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Dynamic Balance and Energy Distribution in Two-nucleus Molecules with Single-Electron Bonding

In discussing the advantages and perspectives of semi-quantitative approach to finding dependencies of electric and, possibly in future, thermal conductivity in metals and non-metals on their ionization potentials reported in [1], some results of our previous basic computational research of energy and configuration of two-nucleus molecules with one- and two bonding electrons have been used. This article gives more complete and consequential review of these results, for a single-electron case.

Simultaneously, these researches have continued exploration of asymmetrical molecules described in article [3] and give new criteria to find more complete and generalized explanation of this phenomenon.

We consider the same basic configuration of the molecule (figure 1):

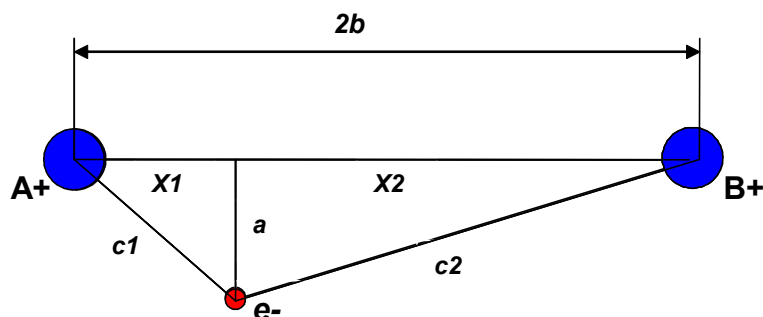


Figure 1

As shown in [3], there is the specific range of charges N_1 and N_2 such that even for $N_1 = N_2$ the molecule can have some asymmetric configuration. In units of the radius of electronic orbit a , such configurations are defined by an equilibrium of electrostatic forces applied along the x-axis.

Absolute dimensions of molecule, in Bohr radii units, have been defined by value of a which, in turn, is defined by the equation (1):

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

where $S_n=0$ if the number of valent electrons $n=1$, $S_n=0.5$ if $n=2$, and $S_n=0.5773$ if $n=3$.

Previously, in article [3], only molecules with balanced configuration have been considered.

Now, we will consider all possible configurations, including unbalanced ones, by changing distance x_1 from 0 up to $2b$.

Using formulas from the article [3], it could be shown that for any charge N_1 and given N_2 the greatest distance x_1 could not be greater than the molecule's length $2b$ and is defined by equation (2):

$$(x_1/a)_{\max} = (N_2/n)^{1/3} / \sqrt{(1-(N_2/n)^{2/3})} \quad \text{Equation (2)}$$

Basically, when x_1 is arbitrarily changed, the molecule becomes unbalanced what means that electric forces are not in equilibrium. It is convenient, using equation (8) from the article [1], to consider the difference between left and right sides of this equation as a measure of this unbalance, or deviation from a balance of forces, Df .

$$Df = \frac{((x_1/a)^2 + 1)^{3/2} [\sqrt{(N_2/n)} ((x_1/a)^2 + 1)^{3/4} - (x_1/a)^{3/2}]}{\{[\sqrt{(N_2/n)} ((x_1/a)^2 + 1)^{3/4} - (x_1/a)^{3/2}]^2 + (x_1/a)\}^{3/2}} - N_1/N_2 \quad (3)$$

When the molecule is balanced, $Df = 0$.

For each particular value of x_1/a , the value of radius 'a' is figured from equation (3) of article (1) as a first iteration. After this, the configuration and its energetic parameters are evaluated using the same formulas as for balanced molecule.

The results of such calculations for bonding energy are shown on figure 2 for homoatomic molecules with FIE = 9, 10, 11, and 12 eV and one valent electron ($n = 1$).

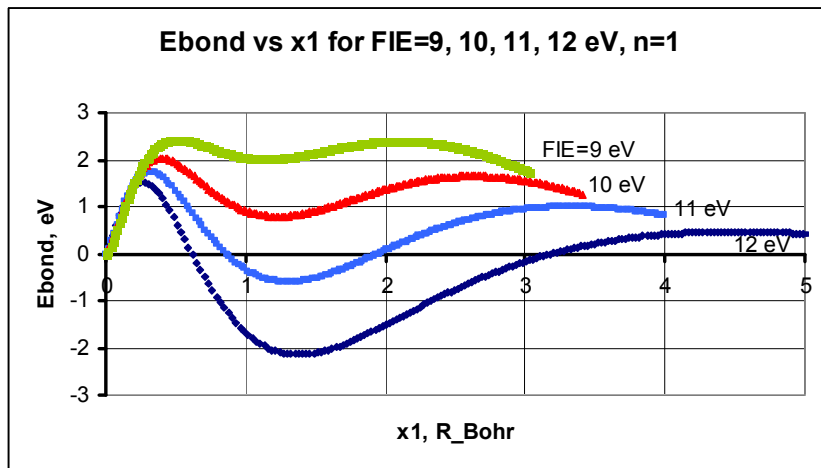


Figure 2

The graphs show clear-cut maximums and minimums of Ebond as it should have been expected in S-zone and, for the first glance, everything looks fine.

However, consideration of the same graphs of Ebond along with parameter Df (figures 3, 4, and 5) shows that the maximums of Ebond nowhere coincide with points of balance, $Df=0$.

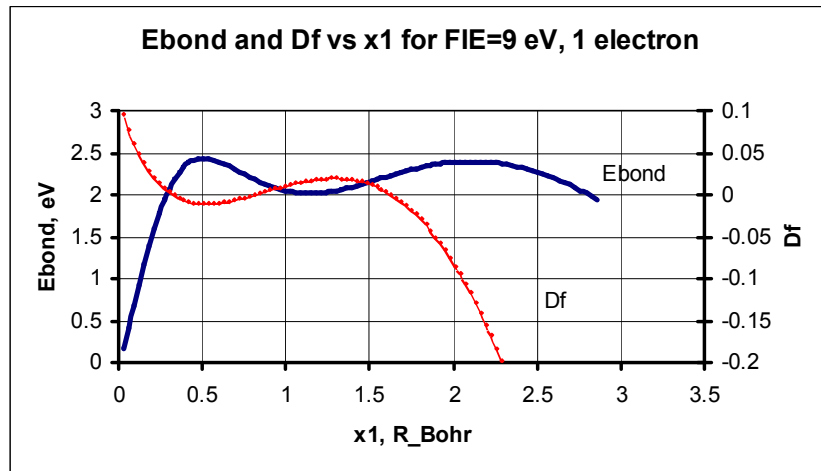


Figure 3

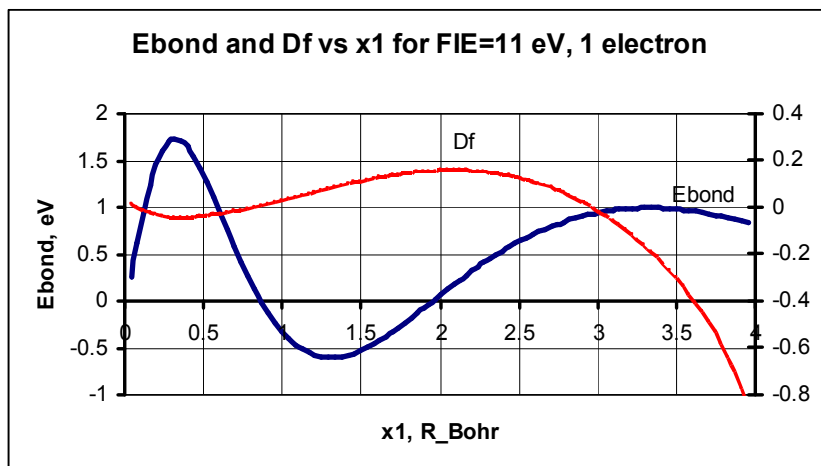


Figure 4

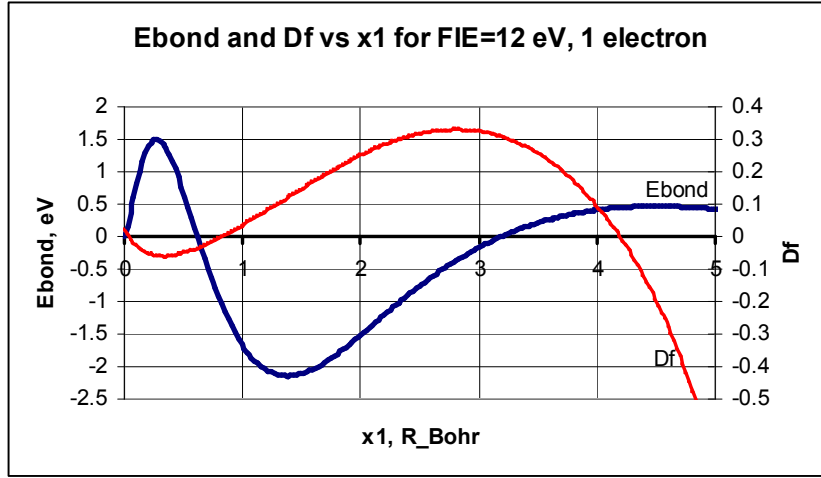


Figure 5

Thus, a bonding energy defined by formulas used in article [3] has no maximum at the point of dynamic balance of a molecule. This unexpected result requires finding another energy relation linked to this point.

Such relation could be found from consideration of potential and kinetic energy in molecule.

For the molecule with one electron shown on figure 1, electrostatic potential energy PE is:

$$PE = K_e e^2 (N_1 N_2 / (2b) - N_1 / c_1 - N_2 / c_2), \quad \text{Equation (4) where:}$$

- $K_e = 8.9876 \times 10^9 \text{ Nm}^2 / \text{C}^2$ - Coulomb constant;
- $e = 1.6022 \times 10^{-27} \text{ C}$ - elementary charge.

Formula for kinetic energy of electron can be developed from equilibrium between vertical components of attraction forces applied to electron from atoms to centrifugal force of electron:

$$K_e e^2 a (N_1 / c_1^3 + N_2 / c_2^3) = mv^2 / a \quad \text{Equation (5)}$$

From this equation, kinetic energy of electron KE is:

$$KE = mv^2 / 2 = K_e e^2 a^2 (N_1 / c_1^3 + N_2 / c_2^3) / 2 \quad \text{Equation (6)}$$

The value of potential energy PE is negative, kinetic energy KE is positive, and their sum equals to:

$$E_{net} = K_e e^2 (N_1 N_2 / (2b) - N_1 / c_1 - N_2 / c_2) + \frac{1}{2} a^2 (N_1 / c_1^3 + N_2 / c_2^3) \quad \text{Equation (7)}$$

Using Bohr radius as a length unit, this formula gives:

$$E_{net} = 27.115(N_1N_2/(2b) - N_1/c_1 - N_2/c_2 + \frac{1}{2}a^2(N_1/c_1^3 + N_2/c_2^3))$$

Equation (7a)

Similarly, for a molecule with two electrons, it may be shown that:

$$E_{net} = 27.115(N_1N_2/(2b) - 2N_1/c_1 - 2N_2/c_2 + 1/(2a) + a^2(N_1/c_1^3 + N_2/c_2^3) - 1/(4a))$$

Equation (7b)

E_{net} value represents an excess of potential energy above kinetic one. Obviously, this variable is directly related to a bonding energy of molecule, so it can be used as a criterion of its stability.

Graph on figure 6 shows E_{net} 's dependence on x_1 illustrated for the same four values of FIE in S-zone as on figure 2.

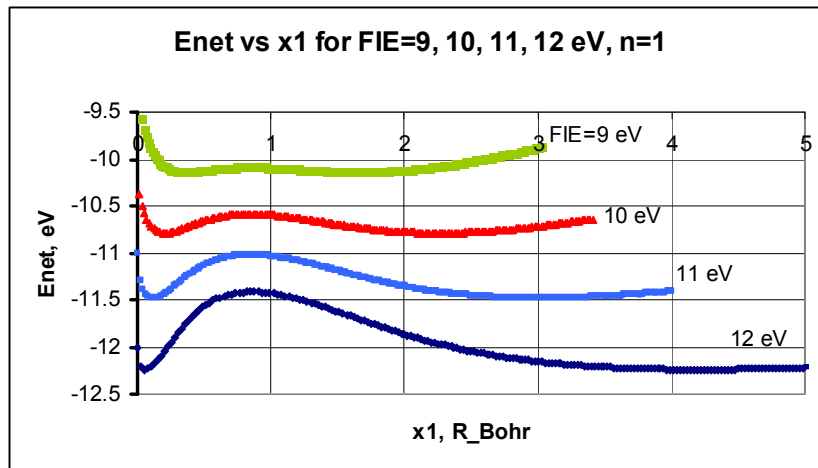


Figure 6

General patterns of these graphs are similar to graphs of E_{bond} vs x_1 shown on figure 2.

But really distinctive and significant, for E_{net} , is the exact coincidence of local extremums with points of $Df=0$. This is illustrated by figures 7 and 8.

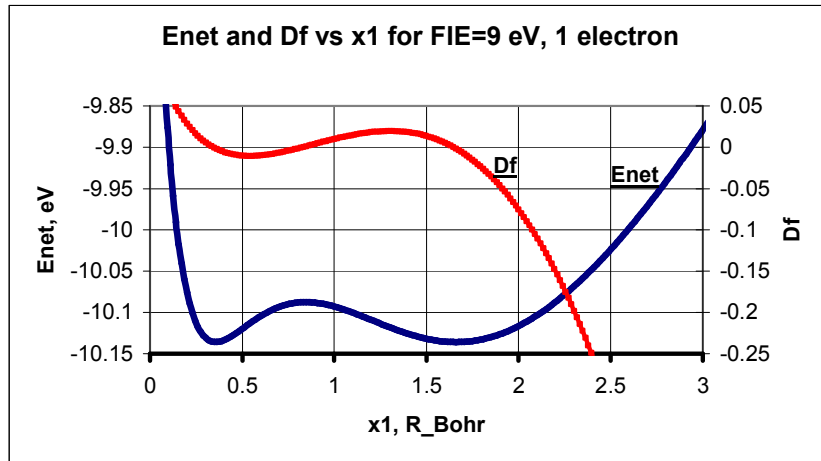


Figure 7

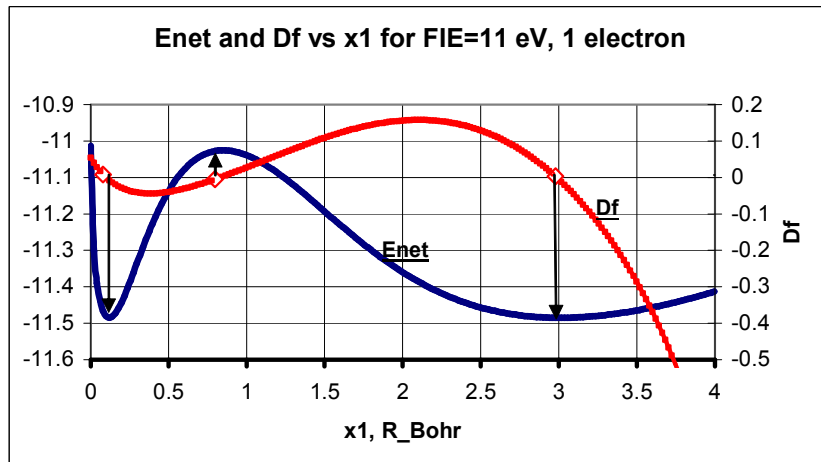


Figure 8

The clear-cut potential wells of E_{net} on both sides of symmetrical configuration have confirmed that asymmetrical ones should be more stable.

From Virial Theorem, for stable molecule, i. e. a molecule in the state of equilibrium, should be:

$|PE / E_{net}| = 2$. So, the variable

$Dv = 2 - |PE / E_{net}|$ can serve as a criterion of the deviation from Virial Theorem, or let's say, "non-'viriality'" of the molecule and the measure of its non-stability. As an example, figure 9 illustrates that Dv and Df are interchangeable as a measure of molecule's stability.

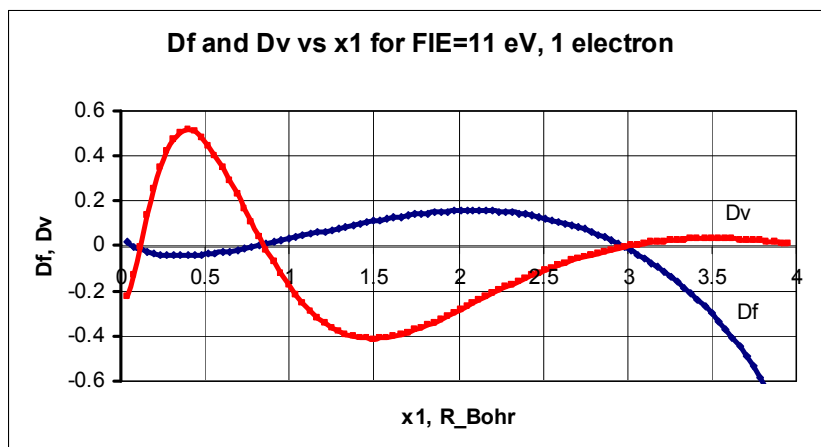


Figure 9

Shapes of E_{net} curves look rather strange because they are not symmetrical with respect to middle vertical axis at $x1/b=1$. The reason of this is that, for every value of $x1$, a geometry of molecule (values of b and a) is different.

These curves look more natural if they are presented as E_{net} vs $x1/b$ instead of E_{net} vs $x1$. This is shown in figure 10 for FIE in the broad range, from 4 to 12 eV.

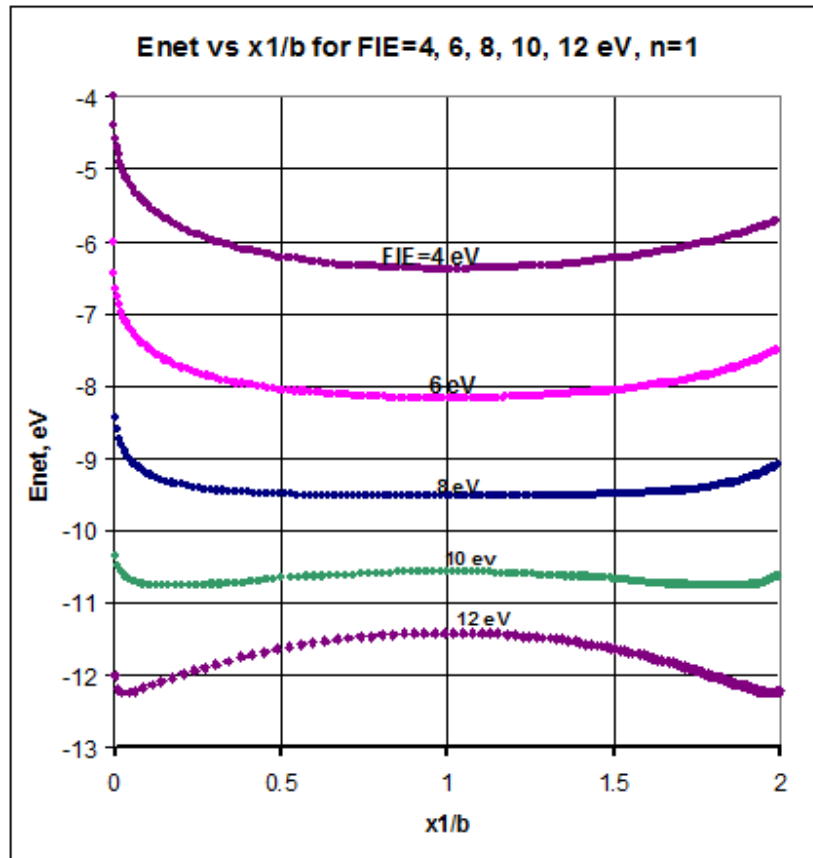


Figure 10

Such curves are almost symmetrical about $x1/b=1$ vertical line as could have been expected. The energetic wells have also been seen clearly for FIE greater than 8 eV (more correctly, 8.056 eV). This kind of dependencies is very convenient for generalized analyses and will be used in future researches.

So far in all calculations of this article, electrons and nuclei were considered as particles of the same mobility as if they have moved instantly and simultaneously from one position to another. However in reality, due to very big difference in their masses, their speed should be also different. One could have got a quantitative idea about this by developing and solving a system of differential equations describing the motion of the particles in the electrostatic field of their own. Such a task seems rather complicated, and we're not aware about any attempt in this direction.

Here, another approach has been used for rough estimation of dynamic of molecule's configuration and energy status. Because nuclei's masses are thousands times greater than that of electron, it is reasonable to assume, as a limiting case, that nuclei do not move while electrons do. We can also

assume that such a situation could retain for a very short time, just about the times of chemical reactions, i. e. 10^{-15} s (femtosecond). We will call this hypothetical situation a model with “frozen” nuclei as opposed to the model with “free” nuclei that has been considered before. We will also refer to them as “schemes with ‘frozen b ’”.

The demonstration of concepts of “free” and “frozen” molecules could be seen at <http://lsanin.dyndns.org/alex/Molecule/gifmolec.htm>

Estimation of main dimensions and energetic parameters for “frozen” models is similar to that of free ones with the exception of internuclei distance b remaining constant. Results of such calculations, together with ones for “free” models, are shown on figure 12.

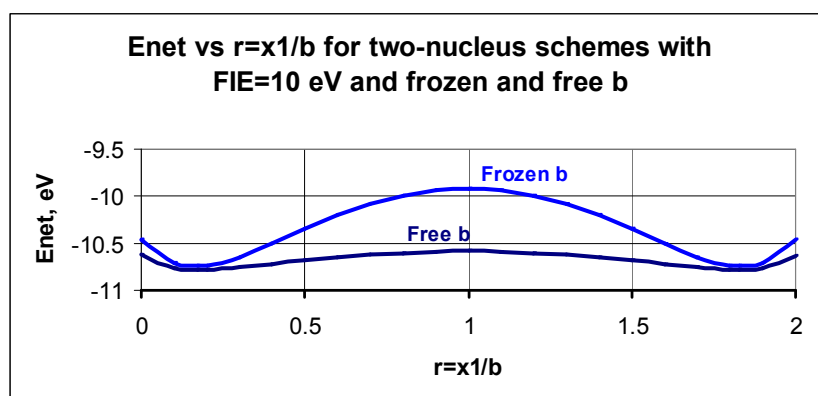


Figure 12

As one can see, “frozen” schemes have greater potential energy, i. e. their stability is less than that for “free” ones.

The calculations have also shown that D_v and D_f criteria for “frozen” schemes are much greater than that for “free” ones which confirms that former schemes are less stable.

In reality, one should expect some interim patterns of nuclei-electron interaction.

Conclusion

1. Stable molecule's configurations including asymmetrical ones correspond to equilibrium of longitudinal forces, i. e. are balanced. These balanced configurations of molecule correspond to its minimum net (total) energy that is the sum of potential and kinetic energy. Extreme

values of bonding energy (E_{bond}) used in the article [1] do not coincide with stable asymmetrical configurations.

2. Deviation criteria D_f and D_v are useful for estimation of molecule's state of force and energetic equilibrium, accordingly.
3. Existence of the asymmetrical zone for a two-nucleus molecule with one valent electron has been confirmed by calculations of change in the molecule's energy while the electron ring is moving along longitudinal axis.
4. For general analysis of molecule's energy, it is convenient to plot graphs of net energy as a function of parameter $x1/b$.
5. The conception of "frozen" nuclei as opposed to "free" one could be useful for exploration and analysis of molecule's energy distribution.

References:

1. Semi-quantitative modeling of electrical conductivity in metals and non-metals.

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(Reported at 232nd ACS National Meeting, San Francisco, CA, September 10-14, 2006.)

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4. How Chemical Bonds Form and Chemical Reactions Proceed

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