + \Delta\chi_{\text{CCl}} = 0.44 + 0.56 = 1.00 \simeq \Delta\chi_{\text{HCl}} = 0.92 \quad (4.57)$$

⁶² Negative ionic resonance energies are occasionally obtained as in the case of the C—S bond above. They are, of course, meaningless and arise from errors in the method, namely, estimating a small quantity (Δ or Δ') by subtracting two large quantities, one of which, the "covalent energy" of C—S, is estimated very crudely. The geometric mean tends to encounter this problem less often than the arithmetic mean method.

⁶³ Neither Δ nor Δ' is additive; *i.e.*, $\Delta_{\text{HCl}} \neq \Delta_{\text{HC}} + \Delta_{\text{CCl}}$, $22.1 \neq 5.9 + 8.0$; for Δ' , $25.6 \neq 6.6 + 9.0$.

⁶⁴ One should be careful to distinguish between the quantity Δ , the ionic resonance energy, and the quantity $\Delta\chi$, the difference in electronegativity.

$$\Delta\chi_{\text{HCl}} + \Delta\chi_{\text{ClF}} = 0.92 + 0.67 = 1.59 \simeq \Delta\chi_{\text{HF}} = 1.56 \quad (4.58)$$

$$\Delta\chi_{\text{CCl}} + \Delta\chi_{\text{ClF}} = 0.56 + 0.67 = 1.23 \simeq \Delta\chi_{\text{CF}} = 1.43 \quad (4.59)$$

$$\Delta\chi_{\text{SCl}} + \Delta\chi_{\text{ClF}} = 0.42 + 0.67 = 1.09 \simeq \Delta\chi_{\text{SF}} = 0.88 \quad (4.60)$$

and we are justified in setting up an electronegativity scale based on:

$$\Delta\chi_{\text{HF}} = \Delta\chi_{\text{HC}} + \Delta\chi_{\text{CF}} \quad (4.61)$$

It is thus possible to set up an additive, linear electronegativity scale in which the difference in electronegativity of two elements is equal to the sum of their differences from a third element.

Pauling set up such a scale, arbitrarily setting hydrogen at 2.1 and arranging the other elements relative to it. It should be obvious from the data in Table 4.9 that there is no unique way to determine the electronegativities of the other elements since the values are not perfectly additive. Nevertheless, by performing very many calculations of this type and choosing electronegativity values such that deviations are minimized, it is possible to obtain a table of electronegativities for general use.⁶⁵ Pauling's values, with minor corrections resulting from improved energy data, are listed in Table 4.10.

Pauling's method of obtaining electronegativity data is probably mainly of historical interest since there are now improved methods of estimating electronegativities.⁶⁶ The concept of covalent-ionic resonance is still quite useful, however. As pointed out above, the fact that a bond with partial ionic character can be stronger than either a purely covalent or purely ionic bond has often been overlooked as alternate methods of treating electronegativity have developed. Energies associated with electronegativity differences can be useful in accounting for the total bonding energy of molecules.⁶⁷

Other methods of estimating electronegativity

Many other methods have been suggested for determining the electronegativity values of the elements. Only two general methods will be discussed here. The first was proposed by Mulliken⁶⁸ shortly after Pauling proposed his method. Mulliken suggested that the attraction of an atom for electrons should be an average of the *ionization energy and electron affinity of the atom*. Mulliken electronegativities can be estimated by the equation:

$$\chi_{\text{M}} = 0.168 (\text{IE}_{\text{v}} + \text{EA}_{\text{v}} - 1.23) \quad (4.62)$$

where the *valence state ionization energy* (IE) and *electron affinity* (EA) are in electron volts. The valence state ionization energy and electron affinity are not the experimentally observed values but those calculated for the atom in its *valence state* as it exists in a molecule. Two short examples will clarify the nature of these quantities.

Divalent beryllium bonds through two equivalent *sp* or *digonal* hybrids. The appropriate ionization energy therefore is not that of ground state beryllium, $1s^2 2s^2$,

⁶⁵ The discussion here is oversimplified. Difficulties are sometimes encountered in obtaining accurate bond energies, and modifications of the above procedures must be resorted to [cf. Pauling, "The Nature of the Chemical Bond," or H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955)].

⁶⁶ Not all chemists would agree with this statement.

⁶⁷ See pages 234–235.

⁶⁸ R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934), **3**, 573 (1935); W. Moffitt, *Proc. Roy. Soc. (London)*, **A202**, 548 (1950).