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Asymmetry Zone for Dual-Atomic Molecules with Single Bonding Electron

1. Molecule Model and Main Equations

This article is devoted to solutions of electrostatic balance equations for dual-atomic molecules developed in the book *How Chemical Bonds Form and Chemical Reactions Proceed* [1].

The basic configuration of the molecule considered in this book is shown on figure 1.

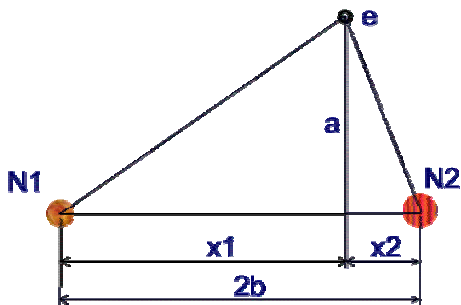


Figure 1

In accordance with the book, the equations of electrostatic balance are as follows:

$$e^2 N_1 n x_1 / (x_1^2 + a^2)^{1.5} = e^2 N_1 N_2 / (x_1 + x_2)^2 \quad \text{Equation (1)}$$

$$e^2 N_2 n x_2 / (x_2^2 + a^2)^{1.5} = e^2 N_1 N_2 / (x_1 + x_2)^2 \quad \text{Equation (2)}$$

$$a = R/F_0 \quad \text{Equation (3)}$$

In these equations, the variables are:

- e – electron charge;
- n – number of bonding (valent) electron
- N_1, N_2 – effective charges of nuclei;
- R – Bohr radius (0.529 Å);
- a – radius of electrons' orbit

- x_1, x_2 – distances between electron orbit's plane and 1st and 2nd nuclei, accordingly.

$$\text{Also, } x_1+x_2 = 2b \quad \text{Equation (3)}$$

where $2b$ is the distance between the two nuclei of the hydrogen-like atoms in the molecule.

Variable F_0 represents the effective positron charge of the two nuclei and can be calculated via the following equation:

$$F_0 = N_1/[(x_1/a)^2+1]^{3/2} + N_2/[(x_2/a)^2+1]^{3/2} - S_n \quad \text{Equation (4)}$$

Here, the value of S_n depends on n : $S_n = 0$ when $n = 1$, $S_n = 0.25$ when $n = 2$, and $S_n = 0.5773$ when $n = 3$.

Equations (1) and (2) describe the balance of the *horizontal* components of the Coulomb forces between the nuclei and electrons (i. e. along the line going through the two nuclei). They constitute a system of equations with three variables x_1, x_2 , and a .

In these two equations, variable a can be excluded by using dimensionless variables: $\chi_1 = x_1/a$, and $\chi_2 = x_2/a$. This makes sense because just these dimensionless variables are used in equation (4) for F_0 , which actually may be illustrated as follows:

$$F_0 = N_1/(\chi_1^2+1)^{3/2} + N_2/(\chi_2^2+1)^{3/2} - S_n \quad \text{Equation (4')}.$$

After the cancellations and the transition to the dimensionless variables, equations (1) and (2) can be written as follows:

$$n\chi_1/(\chi_1^2+1)^{3/2} = N_2/(\chi_1+\chi_2)^2 \quad \text{Equation (5)}$$

and

$$n\chi_2/(\chi_2^2+1)^{3/2} = N_1/(\chi_1+\chi_2)^2 \quad \text{Equation (6)}.$$

Now, we have a system of two equations with two variables χ_1 and χ_2 . We can find the dimensions of the molecule by using Equations (4') or (4), and expressions $x_1 = \chi_1 \cdot a$, and $x_2 = \chi_2 \cdot a$.

The system is solved analytically when the molecule contains two similar atoms (homoatomic molecule). In this case, $N_1 = N_2 = N$. From symmetry considerations, χ_1 and χ_2 are also equal ($\chi_1 = \chi_2 = \chi$) and both equations (5) and (6) offer:

$$n\chi / (\chi^2+1)^{3/2} = N / (4\chi^2).$$

The solution of this equation amounts to the following:

$$\chi = [N / (4n)]^{1/3} / \{1 - [N/(4n)]^{2/3}\}^{1/2}. \quad \text{Equation (7)}$$

Further in this paper, it will be shown that, in some cases, such a solution may not be the only one, and even not the most likely one.

Basically, when N_1 does not equal N_2 and, moreover, in the case of asymmetric molecules, the system has no analytical solution, and the system of two equations (5) and (6) can be reduced to an equation with only one variable, for example — χ_1 .

After solving equation (6) to find χ_2 , making substitutions in equation (5), and simplifications, the resulting single-dimensional equation for χ_1 resembles the following:

$$\frac{(\chi_1^2 + 1)^{3/2} [\sqrt{(N_2/n)} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2}]}{\{[\sqrt{(N_2/n)} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2}]^2 + \chi_1\}^{3/2}} = N_1 / N_2 \quad \text{Eq. (8)}$$

Finding the value of χ_1 , by using also equation (3), one can find the dimensions of the molecule and, finally, its bonding energy. For this, it is necessary to use the first ionization potentials of both nuclei instead of their effective nuclear charges, N_1 and N_2 . The relations between the charges and the ionization potentials of the atoms are expressed in the book [1] by the following Equation:

$$N_i = (FIE_i / FIE_H)^{1/2}.$$

Here, FIE_i is the first ionization energy of the given atom, while $FIE = 13.595$ eV is the first ionization energy of the hydrogen atom. Therefore, in terms of $FIEs$, equation (8) may be illustrated as follows:

$$\frac{(\chi_1^2 + 1)^{3/2} \left[\frac{(FIE_2 / FIE_H)^{1/4}}{\sqrt{n}} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2} \right]}{\left\{ \left[\frac{(FIE_2 / FIE_H)^{1/4}}{\sqrt{n}} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2} \right]^2 + \chi_1 \right\}^{3/2}} = (FIE_1 / FIE)^{1/2}$$

$$\text{Equation (8a)}$$

Equation (8) or its equivalent (8a) are the main working equations that has been used in a calculation program to find χ_1 for the given n and (N_1, N_2) or (FIE_1, FIE_2) .

For convenience, we will consider only such values of N_1 and N_2 where N_1/N_2 is equal to or less than 1, because the enumeration of nuclei is conditional. The same is true for FIE_1 and FIE_2 .

In some parametric researches, it is convenient to use the special term v_2 , then $v_2 = N_2/n = (FIE_2 / FIE_H)^{1/2} / n$, and give it various values. Parameter v_2 represents a value of the positron charge of the second atom per each valence electron, so it can be called a *positron load on the electron*.

For any given v_2 and n :

$$N_2 = v_2 * n \text{ and } FIE_2 = v_2^2 n^2 * (13.595) \text{ eV.}$$

To find the bonding energy of a molecule containing two nuclei with ionization energies FIE_1 and FIE_2 , one should use the following expressions provided in the book *How Chemical Bonds Form and Chemical Reactions proceed*. [1]:

- for a molecule with a single-bonding electron:

$$E_{\text{bond}} = [(1/a^2) * FIE_H - (FIE_I)_{\text{min}}] * 2,$$

where $(FIP_I)_{\text{min}}$ is the minimal ionization potential of the two nuclei, in the molecule;

- for a molecule with two bonding electrons:

$$E_{\text{bond}} = [(1/a^2) * FIE_H * n * (.93 + 0.0114/a) - FIE_1 - FIE_2] * 2.$$

But to use these equations, we have to find χ_1 first. Now let's see how this is done.

2. Solution Methods for Main Equation

For any given N_1 / N_2 or FIE_1 / FIE_2 the right side of equation (8) or (8a) is constant, while the left side depends on variable χ_1 . There is also a constant coefficient v_2 on the left side, which, together with the right side, links the equation to the specific properties of the molecule. Now let's indicate the left-side function as $L(\chi_1)$. Equation (8) can be solved graphically and/or by reiteration.

For reiteration solutions, a special computer program has been developed. With the help of this, we can get information for detailed analyses with various parameters. For reiterations by the Newton method, a derivative of the $L(\chi_1)$ function was used according to the following equation:

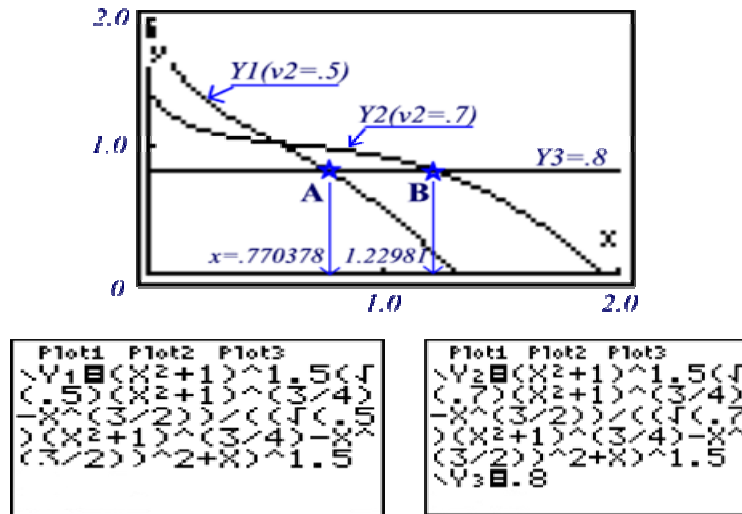
$$L'(\chi_1) / L(\chi_1) = \frac{3\chi_1}{\chi_1^2 + 1} + (3/2) \frac{\sqrt{v_2} \chi_1 / (\chi_1^2 + 1)^{1/4} - \sqrt{\chi_1}}{\sqrt{v_2} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2}} -$$

$$(3/2) \frac{3[\sqrt{v_2} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2}] * [\sqrt{v_2} \chi_1 / (\chi_1^2 + 1)^{1/4} - \sqrt{\chi_1}] + 1}{[\sqrt{v_2} (\chi_1^2 + 1)^{3/4} - \chi_1^{3/2}]^2 + \chi_1}$$

Equation (9)

The graphic method offers an opportunity to find specific, irregular, solutions. Modern graphing calculators provide accuracy and many solutions. Two graphic solutions are given in figure 2.

The two curves shown in this figure are the left sides of equation (8) with values of parameter v_2 equal to 0.5 and 0.7 for functions Y_1 and Y_2 , correspondingly. The functions are shown under the diagram as recorded in the computer's memory. The horizontal line Y_3 represents the right side of the equation for $N_1/N_2 = 0.8$. The intersection points A and B are solutions x for the two values of v_2 .



Figures 2 & 3

The computer offers the same results for χ_1 by iterations.

3. Studies of Irregular Molecule Configurations

Detailed calculations show that there is a specific range of values in parameter $v_2 = N_2/n = [(FIE_1/13.595)^{1/2}/n]^{1/2}$ where the main equation (8), or (8a) has more than one solution. Figure 3 illustrates this graphically. In the following diagrams, the term *FIP*, corresponds to *FIE*.

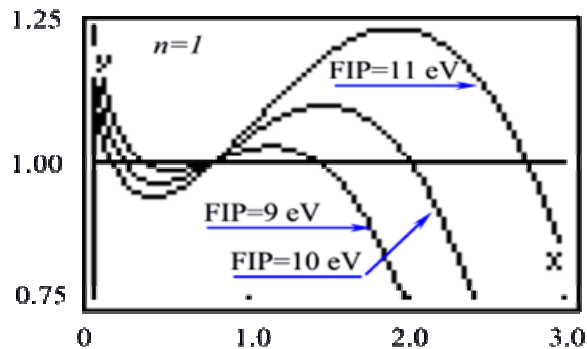


Figure 3 shows the curves of three left-side functions of the main equation for v_2 values equal to 0.89951, 0.85765, and 0.81364. These values expressed in FIE_2/n^2 units are equal to 11.00, 10.00, and 9.00 eV, accordingly. Some horizontal lines, for example, the line $y = 1$ shown in the figure, intersect the diagrams at three different points. This means that three different equation solutions are possible, with relatively different molecular configurations and, as a result, with different bonding energies.

Thus, in the zone where the first ionization energy for one of two nuclei, creating a molecule, has a value of about $10 \cdot n^2$ eV, it is possible to have a multiple choice of molecular configurations and bonding energies. This zone is called a *split-zone* or an *S-zone*, because the letter **S** reminds one of the shape of the diagram in this zone.

Further the discussion concerns two special cases for molecules in the S-zone: homoatomic molecules and heteroatomic molecules. Let's take them separately.

3.1. Homoatomic Molecules in the S-Zone

First let's evaluate the reality of the existence of the S-zone.

The atoms of a homoatomic molecule should have a *FIE* magnitude of about $10 \cdot n^2$ eV, in order to fall into the category fit for the S-zone. That is, only molecules with one bonding electron can be considered. For $n = 2$ and higher, the *FIE* value has an order of magnitude of about 40 eV, which is not the case for ordinary atoms.

Now, let's take a specific homoatomic molecule in the S-zone; for example, let's take one with a *FIE* = 10 eV, $n = 1$.

Figure 4 shows a diagram that corresponds to the left-side function and three points of its intersection with the line $y = 1$.

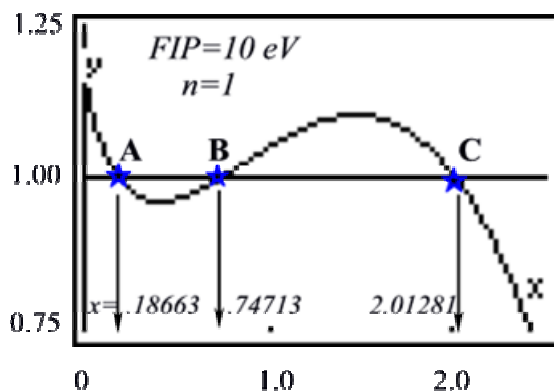


Figure 4

Now we can calculate the corresponding configurations and bonding energies. The results of the calculations are shown in table 1.

Table 1

Point	a	2b	x1	x2	E bond	
	R_Bohr	R_Bohr	R_Bohr	R_Bohr	eV	kJ/mole
A	1.123	2.471	0.210	2.261	1.550	149.51
B	1.134	1.694	0.847	0.847	1.144	110.37
C	1.123	2.471	2.261	0.210	1.550	149.51

Intersection points A and C actually represent one point with mutually interchanged coordinates x_1 and x_2 . Surprisingly, the configuration in point A/C is asymmetric even though the atomic charges are equal. Furthermore, this asymmetric configuration provides more stability, than the symmetric one represented by point B, as a result of the greater bonding energy.

The dimensions of the symmetrical configuration at point B coincide with the values given by theoretical equation (7).

In the specific case when $FIE = 10 \text{ eV}$, we get:

$$\chi = [(10 / 13.595)^{1/2} / 4]^{1/3} / \{1 - [(10 / 13.595)^{1/2} / 4]^{2/3}\}^{1/2} = 0.74713,$$

i.e., the same value as shown on figure 4.

We will speak about *forced symmetry* when the configuration of the homoatomic molecule is calculated with the help of equation (7) rather than by reiteration or by the graphic method.

It is of interest to note that, unlike points A and C, point B could not be calculated by the reiteration program, therefore the graphic solution or equation (7) are the only means for calculating symmetrical configurations in S-zone.

The calculation results for homoatomic molecules, with or without forced symmetry, in the whole range of *FIEs* corresponding to positive values of bonding energies, are shown in table 2 and in schemes (figures 5 and 6).

Table 2

**Molecular Structures vs FIE for Homoatomic Molecules
with one electron**

a. No Forced Symmetry						
FIE	A	2b	x1	x2	E bond	
eV	R_Bohr	R_Bohr	R_Bohr	R_Bohr	eV	
1	2.422	2.163	1.082	1.082	2.636	
2	1.855	1.91	0.955	0.955	3.904	
3	1.606	1.804	0.902	0.902	4.543	
4	1.46	1.748	0.874	0.874	4.761	
5	1.362	1.717	0.858	0.858	4.662	
6	1.291	1.699	0.849	0.849	4.313	
7	1.237	1.69	0.845	0.845	3.741	
8	1.195	1.688	0.843	0.845	3.029	
9	1.159	2.017	0.356	1.661	2.249	
10	1.123	2.471	0.21	2.261	1.55	
11	1.089	3.129	0.121	3.008	0.944	
12	1.055	4.281	0.06	4.221	0.45	
13	1.021	7.564	0.018	7.546	0.101	
13.595	1	Infinite	0	infinite	0	

b. Forced Symmetry						
FIE	A	2b	x1	x2	E bond	
eV	R_Bohr	R_Bohr	R_Bohr	R_Bohr	eV	
1	2.422	2.163	1.082	1.082	2.636	
2	1.855	1.91	0.955	0.955	3.904	
3	1.606	1.804	0.902	0.902	4.543	
4	1.46	1.748	0.874	0.874	4.761	
5	1.362	1.717	0.858	0.858	4.662	
6	1.291	1.699	0.849	0.849	4.313	
7	1.238	1.692	0.846	0.846	3.741	
8	1.196	1.689	0.8445	0.8445	3.008	
9	1.162	1.6756	0.8378	0.8378	2.137	
10	1.134	1.6942	0.8471	0.8471	1.144	
11	1.111	1.7875	0.8938	0.8938	0.028	
12	1.092	1.7123	0.8561	0.8561	-1.198	
13	1.075	1.7222	0.8611	0.8611	-2.472	
13.595	1.067	1.7317	0.8658	0.8658	-3.326	

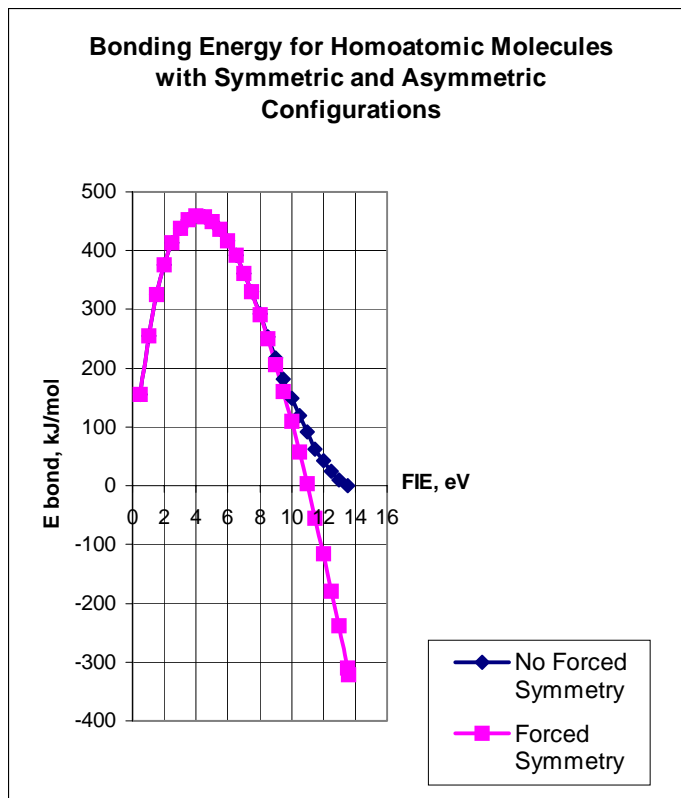


Figure 5

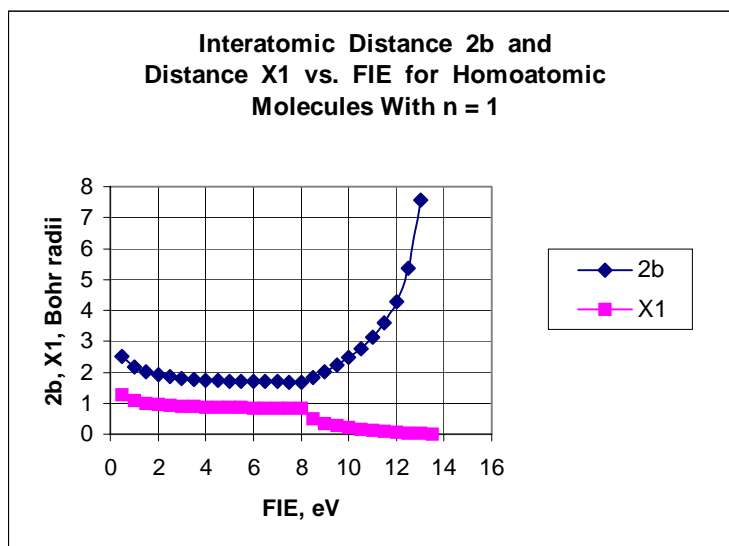


Figure 6

For homoatomic molecules, the point where the split begins (let's call it the *critical point*) can be found analytically. For this, equation (9) should be used as a derivative of equation (8).

In the critical point, two things should happen:

- the derivative (along with a second derivative) equals zero (inflection step);
- the configuration of the molecule is still a symmetric one, thus equation (7) is applicable.

With these two conditions, the following equation offers the critical value of *FIE*:

$$FIE_{cr} = (16/27) n^2 (FIE_H) = 8.0563n^2 \text{ eV} \quad \text{Equation (10)}$$

For $n = 1$, electron $FIE_{cr} = 8.0563 \text{ eV}$.

Thus, when the positron load on the bonding electron reaches the critical value of about 8 eV, asymmetric configurations become more efficient than symmetric ones, in terms of bonding energy.

In such configurations, the interatomic distance increases, causing a decrease in the repulsive forces between the atoms; and the electron approaches one of the atoms. As a result, the electron bonds stronger to this atom, its orbit radius decreases, causing an overall increase in the bonding energy; even though the distance between the nuclei increases.

From this data, the following conclusions can be made.

For homoatomic molecules having one bonding electron with a *FIE* value greater than 8.06 eV, the energetically balanced molecule tends to become asymmetric, and the internuclear distance sharply increases. The bonding energy of an asymmetric molecule is always higher than that of a symmetric one.

Asymmetric molecules have positive bonding energies for *FIEs* up to those of hydrogen atoms (13.595 eV), while symmetric molecules have negative bonding energies for *FIEs* equal to about 11 eV.

3.2. Heteroatomic Molecules in the S-Zone

The ratios N_1/N_2 or FIE_1/FIE_2 are close to 1 in the case when heteroatomic molecules fall into the S-zone.

Let's consider some specific examples with $FIE_1/FIE_2 = 0.95652$ assuming that $FIE_1 = 11 \text{ eV}$ and $FIE_2 = 11.5 \text{ eV}$. The graphic solution of this case is shown on figure 7.

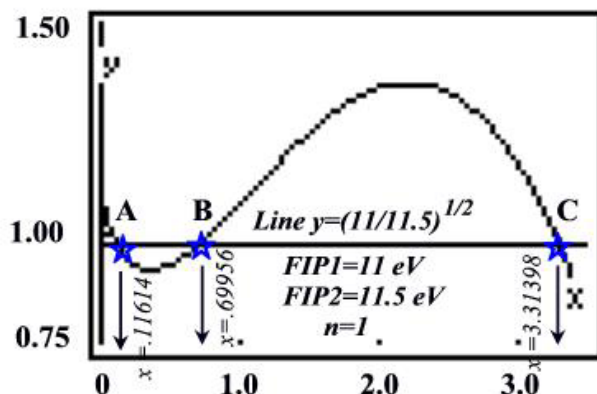


Figure 7

Solutions corresponding to these three intersection points on the diagram are shown in table 3.

Schematic images of these three configurations are shown in figure 8.

Table 3

Point	a	2b	x1	x2	E_bond	
	R_Bohr	R_Bohr	R_Bohr	R_Bohr	eV	kJ/mole
A	1.088	3.092	0.126	2.966	0.972	93.78
B	1.106	1.710	0.769	0.941	0.218	21.03
C	1.072	3.314	3.237	0.077	1.664	160.54

As we see, in the case of heteroatomic molecules, there are three different solutions at points A, B, and C rather than two as in the case of homoatomic molecules.

The main tendency does not change: more asymmetry means higher bonding energy. The interatomic distance along the asymmetry increases greatly.

The middle point B is the point of minimal asymmetry caused by the different charges of atoms in the molecule.

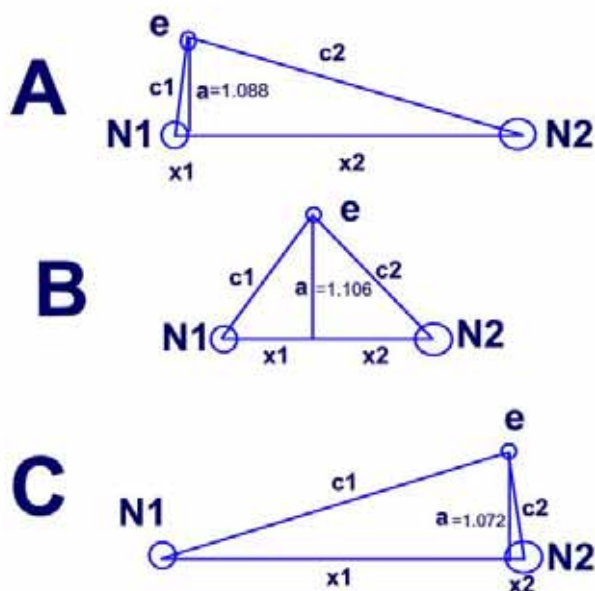


Figure 8

It is of interest to estimate the range and borders of an S-zone in terms of first ionization energy values for FIE_1 and FIE_2 . We can consider FIE_2 as an independent variable because it determines the shape of the main function (together with n). For any given value of FIE_2 , the corresponding minimal and maximal values of FIE_1 can be found from the $L(\chi_1)$ function scheme. The graphic calculator allows finding values with high accuracy. Knowing the extreme values of $L(\chi_1)$, it is easy to find FIE_1 as:

$$FIE_1 = [L(\chi_1)]^2 * FIE_2.$$

Thus, the plot of FIE_1 minimal and FIE_1 maximal as functions of FIE_2 can be built as shown on figure 9 along with the line $FIE_1 = FIE_2$ relative to the case of homoatomic molecules.

In some molecules (for any given FIE_2 , if the FIE_1 value falls between the two FIE_1 minimal and maximal curves) we can be sure that the molecule will hit the S-zone, and it has a good chance of becoming strongly asymmetric. Because value FIE_2 is, by convention, greater or equal to that of FIE_1 , the upper border of the S-zone is on the line of $FIE_1 = FIE_2$.

Having the borders of the S-zone expressed in terms of FIE_1 and FIE_2 , it is possible to define the borders in terms of bonding energy.

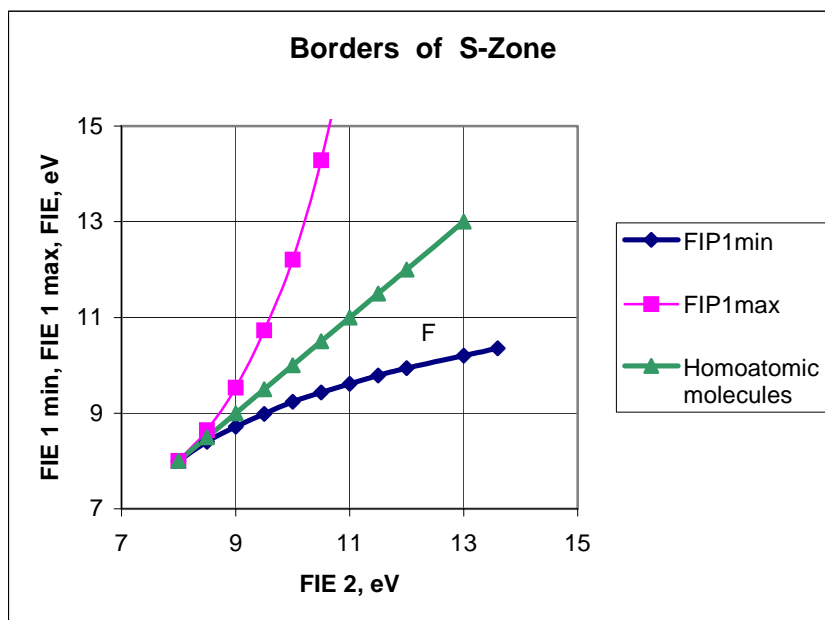


Figure 9

However, as figure 10 shows, for every minimal function of $L(\chi_1)$, there is another solution with the same functional value, with a greater bonding energy due to greater asymmetry (points B and C, accordingly).

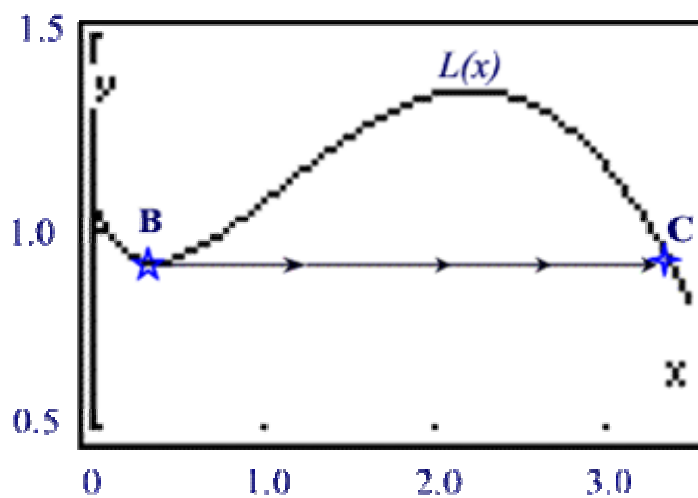


Figure 10

The upper energy border of the S-zone is split. The lower energy border represents the bonding energies of homoatomic molecules in the S-zone. This is the upper branch of scheme E_{bond} vs. FIE (figure 5).

With these considerations, the scheme of energy borders in the S-zone exists as shown in figure 11.

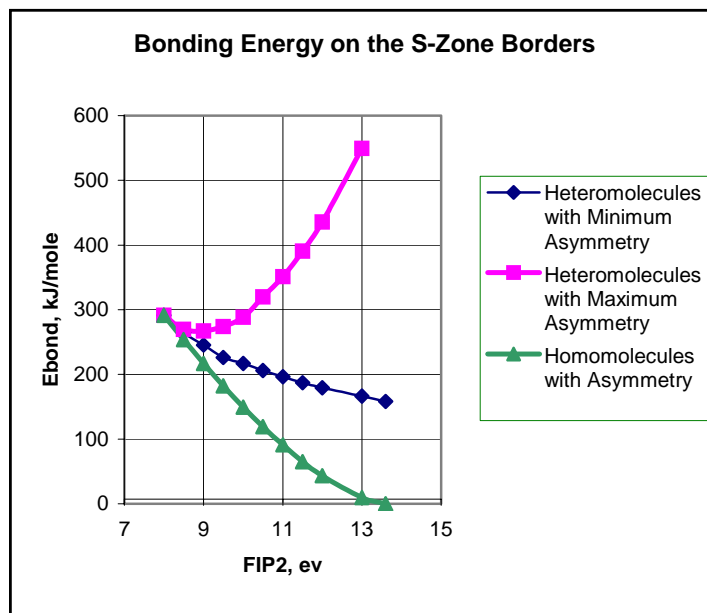


Figure 11

From this figure, it is obvious that, in the general case of heteroatomic molecules, the efficiency of asymmetry, in regard to bonding energy gains, is even greater than in the case of homoatomic molecules.

References:

How Chemical Bonds Form and Chemical Reactions Proceed
By Victor Y. Gankin and Yuriy V. Gankin, ITC, 1998