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FULL PAPER

Unconventional semiclassical method for calculating the energetic values of diatomic molecules

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In previous papers we proved that the geometrical elements of the wave described by the Schrödinger equation, namely the wave surfaces and their normals, denoted by C curves, are solutions of the Hamilton-Jacobi equations, written for the same system, in the case of stationary systems. The C curves correspond to the same constants of motion as the eigenvalues of the Schrödinger equation. In two recent papers we presented a central field method for the calculation of the C curves, and of the corresponding energetic values. The method was verified for the atoms He , Li , Be , B , C , N and O . In this paper we extend this method, using the symmetry properties of the systems, in the case of the diatomic molecules, with exemplification for Li_2 , Be_2 , B_2 , C_2 , LiH , BeH , BH and CH . The accuracy of the method is, as in the case of the atoms, comparable to the accuracy of the Hartree-Fock method, for the same system. This could be a potential useful result, because our approach predicts also basic properties of the molecules in discussion.

Keywords: diatomic molecules; energetic values; unconventional semiclassical method

1. Introduction

Over the last few years, a large number of semiclassical approaches were published in the field of atomic and molecular systems [1]-[5]. The semiclassical methods lead to solutions which are relatively easy to calculate, using the information obtained from the study of classical trajectories. In numerous papers the semiclassical eigenvalues of the bond states are related to the periodic trajectories [6]-[12], in others they are related to the phase manifolds generated by quasiperiodic trajectories [13]-[15]. In this family of topics we can consider also the study of the semiclassical trajectories with the aid of the propagator functions [16]-[20] or the application of a generalized semiclassical theory to multidimensional dynamical systems [21]. In this paper we present a multidimensional semiclassical analysis which applies to a wide class of atoms and molecules.

In a series of papers [22]-[24] we presented a method for calculating the energetic values of atomic and molecular systems, which is based on the following property [22]: the energy of the Schrödinger equation can be rigorously calculated by line integrals of analytical functions, if the Hamilton-Jacobi equation, written for the same system, is satisfied by a periodical trajectory. We proved [24] that this property is a consequence of the fact that, for stationary systems, the Schrödinger

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equation is equivalent to the wave equation. Starting from this equivalence, we have proposed [24]-[26] a wave model for stationary atomic and molecular systems. In recent papers [27, 28] we have elaborated a central field method for calculation of energetic values of atomic systems, which is based on the above wave model. The central point of this method is the the following property [25, 26]: the geometrical elements of the wave described by the Schrödinger equation, namely the wave surfaces and their normals (the C curves) are rigorously solutions of the Hamilton-Jacobi equation, written for the same system. We have verified this method for a large number of atoms, and we found that its accuracy is comparable to the accuracy of the Hartree-Fock method applied to the same atoms.

In this paper we use symmetry properties of the systems to show that the central field method for calculating the energetic values [27, 28] can be extended to diatomic molecules, both homonuclear and heteronuclear, with the same accuracy as that of the Hartree-Fock method. We compare our data with theoretical data taken from The Computational Chemistry Comparison and Benchmark Database (CCCBDB) [29]. In addition, the method presented in this paper predicts basic properties of the molecules [30, 31], such as the existence of the simple, double and triple bonds in the case of the $C - C$ bond, the symmetry properties of these bonds, the fact that in the case of the C_2 molecule the bond is double, and it also explains the ionic character of the LiH bond.

The paper is structured as follows. In Section 2 we present briefly the relations and results from previous papers which are necessary in this paper. In Section 3 we give exact solutions to the equations of the C curves, in the case of simple, double and triple covalent bonds of homonuclear molecules and in the case of ionic and covalent bonds of heteronuclear molecules. In Section 4 we present the method for calculating the energetic values, and in Section 5 we apply the method to several molecules. We present the computation details in two typical cases, Li_2 and Be_2 , and we give the results of the computation in the other cases investigated: the B_2 , C_2 , LiH , BeH , BH and CH . Details of the computation for the these molecules are given in the Supplementary Online Material for this article, where we also give the Mathematica 7 scripts containing all the calculations from this paper.

Throughout the paper the equations are written in the International System.

2. Preliminary results

In this section we present the relations which have been deduced in previous papers [25]-[28] and which are necessary in this paper. In Refs. [25, 26] we studied the wave properties of a discrete system composed of N electrons and N' nuclei. The Cartesian coordinates of the electrons are x_a, y_a, z_a , where a takes values between 1 and N . Our analysis is made in the space R^{3N} of the electron coordinates, which are denoted by q_j (where $q_1 = x_1, q_2 = y_1, q_3 = z_1, \dots, q_{3N} = z_N$), j taking values between 1 and $3N$. We denote by $q = (q_1, q_2, \dots, q_{3N})$ the coordinates of a point in the space R^{3N} .

We consider a system which fulfills the following initial hypotheses: (h1) The system is closed and conservative (i.e. the total energy, denoted by E , is constant and the potential energy, denoted by U , does not depend explicitly on time); (h2) The total energy has real negative values (i.e. the system is in a bound state); (h3) The behavior of the system is completely described by the Schrödinger equation; (h4) The relativistic and magnetic effects are neglected; (h5) The nuclei motion is neglected. We proved [25, 26] that the following properties are valid for this system:

(p1) In the case of the stationary systems, the Schrödinger and wave equations are rigorously equivalent, and the characteristic surface of the wave equation (which has

1 the significance of a wave surface), denoted by Σ , and its normals, denoted by C , are
2 solutions of the Hamilton-Jacobi, written for the same system, and corresponding
3 to constants of motion identical to the eigenvalues of the Schrödinger equation.

4 (p2) The motion of the surface Σ is periodical, and the C curves are closed (see
5 Section 4 of Ref. [25]).

6 (p3) The generalized Bohr quantization condition
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$$12 \quad \Delta_C S_0 = nh \quad (1)$$

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18 is valid for the C curve (see Section 5 of Ref. [26]). Here S_0 is the reduced action
19 function, $\Delta_C S_0$ is the variation of the function S_0 which corresponds to the curve
20 C and n is the principal quantum number.

21 In the case of systems for which the separation of variables is possible, namely
22 when the function S_0 can be written $S_0 = \sum_a S_{0a}$, where $S_{0a} = S_{0a}(x_a, y_a, z_a)$, the
23 following quantization relation is valid [26]
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$$29 \quad \Delta_{C_a} S_{0a} = n_a h \quad (2)$$

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35 where n_a is the principal quantum number associated to the motion of the electron
36 a and C_a is the curve corresponding to the electron a .

37 The property (p1) establishes a direct connection between the Schrödinger and
38 Hamilton-Jacobi equations in the case of the stationary systems. A similar con-
39 nection, which has been derived through entirely different method, is presented
40 in [32], where it is shown that the discontinuities of the partial second deriva-
41 tives of the wave function propagate following the trajectories determined by the
42 Hamilton-Jacobi equation, written for the same system.

43 The particular curve of a given electron is obtained from the projection of the
44 trajectory C from the R^{3N} space of coordinates to the three dimensional space of
45 that electron. For example, the curve of electron a is obtained from the projection
46 of the curve C to the space of coordinates x_a, y_a, z_a . The projection is also a closed
47 curve, denoted by C'_a , where $a = 1, 2, \dots, N$. When the separation of variables is
48 possible, we have $C'_a \equiv C_a$.

49 The above properties imply that the problem of calculating the energetic values
50 of atomic and molecular systems reduces to the calculation of the C'_a or C_a curves,
51 or, in other words, to the calculation of the systems' periodic solutions. In previous
52 papers [27, 28] we have shown that the problem can be solved exactly, or with
53 good accuracy, by a central field method, which makes possible the separation of
54 the variables, and, consequently, the calculation of the C_a curves. In this case we
55 have applied the quantization condition, namely (2) for each C_a curve and have
56 obtained the following relations for the calculation of the total energy, which are
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valid for all the atoms which have been analyzed in Refs. [27, 28]:

$$E = E_1 + E_2 + \sum_{a \geq 3} E_a \quad (3)$$

$$E_1 = E_2 = -\frac{Z_1 K_1}{r_1} + \frac{m}{2} \left(\frac{dr_1}{dt} \right)^2 = -\frac{R_\infty Z_1^2}{n_1^2} \quad (4)$$

$$E_a = -\frac{Z_a K_1}{r_a} + \frac{m}{2} \left(\frac{dr_a}{dt} \right)^2 = -\frac{R_\infty Z_a^2}{n_a^2} \quad (5)$$

$$Z_1 = Z_2 = Z - s_{12e} - \sum_{a \geq 3} s_{1ae} \quad \text{with} \quad s_{12e} = \frac{1}{4} \quad (6)$$

$$Z_a = Z - 2s_{a1e} - \sum_{b \geq 3; b \neq a} s_{abe} \quad (7)$$

Here r_a is the norm of position vector of the electron e_a in a Cartesian system of coordinates with origin at the nucleus, m is the electron mass, t is the time, Z is the order number of the nucleus, and K_1 is a constant given by the relation

$$K_1 = \frac{e^2}{4\pi\epsilon_0} \quad (8)$$

where e and ϵ_0 are the absolute value of the electron charge and the vacuum permittivity, respectively. In these equations E_1 and E_2 are the energies of the 1s electrons, E_a is the energy of the valence electron a , where $a \geq 3$ for $Z \geq 3$, Z_1 and Z_2 are the effective order numbers of nucleus, which enter in the motion equations of the 1s electrons, Z_a is the effective order number of nucleus which enters in the equation of electron a and R_∞ is the Rydberg energy. The quantities s_{1ae} and s_{a1e} are the effective reciprocal screening coefficients between the 1s electrons and the valence electrons e_a , which are calculated with the aid of the equation system (59)-(62) from Ref. [27], when eccentricity of the curve C_a is very closed to unit, and with the aid of the system (73)-(77) from Ref. [27], when C_a is an elliptic curve. The quantities s_{12e} and s_{abe} are, respectively, the effective reciprocal screening coefficients between the 1s electrons and between the valence electrons, which are calculated with the aid of the relation (7) from Ref. [28], which is:

$$s_{abe} = s_{bae} = \frac{1}{4 \sin(\alpha_{ab}/2)} \quad (9)$$

where α_{ab} is the angle between the two straight lines which pass through nucleus and the average positions of the two electrons.

The interaction energy between two electrons, let us say e_a and e_b , can be written: [27, 28]

$$U_{abe} = \frac{K_1}{|\bar{r}_a - \bar{r}_b|} = \frac{K_1 s_{abe}}{r_a} + \frac{K_1 s_{bae}}{r_b} \quad (10)$$

From this relation and from (4)-(7), it follows that part of the interaction energy enters in the expression of E_a , by the term $K_1 s_{abe}/r_a$, while the other part, $K_1 s_{bae}/r_b$, enters in the expression of E_b .

The expression of the total energy, given by (3), contains, in addition, a correction energy due to the spin magnetic interaction of the 1s electrons, which has been

deduced in Ref. [27]. This term is

$$E_{m1s} = R_{\infty} \frac{Z_1^3}{8n_1^3} \quad \text{with } n_1 = 1 \quad (11)$$

The model represented by equations (3)-(10) has two properties which are both attributes of a central field type solution. The first is that the motion of an arbitrary electron is similar to that in a hydrogenoid system, and it takes place in the averaged field of the other electrons. The effect of the interaction with these electrons is included in the effective order number of the nucleus. The second property, which is useful in applications, is that adding a supplementary electron to the system leads only to the modification of the effective order numbers corresponding to the other electrons, while their equations remain unchanged.

On the other hand, in Ref. [33] it is shown that, for a multielectron system, the energetically most favorable geometric configuration minimizes the electron-electron repulsion and, generally, this configuration corresponds to the maximum symmetry of the geometrical configuration of the electrons. Our results [27, 28] confirm this property, because the C_a curves, as result from our treatment, have also a configuration with maximum symmetry. For example, the C_a curves of the valence electrons in the case of helium and beryllium are two symmetrical ellipses, having eccentricities very close to unity, for boron the C_a curves are three symmetrical ellipses, whose axes are oriented toward the corners of an equilateral triangle, and so on. A strong simplification of the calculation of the total energy results if we apply this property. In this case we suppose the average positions of the electrons, which have maximum symmetry, calculate the s_{1ae} , s_{a1e} and s_{abe} and the total energy results directly from the equations (4) and (5). The average distance and the maximum distance of the electron from the nucleus, denoted, respectively, by \tilde{r}_a and r_M , are [28]

$$\tilde{r}_a = \frac{n_a^2 a_0}{Z_a} \left(1 + \frac{e^2}{2} \right) \quad \text{and} \quad r_M = \frac{n_a^2 a_0}{Z_a} (1 + e) \quad (12)$$

where a_0 is the Bohr radius and e is the eccentricity of the C_a curve.

We have applied this method and resulted that the accuracy of the calculation of the energy is comparable with the accuracy of the Hartree-Fock method for the atoms *He*, *Li*, *Be*, *B*, *C*, *N* and *O* (see Table 1 from Ref. [27] and Table 4 from Ref. [28]). We will use this method in the case of molecules, for the calculation of the energies of the electrons which do not participate directly to the bonds.

3. Calculation of the C_a curves corresponding to simple, double and triple bonds of homonuclear molecules and to ionic and covalent bonds of heteronuclear molecules

In this section we present calculations of the C_a curves corresponding to the bond electrons in homonuclear and heteronuclear molecules. The C_a curves for the simple bond of homonuclear molecules were presented in Refs. [23, 24]. In this paper we present them, taking into account the new data resulted from the central field method, applied in the case of atoms. The new topics presented in this paper refers to the double and triple bonds of the homonuclear molecules, to the modeling of the heteronuclear molecules and to the explaining of a lot of properties of the molecules, which result from our calculations.

Notations.

The symbols used in the equations that describe the behavior of the molecules contain supplementary indexes, which refer to different nuclei of the molecule. These indexes are, as follows.

1) The $1s$ electrons which move in the field of the nucleus n_A are denoted by e_{A1} , e_{A2} , while the valence electrons which move in the field of the nucleus n_A and do not participate to the bond are denoted by e_{A3} , e_{A4} , e_{A5} , and so on. Similar notations correspond to electrons which move in the field of the nucleus n_B . The bond electrons are denoted by e_1 , e_2 , e_3 , and so on.

2) In the case of the homonuclear diatomic molecules, the nuclei order numbers, denoted by Z_A and Z_B , are equal. In this case, the order numbers corresponding to the electrons e_{Ai} and e_j , where $i, j = 1, 2, \dots$, are denoted, respectively, by Z_{Ai} and Z_j . The screening coefficients between electrons e_{Ai} and e_{Ak} are denoted by $s_{Ai,Ak}$ and $s_{Ak,Ai}$, those between the bond electrons e_j and e_k are denoted by $s_{j,k}$ and $s_{k,j}$, and the screening coefficients between the electrons e_{Ai} and e_j are denoted by $s_{Ai,j}$ and $s_{j,Ai}$.

3) The effective order number of the nucleus n_A in interactions between nuclei includes the effect of the $1s$ electrons and the effect of the electrons that do not participate to the bond. In this case the effective order number of n_A is denoted by Z_{nA} .

3.1. C_a curves for simple, double and triple bonds of homonuclear molecules

We consider a molecule composed of two fixed identical nuclei, denoted by n_A and n_B , two $1s$ electrons in the vicinity of the n_A nucleus, denoted by e_{A1} and e_{A2} , two $1s$ electrons in the vicinity of the n_B nucleus, denoted by e_{B1} and e_{B2} , and N_b valence electrons which participate to the bond, denoted by e_1, e_2, \dots, e_{N_b} . The Cartesian coordinates of the nuclei are $n_A(-\sigma, 0, 0)$ and $n_B(\sigma, 0, 0)$ and their order number is equal to Z_A . The equations of motion for the electrons are as follows:

$$-\frac{K_1 Z'(\bar{r}_a - \sigma \bar{i})}{|\bar{r}_a - \sigma \bar{i}|^3} - \frac{K_1 Z'(\bar{r}_a + \sigma \bar{i})}{|\bar{r}_a + \sigma \bar{i}|^3} + \sum_b \frac{K_1(\bar{r}_a - \bar{r}_b)}{|\bar{r}_a - \bar{r}_b|^3} = m \frac{d^2 \bar{r}_a}{dt^2} \quad (13)$$

where $a, b = 1, 2, \dots, N_b$ and $a \neq b$

Here \bar{r}_a are the position vectors of the e_a electrons, which have their origin in the origin of the Cartesian coordinate axes, whose versors are denoted by $\bar{i}, \bar{j}, \bar{k}$, and Z' is an order number which includes the effect of the $1s$ electrons. It is given by the relation $Z' = Z_A - 2s_{a,A1}$.

This system has three exact solutions similar to the solutions of the valence bond electrons. More precisely, there is one solution for each one of the following three cases: a) for $N_b = 2$, which corresponds to simple bond; b) for $N_b = 4$, which corresponds to the double bond and c) for $N_b = 6$, which corresponds to the triple bond.

3.1.1. Simple bond ($N_b = 2$)

The solution of the system in this case is presented in Section 3 of Ref. [23]. This solution is:

$$\bar{r}_1 = -\bar{r}_2 = \bar{r} \quad \text{for} \quad \bar{r} \cdot \bar{k} = 0 \quad (14)$$

It is easy to show that, in virtue of (14), the solution the system represented by

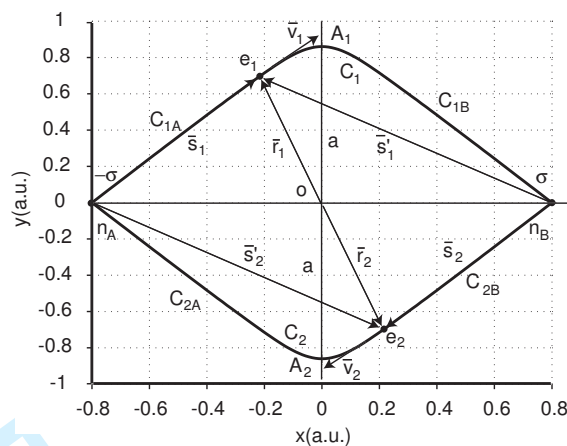


Figure 1. C_a curves for simple bond in homonuclear diatomic molecules.

(13) reduces to the solution of the following equation

$$-\frac{K_1 Z'(\bar{r}_a - \sigma \bar{i})}{|\bar{r}_a - \sigma \bar{i}|^3} - \frac{K_1 Z'(\bar{r}_a + \sigma \bar{i})}{|\bar{r}_a + \sigma \bar{i}|^3} + \frac{K_1 \bar{r}_a}{4|\bar{r}_a|^3} = m \frac{d^2 \bar{r}_a}{dt^2} \quad (15)$$

which is valid for $a = 1$ or $a = 2$. This solution corresponds to symmetrical velocities. The symmetry of the velocities results from the total derivative of (14) with respect to time, which gives $\bar{v}_1 = -\bar{v}_2 = \bar{v}$. In virtue of (14), (15) is equivalent to the following two scalar equations, in the plane (x, y) :

$$-\frac{K_1 Z'(x - \sigma)}{[(x - \sigma)^2 + y^2]^{3/2}} - \frac{K_1 Z'(x + \sigma)}{[(x + \sigma)^2 + y^2]^{3/2}} + \frac{1}{4} \frac{K_1 x}{(x^2 + y^2)^{3/2}} = m \frac{d^2 x}{dt^2} \quad (16)$$

$$-\frac{K_1 Z'y}{[(x - \sigma)^2 + y^2]^{3/2}} - \frac{K_1 Z'y}{[(x + \sigma)^2 + y^2]^{3/2}} + \frac{1}{4} \frac{K_1 y}{(x^2 + y^2)^{3/2}} = m \frac{d^2 y}{dt^2} \quad (17)$$

The numerical solution of the above system of equations is given in Ref. [23], and it leads to the curve C_1 that corresponds to electron e_1 . The curve C_2 , corresponding to electron e_2 , is symmetrical to the curve C_1 .

The atomic curves for the fundamental states of atoms, calculated in Refs. [27] and [28], are ellipses with eccentricities very close to unity. For this reason, in this paper we restrict ourselves to the case in which the molecular C_1 curve is composed of two atomic curves, denoted by C_{1A} and C_{1B} , which are ellipses with eccentricities very close to unity, as shown in Fig. 1. At the scale of the figure, these ellipses are drawn as straight lines in the vicinities of the nuclei, in spite of the fact that the curve C_{1A} surrounds the nucleus n_A , while the curve C_{1B} surrounds the nucleus n_B . The curves C_1 and C_2 depend on three parameters: E_b , σ and a , where E_b is the total energy of the particles that participate to the bond, and a is the maximum distance between the electron and the line on which the two nuclei are situated [23]. In Fig. 1 the electrons are situated in average positions, in agreement with (12).

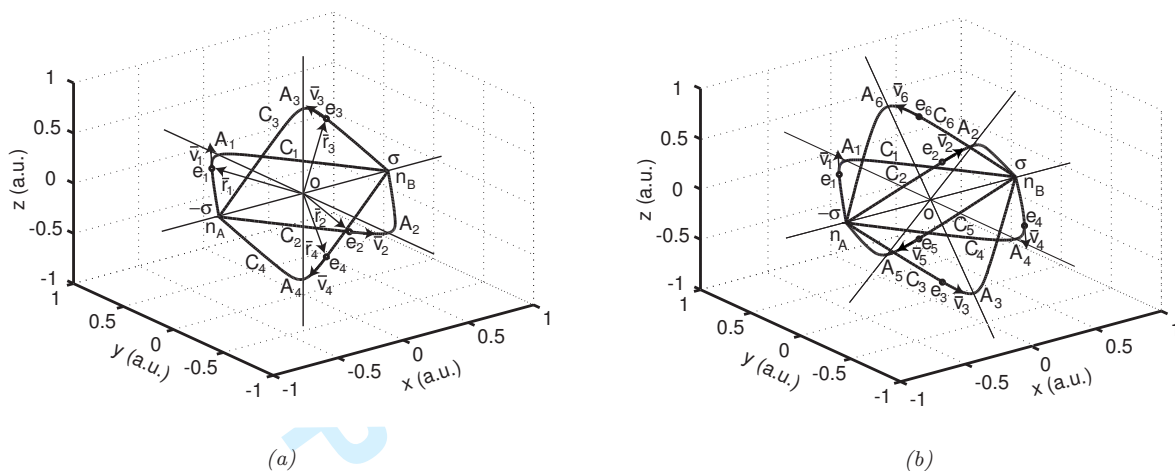


Figure 2. C_a curves for (a) double bond and (b) triple bond in homonuclear diatomic molecules.

3.1.2. Double bond ($N_b = 4$)

In this case the solution of the system represented by (13) is very similar to the solution for the simple bond. This solution is:

$$\bar{r}_1 = -\alpha\bar{i} + \beta\bar{j} \quad (18)$$

$$\bar{r}_2 = -\alpha\bar{i} - \beta\bar{j} \quad (19)$$

$$\bar{r}_3 = \alpha\bar{i} + \beta\bar{k} \quad (20)$$

$$\bar{r}_4 = \alpha\bar{i} - \beta\bar{k} \quad (21)$$

where α and β are real variables. It is easy to show that, in virtue of (18)-(21), the solution of the system represented by (13) reduces to the solution of the following equation, in which the unknown is \bar{r}_a

$$-\frac{K_1 Z'(\bar{r}_a - \sigma\bar{i})}{|\bar{r}_a - \sigma\bar{i}|^3} - \frac{K_1 Z'(\bar{r}_a + \sigma\bar{i})}{|\bar{r}_a + \sigma\bar{i}|^3} + \frac{\bar{r}_a - (\bar{r}_a \cdot \bar{i})\bar{i}}{4[\bar{r}_a^2 - (\bar{r}_a \cdot \bar{i})^2]^{3/2}} + \frac{\bar{r}_a + (\bar{r}_a \cdot \bar{i})\bar{i}}{\sqrt{2}[\bar{r}_a^2 + (\bar{r}_a \cdot \bar{i})^2]^{3/2}} = m \frac{d^2 \bar{r}_a}{dt^2} \quad (22)$$

This equation is valid for any bond electron. For example, Eq. (22) written for \bar{r}_1 (i.e. $a = 1$) is obtained from (13) in which we plug in the solutions of \bar{r}_2 , \bar{r}_3 and \bar{r}_4 given by (19)-(21). Same procedure can be used to derive (22) for $a = 2, 3, 4$. The solution to (22) corresponds to symmetrical velocities. The symmetry of the velocities results from the total derivative of (18)-(21) with respect to time.

Equation (22) leads again to a plane C_1 curve, for the electron e_1 . It is equivalent to two scalar equations, very similar to (16, 17). An identical numerical solution,

as that shown in Ref. [23], leads again to a molecular curve, which is composed of two elliptic quasilinear curves, when the minimum distance between electron and the nucleus is negligible. The curves for the other electrons are symmetrical, in agreement to (18)-(21). These curves, which result from (22), are represented in Fig. 2(a). From this figure we see that, in the vicinities of the nuclei, C_1 and C_2 are two symmetrical curves, in the plane (x, y) , similar to the valence curves in the case of the helium atom, or in the case of beryllium. The other curves, C_3 and C_4 are two symmetrical curves, with the same properties, situated in the plane (x, z) .

3.1.3. Triple bond ($N_b = 6$)

In this case the symmetrical solution of the system represented by (13) is as follows:

$$\bar{r}_1 = -\alpha\bar{i} + \beta\bar{j} \tag{23}$$

$$\bar{r}_2 = -\alpha\bar{i} - \frac{1}{2}\beta\bar{j} + \frac{\sqrt{3}}{2}\beta\bar{k} \tag{24}$$

$$\bar{r}_3 = -\alpha\bar{i} - \frac{1}{2}\beta\bar{j} - \frac{\sqrt{3}}{2}\beta\bar{k} \tag{25}$$

$$\bar{r}_4 = \alpha\bar{i} - \beta\bar{j} \tag{26}$$

$$\bar{r}_5 = \alpha\bar{i} + \frac{1}{2}\beta\bar{j} - \frac{\sqrt{3}}{2}\beta\bar{k} \tag{27}$$

$$\bar{r}_6 = \alpha\bar{i} + \frac{1}{2}\beta\bar{j} + \frac{\sqrt{3}}{2}\beta\bar{k} \tag{28}$$

where α and β are real variables. It is easy to show that, as in the previous case, in virtue of (23)-(28), the solution the system represented by (13) reduces to the solution of the following equation in which the unknown is \bar{r}_a

$$-\frac{K_1 Z'(\bar{r}_a - \sigma\bar{i})}{|\bar{r}_a - \sigma\bar{i}|^3} - \frac{K_1 Z'(\bar{r}_a + \sigma\bar{i})}{|\bar{r}_a + \sigma\bar{i}|^3} + \frac{\bar{r}_a}{4|r_a|^3} + \frac{\bar{r}_a + 3(\bar{r}_a \cdot \bar{i})\bar{i}}{[\bar{r}_a^2 + 3(\bar{r}_a \cdot \bar{i})^2]^{3/2}} + \frac{\bar{r}_a - (\bar{r}_a \cdot \bar{i})\bar{i}}{\sqrt{3}[\bar{r}_a^2 - (\bar{r}_a \cdot \bar{i})^2]^{3/2}} = m \frac{d^2 \bar{r}_a}{dt^2} \tag{29}$$

This equation is valid for any value of a . For example we obtain (29) for $a = 1$ by introducing the solutions for $\bar{r}_2, \bar{r}_3, \dots, \bar{r}_6$, given by (24)-(28), in (13) written for the electron e_1 . In the same manner we obtain the above equation for $a = 2, \dots, 6$. The solution to (29) corresponds again to symmetrical velocities.

Equation (29) leads to a plane C_1 curve for electron e_1 . It is equivalent, as in the previous case, to two scalar equations, very similar to (16), (17). An identical numerical solution, as that shown in Ref. [23], leads again to a molecular curve, which is composed of two elliptic quasilinear curves. The curves for the other electrons are symmetrical, in agreement to (23)-(28). These curves, which result from (29), are represented in Fig. 2(b). From this figure we see that, in the vicinities of the nuclei, C_1, C_2, C_3 are three symmetrical curves, similar to the curves of the valence electrons, in the case of the boron atom. The other curves, C_4, C_5 and C_6 are three symmetrical curves, with the same properties.

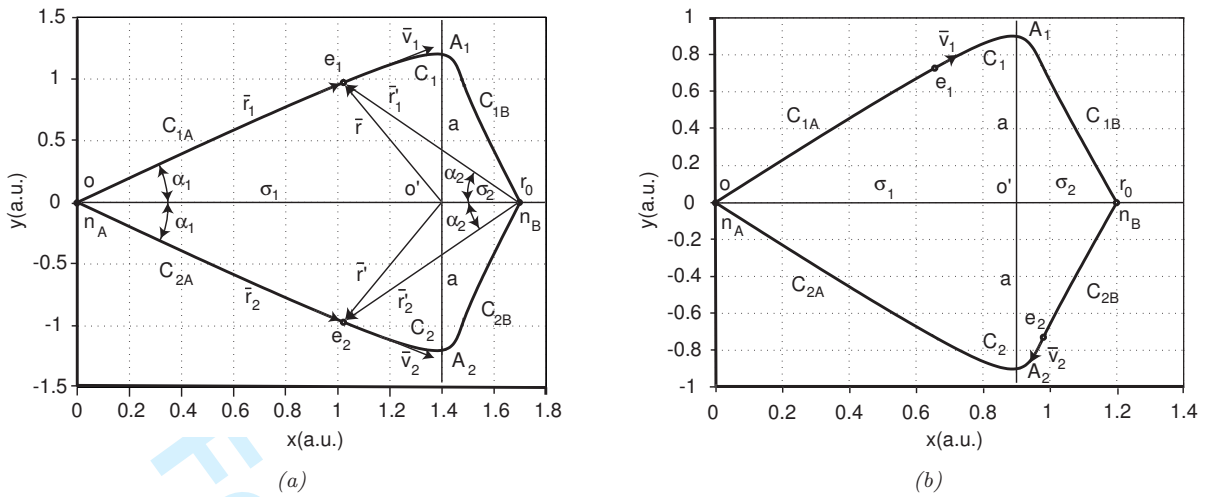


Figure 3. C_a curves for (a) ionic bond and (b) covalent bond in heteronuclear diatomic molecules.

3.2. C_a curves for ionic and covalent bonds in heteronuclear molecules

We consider a heteronuclear molecule composed of two fixed different nuclei, denoted by n_A and n_B , two $1s$ electrons in the vicinity of the n_A nucleus, denoted by e_{A1} and e_{A2} , and two valence electrons which participate to the bond, denoted by e_1 and e_2 , as shown in Fig. 3(a). The Cartesian coordinates of the nuclei are $n_A(0, 0, 0)$ and $n_B(r_0, 0, 0)$ and their order numbers are, respectively, equal to Z_A and Z_B , where $Z_A > Z_B$. The equations of motion for electrons are as follows:

$$-\frac{K_1 Z'_A \bar{r}_a}{|\bar{r}_a|^3} - \frac{K_1 Z_B (\bar{r}_a - r_0 \bar{i})}{|\bar{r}_a - r_0 \bar{i}|^3} + \sum_b \frac{K_1 (\bar{r}_a - \bar{r}_b)}{|\bar{r}_a - \bar{r}_b|^3} = m \frac{d^2 \bar{r}_a}{dt^2} \quad (30)$$

where $a, b = 1, 2$ and $a \neq b$

Here \bar{r}_a are the position vectors of the electrons having the origin in the origin of the Cartesian coordinate axes, and Z'_A is an effective order number which includes the effect of the $1s$ electrons.

This system has the following symmetrical solution:

$$x_1 = x_2, \quad y_1 = -y_2 \quad \text{and} \quad z_1 = z_2 = 0 \quad (31)$$

The symmetry of the velocities results from the total derivative of these relations with respect to time.

An identical procedure, as that presented in the previous subsection, shows that, for this solution, the above system reduces to the following two scalar equations in the plane (x, y) :

$$-\frac{K_1 Z'_A x_a}{(x_a^2 + y_a^2)^{3/2}} - \frac{K_1 Z_B (x_a - r_0)}{[(x_a - r_0)^2 + y_a^2]^{3/2}} = m \frac{d^2 x_a}{dt^2} \quad (32)$$

$$-\frac{K_1 Z'_A y_a}{(x_a^2 + y_a^2)^{3/2}} - \frac{K_1 Z_B y_a}{[(x_a - r_0)^2 + y_a^2]^{3/2}} + \frac{K_1 y_a}{4|y_a|^3} = m \frac{d^2 y_a}{dt^2} \quad (33)$$

which are valid for $a = 1, 2$.

The numerical solution of the above system of equations is almost identical to

1 the solution of the system represented by (16), (17), which is given in Ref. [23].
2 Same numerical method presented in Ref. [23] can be used to compute curves C_1
3 and C_2 corresponding to the electrons e_1 and e_2 , which are shown in Fig. 3(a). In
4 this figure, the coordinates of the points A_1 and A_2 are, respectively, $(\sigma_1, a, 0)$ and
5 $(\sigma_1, -a, 0)$. We have also $\sigma_2 = r_0 - \sigma_1$. The difference between the curve C_1 resulted
6 from (16), (17) and the curve C_1 resulted from (32), (33) is that the latter does not
7 have an axis of symmetry parallel to the oy axis, as illustrated by the comparison
8 between Figs. 1 and 3(a), respectively. On the other hand the curves C_1 and C_2
9 shown in Fig. 3(a) are symmetric to each other with respect to the ox axis. Each
10 of these curves is composed of two quasilinear ellipses. The analysis of this figure
11 shows the existence of two phases, the phase A , when the electrons are situated on
12 the curves C_{1A} and C_{2A} , in the vicinity of the nucleus n_A , and the phase B , when
13 the electrons are situated on the curves C_{1B} and C_{2B} , in the vicinity of the nucleus
14 n_B . These curves correspond to the ionic bond because, due to the nonsymmetry,
15 in the majority of the time, the electrons are in the vicinity of the nucleus whose
16 order number is smaller.

17
18
19 A similar analysis, as that presented above, leads to the C_a curves corresponding
20 to the covalent bond in heteronuclear diatomic molecule. In this case the e_1 and
21 e_2 electrons are situated in the vicinities of different nuclei, as shown in Fig. 3(b).
22 Unlike the ionic bond, in the covalent bond the electrons move alternatively in the
23 fields of different nuclei, and their charge is disposed in the vicinities of both nuclei.

24
25 In this section we have calculated the C_a curves when the bond electrons move
26 in the fields of two nuclei and the system contains only valence electrons which
27 participate to the bond. In Appendix we proved that the motion of a bond elec-
28 tron in the case of homonuclear molecules with simple bond is similar to that in
29 a central field. An example of such an electron is e_1 which moves on curves C_{1A}
30 and C_{1B} . This property results from relation (A3). Identical properties are proved
31 in the Supplementary Online Material for other types of bonds. It follows from
32 Section 2 that, in virtue of the second property of motion in the central field,
33 adding a supplementary electron that does not participate to the bond in the field
34 of the nucleus n_A does not change the equation of motion of the electron e_1 . The
35 only change is the fact that the expression of Z_1 contains a supplementary screen-
36 ing coefficient corresponding to the interaction between e_1 and the supplementary
37 electron. In the next section we will see that for the general case of the molecules
38 which contains electrons which do not participate to the bond, the relations from
39 Appendix remain valid, with the only difference that the expressions of the order
40 numbers are changed.
41
42

44 4. Analytical method for the calculation of energetic values of diatomic 45 molecules

46
47
48 In this section, we present a general analytical method for the calculation of the
49 energetic values and geometric parameters of diatomic molecules, which leads to
50 values in close agreement with the experimental values for all the molecules ana-
51 lyzed in this paper.

52 The structure of the molecule is illustrated by Fig. 4. Despite the fact that in
53 this figure we consider the case of a homonuclear molecule with a simple bond,
54 the method presented in this section is valid for all types of bonds. The molecule
55 shown in Fig. 4 is composed of two nuclei denoted by n_A and n_B and having
56 $Z_A = Z_B$, four $1s$ electrons, denoted by e_{A1} , e_{A2} , e_{B1} and e_{B2} , two electrons which
57 participate to the bond, denoted by e_1 and e_2 , N_A electrons which move in the
58 field of the nucleus n_A and do not participate to the bond, denoted by e_{Ai} , and N_B
59
60

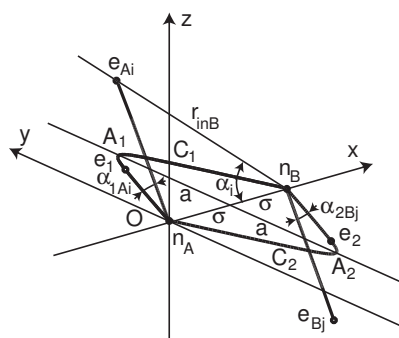


Figure 4. General structure of a homonuclear diatomic molecule.

electrons which move in the field of the nucleus n_B and do not participate to the bond, denoted by e_{Bj} . The electrons e_{Ai} and e_{Bj} are shown in average positions in Fig. 4. We suppose that the molecule is symmetrical, and have $N_A = N_B$ and $i, j = 3, 4, \dots, N_A$.

The calculation of the energetic values and geometric parameters of the diatomic molecule is performed in two stages, as follows.

1) In the first stage we calculate the values of E_b , σ and a with the aid of (A6), (A9) and (A10) in the Appendix. The method of computation originates in Refs. [23, 24], and in Appendix A we present an improved version of this method in the typical case of the simple bond of homonuclear diatomic molecules.

We use normalized quantities. The energies are normalized to R_∞ and the distances to $2a_0$, as follows: $\underline{E}_b = E_b/R_\infty$, $\underline{\sigma} = \sigma/(2a_0)$ and $\underline{a} = a/(2a_0)$. Taking into account these relations, together with the relations $R_\infty = (mK_1^2)/(2\hbar^2) = K_1/(2a_0)$ (see Appendix A of Ref. [27]), (A6), (A9) and (A10) become

$$\underline{E}_b = -2 \frac{Z_1^2}{n_1^2} - \frac{8Z_{1M}}{\sqrt{9\underline{a}^2 + 25\underline{\sigma}^2}} + \frac{2}{\sqrt{9\underline{a}^2 + \underline{\sigma}^2}} + \frac{Z_{nA}^2}{2\underline{\sigma}} \quad (34)$$

$$\underline{E}_b = -\frac{2n_1\sqrt{Z_{1M}}}{(\underline{a}^2 + \underline{\sigma}^2)^{3/4}} \quad (35)$$

$$\underline{E}_b = -\frac{4Z_{1M}}{\sqrt{\underline{a}^2 + \underline{\sigma}^2}} + \frac{1}{2\underline{a}} + \frac{Z_{nA}^2}{2\underline{\sigma}} \quad (36)$$

This is a system of three equations with three unknowns: \underline{E}_b , $\underline{\sigma}$ and \underline{a} . In this case, taking into account the structure of the molecule (shown in Fig. 4) the expression of Z_1 must contain the screening coefficients due to the e_{Ai} electrons and it can be written:

$$Z_1 = Z_A - 2s_{1,A1} - \sum_{i=3}^{N_A} s_{1,Ai} \quad (37)$$

where $s_{1,A1}$ is approximated very well by s_{31e} , calculated for atoms, while $s_{1,Ai}$ is

calculated with (9). The expression of Z_{1M} is modified, as follows:

$$Z_{1M} = Z_A - 2 - \sum_{i=3}^{N_A} s_{1,Ai} \quad (38)$$

Also, the expression of Z_{nA} must be modified, in order to take into account the effect of the screening due to the electrons e_{Ai} . This expression is deduced in Ref. [24] and it is given by Eq. (4.8) from that paper. With the notations from Fig. 4, where r_{inB} is the average distance between n_B and e_{Ai} and α_i is the angle between the two lines which pass, respectively, through n_B and e_{Ai} and through n_B and n_A , this relation can be written, as follows

$$Z_{nA} = Z_A - 2 - \sum_{i=3}^{N_A} \frac{(2\sigma)^2}{r_{inB}^2} \cos \alpha_i \quad (39)$$

2) In the second stage, we calculate directly the normalized expression of the total energy, corresponding to the average positions of the electrons. We assume that the average positions of the electrons which do not participate to the bond are disposed in a configuration having maximum symmetry. The average normalized distance between the e_{Ai} electron and the nucleus is calculated from (12), which can be written:

$$r_{Ai} = \frac{n_{Ai}^2}{2Z_{Ai}} \left(1 + \frac{e^2}{2} \right) \quad (40)$$

where Z_{Ai} is the order number corresponding to the electron e_{Ai} .

Taking into account the symmetry of the system, where $\underline{E}_1 = \underline{E}_2$, $\underline{E}_{Ai} = \underline{E}_{Bi}$, $\underline{E}_{A1} = \underline{E}_{A2} = \underline{E}_{B1} = \underline{E}_{B2}$, $\underline{U}_{e_1 n_B} = \underline{U}_{e_2 n_A}$, $\underline{U}_{e_{Ai} n_B} = \underline{U}_{e_{Bi} n_A}$ and $\underline{U}_{e_{Ai} e_2} = \underline{U}_{e_{Bi} e_1}$, the normalized expression of the total energy can be written as follows:

$$\begin{aligned} \underline{E} = & 2\underline{E}_1 + 2 \sum_{i=3}^{N_A} \underline{E}_{Ai} + 4\underline{E}_{A1} + \underline{U}_{e_1 e_2} + 2\underline{U}_{e_1 n_B} + 2 \sum_{i=3}^{N_A} \underline{U}_{e_{Ai} e_2} + \quad (41) \\ & 2 \sum_{i=3}^{N_A} \underline{U}_{e_{Ai} n_B} + \sum_{i=3}^{N_A} \sum_{j=3}^{N_B} \underline{U}_{e_{Ai} e_{Bj}} + \underline{U}_{n_A n_B} + 2\underline{E}_{m1s} = -2 \frac{Z_1^2}{n_1^2} - 2 \sum_{i=3}^{N_A} \frac{Z_{Ai}^2}{n_{Ai}^2} - \\ & 4 \frac{Z_{A1}^2}{n_{A1}^2} + \frac{1}{|\bar{r}(e_1) - \bar{r}(e_2)|} - \frac{2(Z_A - 2)}{|\bar{r}(e_1) - \bar{r}(n_B)|} + 2 \sum_{i=3}^{N_A} \frac{1}{|\bar{r}(e_{Ai}) - \bar{r}(e_2)|} - \\ & 2 \sum_{i=3}^{N_A} \frac{Z_A - 2}{|\bar{r}(e_{Ai}) - \bar{r}(n_B)|} + \sum_{i=3}^{N_A} \sum_{j=3}^{N_B} \frac{1}{|\bar{r}(e_{Ai}) - \bar{r}(e_{Bj})|} + \frac{(Z_A - 2)^2}{|\bar{r}(n_A) - \bar{r}(n_B)|} + \\ & 2 \frac{Z_{A1}^{3/2}}{8n_{A1}^3} \end{aligned}$$

where $\bar{r}(e_1)$ and $\bar{r}(n_A)$ are, respectively, the average normalized position vectors of the electron e_1 and nucleus n_A , $\underline{U}_{e_1 e_2}$ is the normalized potential energy of electrostatic interaction between the electron e_1 and nucleus e_2 , and so on. The

expressions of the order numbers are Z_1 given by (37) and

$$Z_{A1} = Z_A - s_{A1,A2} - s_{A1,1} - \sum_{i=3}^{N_A} s_{A1,Ai} \quad (42)$$

$$Z_{Ai} = Z_A - 2s_{Ai,A1} - s_{Ai,1} - \sum_{j=3; i \neq j}^{N_A} s_{Ai,Aj} \quad \text{for } i \geq 3 \quad (43)$$

where $s_{Ai,A1}$ are, with good approximation, equal to s_{31e} , calculated in the case of atoms, while $s_{A1,1}$ and $s_{A1,Ai}$ are equal to s_{13e} . The coefficients $s_{1,Ai}$, $s_{Ai,Aj}$ and $s_{A1,A2}$ are calculated with (9).

The first, second and third terms of the second member in (41) are the total normalized energies of the electrons which move in the field of the same nucleus. Their significance is identical to the significance of electron energies in an atomic system (see Section 2), taking into account that new indexes are introduced in the case of molecular systems, as it is shown in Section 3. We recall that the components of the energies, denoted by E_1 , E_{Ai} or E_{A1} , are given by the equations (4) and (5). The other terms represent the normalized electrostatic interaction energies, corresponding to interactions at distance between electrons that do not move in the field of the same nucleus, between electrons and nuclei which are situated at distance from them, and between nuclei, having order numbers which include the screening effects of the $1s$ electrons. The last term is given by (11) and represents the normalized correction energies due to the spin magnetic interaction of the $1s$ electrons. An analysis of equation (41) shows that all the components of the interaction energies are taken into account.

In virtue of the hypothesis (h5), the kinetic energy of the nuclei is zero. It follows that the distance between nuclei, denoted by r_0 and calculated with the relation

$$r_0 = 2\sigma \quad (44)$$

corresponds to values of the nuclei velocities of zero. On the other hand, the experimental value of the distance between nuclei, denoted by r_e , corresponds to the minimum of the Morse curve [34]. The theory of the harmonic oscillation of the nuclei shows that this minimum corresponds to maximum velocities of the nuclei. It follows that r_0 is different from r_e because the first corresponds to zero velocities of the nuclei, while the last corresponds to the maximum velocities of the nuclei.

The normalized experimental values of the total energy are obtained with the aid of the relation

$$\underline{E}_{exp} = -2\underline{S}_{EiA} - \underline{D}_0^0 \quad (45)$$

where S_{EiA} and D_0^0 are, respectively, the sum of the ionization energies of the atom A and the observed dissociation energy. The values of S_{EiA} and D_0^0 are taken, respectively, from Refs. [35] and [36]. Since our calculation method is based on the central field approximation under the assumption that a given electron moves in the averaged field of the other electrons, in Table 1 we will compare our theoretical results, with similar results reported in literature [29], obtained with the aid of the Hartree-Fock method.

The calculations are made with the aid of Mathematica 7, the absolute error being of the order 10^{-16} .

Table 1. Normalized values of the total energies \underline{E} , calculated for homonuclear and heteronuclear diatomic molecules. For comparison, are given the best two values of the normalized values of the total energies from CCCBDB [29], denoted by \underline{E}_{HF} , which are calculated with the aid of the Hartree-Fock method and the corresponding experimental values \underline{E}_{exp} . All the values are given in Rydbergs.

| Molecule | \underline{E} | \underline{E}_{HF} [29] | \underline{E}_{exp} |
|----------|-----------------|----------------------------|-----------------------|
| Li_2 | -30.0919 | -29.73625 -29.736246 | -29.9896 |
| Be_2 | -58.7676 | -58.486596 -58.48645 | -58.8396 |
| B_2 | -98.3341 | -98.182662 -98.18259 | -98.8574 |
| C_2 | -151.148 | -150.804028 -150.803916 | -151.883 |
| LiH | -16.1821 | -15.967824 -15.96775 | -16.1348 |
| BeH | -30.4238 | -30.300286 -30.300248 | -30.4872 |
| BH | -50.4587 | -50.256246 -50.256092 | -50.5691 |
| CH | -76.6349 | -76.561468 -76.560994 | -76.968 |

Table 2. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of Li_2 and Be_2 molecules.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|--|---|
| Li_2 | |
| $n_A(-\underline{\sigma}, 0, 0); n_B(\underline{\sigma}, 0, 0)$ | $s_{1,A1} = 0.854942$ [27]; $s_{A1,1} = 0.0013792$ [27] |
| $e_1(-\frac{1}{4}\underline{\sigma}, \frac{3}{4}\underline{a}, 0); e_2(\frac{1}{4}\underline{\sigma}, -\frac{3}{4}\underline{a}, 0)$ | $s_{A1,A2} = 0.25$ |
| $n_1 = 2; n_{A1} = n_{A2} = 1$ | $Z_1 = Z_2 = Z_A - 2s_{1,A1}$ |
| $\underline{E}_b = -1.0115$ | $Z_{1M} = Z_{2M} = Z_A - 2$ |
| $\underline{\sigma} = 1.46474; \underline{a} = 2.02683$ | $Z_{A1} = Z_{A2} = Z_A - s_{A1,A2} - s_{A1,1}$ |
| $\underline{S}_{EiA} = 14.9563$ [35]; $\underline{D}_0^0 = 0.0768815$ [36] | $Z_{nA} = Z_{nB} = Z_A - 2$ |
| Be_2 | |
| $n_A(0, 0, 0); n_B(2\underline{\sigma}, 0, 0)$ | $s_{1,A1} = s_{A3,A1} = 0.83882$ [27] |
| $e_1(\frac{3}{4}\underline{\sigma}, \frac{3}{4}\underline{a}, 0); e_2(\frac{5}{4}\underline{\sigma}, -\frac{3}{4}\underline{a}, 0)$ | $s_{A1,1} = s_{A1,A3} = 0.00221203$ [27] |
| $e_{A3}(-r_{A3}, 0, 0); e_{B3}(2\underline{\sigma} + r_{A3}, 0, 0)$ | $s_{A1,A2} = .25$ |
| $n_1 = n_{A3} = 2; n_{A1} = n_{A2} = 1$ | $s_{1,A3} = (\sqrt{2}/4) / \sqrt{1 + \frac{\underline{\sigma}}{\sqrt{\underline{\sigma}^2 + \underline{a}^2}}}$ |
| $\underline{E}_b = -2.39104$ | $Z_1 = Z_2 = Z_A - 2s_{1,A1} - s_{1,A3}$ |
| $\underline{\sigma} = 1.04502; \underline{a} = 1.32709$ | $Z_{1M} = Z_{2M} = Z_A - 2 - s_{1,A3}$ |
| $\underline{S}_{EiA} = 29.3377$ [35]; $\underline{D}_0^0 = 0.1643$ [37] | $Z_{A1} = Z_{A2} = Z_A - s_{A1,A2} - 2s_{A1,1}$ |
| | $Z_{A3} = Z_{B3} = Z_1 = Z_2$ |
| | $r_{A3} = 3/Z_{A3}$ |
| | $Z_{nA} = Z_{nB} = Z_A - 2 - \frac{(2\underline{\sigma})^2}{(2\underline{\sigma} + r_{A3})^2}$ |

5. Typical examples of applications

a) Li_2 molecule.

This molecule contains only valence electrons that participate to the bond. Its structure is shown in Fig. 1. We follow the algorithm presented in Section 4 and calculate the screening coefficients, order numbers and then solve the system (34)-(36). All these values are given in Table 2. The screening coefficients between the 1s electrons and the e_1 and e_2 electrons, namely $s_{1,A1}$ and $s_{A1,1}$ are identical, respectively, to s_{31e} and s_{13e} , which have been calculated in Ref. [27] for the $1s^22s$ state of lithium atom. The coefficient $s_{A1,A2}$ is calculated from equation (9). Since 2s valence electrons participate to the bond, we have $n_1 = 2$. Also, we have $n_{A1} = 1$ because this number corresponds to 1s electrons. We solve the system (34)-(36) in order to obtain \underline{E}_b , $\underline{\sigma}$ and \underline{a} .

Table 3. Values of r_0 calculated in this paper compared with the experimental values of r_e [29], and also with the range of values for r_{eHF} calculated using Hartree-Fock methods [29]. All the values are given in angstroms.

| Molecule | r_0 | r_e | r_{eHF} |
|----------|---------|--------|-------------|
| Li_2 | 3.10043 | 2.673 | 2.696-2.816 |
| Be_2 | 2.212 | 2.460 | 1.780-2.049 |
| B_2 | 1.7883 | 1.590 | 1.512-1.562 |
| C_2 | 1.35694 | 1.243 | 1.240-1.308 |
| LiH | 1.84635 | 1.5957 | 1.511-1.636 |
| BeH | 1.4389 | 1.3426 | 1.301-1.356 |
| BH | 1.21642 | 1.2324 | 1.213-1.232 |
| CH | 1.07572 | 1.1199 | 1.111-1.127 |

Since in this case E_b has the significance of the total energy from which the energies of the 1s electrons are subtracted, we have:

$$\underline{E} = \underline{E}_b + 4\underline{E}_{A1} + 2\underline{E}_{m1s} = \underline{E}_b - 4\frac{Z_{A1}^2}{n_{A1}^2} + 2\frac{Z_{A1}^{3/2}}{8n_{A1}^3} \quad (46)$$

The values of r_0 , calculated from (44), and the experimental value of the distance between nuclei, denoted by r_e and taken from Ref. [29], are given in angstroms in Table 3. Table 3 also gives the range of values for the distances between nuclei, denoted by r_{eHF} , calculated with the Hartree-Fock method and taken from [29].

The normalized value of the total energy, \underline{E} , obtained from equation (46), together with the experimental value, denoted by \underline{E}_{exp} , are presented in Table 1. We also present in this table the best two values of the normalized total energies, calculated with the aid of the Hartree-Fock method, denoted by \underline{E}_{HF} , which are taken from *CCCBDB* [29]. The experimental values of the total energy are obtained with the aid of equation (45), where S_{EiA} and D_0^0 which are taken, respectively, from Refs. [35] and [36], are given in Table 2. The analysis of the data from Table 1 shows that the value of \underline{E} is closer to the experimental value, \underline{E}_{exp} , than the values of \underline{E}_{HF} . The relative errors in the two cases are, respectively, $|(\underline{E} - \underline{E}_{exp}) / \underline{E}_{exp}| = 0.003$ and $|(\underline{E}_{HF} - \underline{E}_{exp}) / \underline{E}_{exp}| = 0.008$.

b) Be_2 molecule.

The structure of this molecule is shown in Fig. 5. This molecule contains two electrons, denoted by e_{A3} and e_{B3} , which do not participate to the bond. The geometrical structure of the molecule results from the system (34)-(36), where the expressions of Z_1 , Z_{1M} , Z_{nA} and the value of n_1 are given in Table 2. The screening coefficients between the 1s electrons and the e_1 , e_2 , e_{A3} and e_{B3} electrons, namely $s_{1,A1}$, $s_{A1,1}$, $s_{A3,A1}$, $s_{A1,A3}$, and so on, are identical, respectively to s_{31e} and s_{13e} , which have been calculated in Ref. [27] for the $1s^2 2s^2$ state of beryllium atom. The coefficient $s_{1,A3}$ is calculated with (9). This calculation reduces to the evaluation of the angle between the two lines which pass, respectively, through nucleus n_A and electron e_1 and through nucleus n_A and electron e_{A3} , with the aid of the coordinates of the particles, which are shown in Table 2. All the other necessary data are given in Table 2.

The normalized value of the total energy is calculated with the aid of equation (41), and can be written for Be_2 molecule in the following form, taking into account the symmetry of the system (namely $\underline{E}_1 = \underline{E}_2$, $\underline{E}_{A3} = \underline{E}_{B3}$, $\underline{E}_{A1} = \underline{E}_{A2} = \underline{E}_{B1} =$

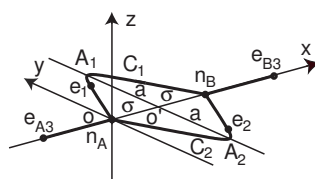


Figure 5. Structure of Be_2 molecule.

$$\underline{E}_{B_2}, \underline{U}_{e_1 n_B} = \underline{U}_{e_2 n_A}, \underline{U}_{e_{A_3} e_2} = \underline{U}_{e_{B_3} e_1} \text{ and } \underline{U}_{e_{A_3} n_B} = \underline{U}_{e_{B_3} n_A}:$$

$$\begin{aligned} \underline{E} = & 2\underline{E}_1 + 2\underline{E}_{A_3} + 4\underline{E}_{A_1} + \underline{U}_{e_1 e_2} + 2\underline{U}_{e_1 n_B} + 2\underline{U}_{e_{A_3} e_2} + 2\underline{U}_{e_{A_3} n_B} + (47) \\ \underline{U}_{e_{A_3} e_{B_3}} + \underline{U}_{n_A n_B} + 2\underline{E}_{m1s} = & -2 \frac{Z_1^2}{n_1^2} - 2 \frac{Z_{A_3}^2}{n_{A_3}^2} - 4 \frac{Z_{A_1}^2}{n_{A_1}^2} + \frac{1}{2\sqrt{(\frac{1}{4}\sigma)^2 + (\frac{3}{4}a)^2}} - \\ & \frac{2(Z_A - 2)}{\sqrt{(\frac{5}{4}\sigma)^2 + (\frac{3}{4}a)^2}} + \frac{2}{\sqrt{(\frac{5}{4}\sigma + r_{A_3})^2 + (\frac{3}{4}a)^2}} - \frac{2(Z_A - 2)}{2\sigma + r_{A_3}} + \\ & \frac{1}{2\sigma + 2r_{A_3}} + \frac{(Z_A - 2)^2}{2\sigma} + 2 \frac{Z_{A_1}^{3/2}}{8n_{A_1}^3} \end{aligned}$$

In this case \underline{E}_{exp} is obtained from equation (45), where S_{EiA} is taken from Ref. [35], but the value of D_0^0 is obtained from Fig. 6-2 of Ref. [37] (Ref. [36] does not contain this data). The values of r_0 and r_e are given in Table 3, while \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} are shown in Table 1. The relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, $|(\underline{E} - \underline{E}_{exp}) / \underline{E}_{exp}| = 0.001$ and $|(\underline{E}_{HF} - \underline{E}_{exp}) / \underline{E}_{exp}| = 0.006$.

c) Other molecules.

The procedure for calculating the energetic values of B_2 , C_2 , LiH , BeH , BH and CH molecules is almost identical to that shown in the above examples. The values of \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} , corresponding to these molecules are shown also in Table 1. The specific differences, referring to these molecules are given briefly below.

The B_2 molecule contains four electrons, denoted by e_{A_3} , e_{A_4} , e_{B_3} and e_{B_4} which do not participate to the bond. Taking into account this difference, the procedure for calculating the energetic values is identical to that for the Be_2 molecule.

We have analyzed the C_2 molecule in three cases: when the bond is simple, double and triple and found that the total energy is minimum in the case of the double bond, resulting that the real bond of the C_2 molecule is double. This result is identical to that obtained by pure quantum evaluations (see, for example pag. 97 of Ref. [31]). In Table 1 it is shown the value of \underline{E} corresponding to the C_2 molecule with double bond, together with \underline{E}_{HF} and \underline{E}_{exp} . We have found also that the symmetry properties of the C_2 molecules, corresponding to simple, double and triple bonds are identical, respectively, to the experimental symmetry properties of the ethane, ethylene and acetylene molecules, namely C_2H_6 , C_2H_4 and C_2H_2 (see Ref. [29]). This explains why adding 6, 4 and, respectively, 2 hydrogen atoms to the structures of C_2 with simple, double and triple bonds leads to the formation of the C_2H_6 , C_2H_4 and, respectively, C_2H_2 molecules. Also, our calculations explain

the property that the length of the bond decreases as the bond order increases.

We have analyzed the following heteronuclear diatomic molecules: LiH , BeH , BH and CH . The model of ionic bond, as it results from Fig. 3(a), is in agreement with the experimental data for LiH , BeH , while the model of covalent bond, which is shown in Fig. 3(b), is in agreement with the experimental data only for BH and CH . For example, if we apply the covalent model in the case of LiH , it will lead to a symmetrical molecule, for which $\sigma_1 = \sigma_2$, which is in strong disagreement with the fact that this molecule has a strong ionic character [31]. Outside of these differences, the procedure of calculation of the energetic values is almost identical to that shown in the above examples.

All the details of the computations and the Mathematica 7 scripts used for all the molecules are given in the Supplementary Online Material for this article.

6. Conclusions

We presented a semiclassical central field method for the calculation of the energetic values of the diatomic molecules Li_2 , Be_2 , B_2 , C_2 , LiH , BeH , BH and CH , which is based on an exact theoretical connection between the geometric elements of the wave described by the Schrödinger equation and the Hamilton-Jacobi equation, written for the same system. This connection was proved and was checked on atomic systems in previous papers. The accuracy of our method is comparable with the accuracy of the standard central field Hartree-Fock method, for both, atomic systems and diatomic molecules. Our method reveals a series of other properties of the diatomic molecules, such as the fact that the bond of C_2 is double, or LiH has a strong ionic character, which is in agreement with experimental measurements.

Appendix A. Analytical calculation method for geometric parameters in the typical case of the simple bond of homonuclear diatomic molecules.

We consider a molecule composed of two fixed identical nuclei, denoted by n_A and n_B , four $1s$ electrons and two valence electrons which participate to the bond, denoted by e_1 and e_2 . The Cartesian coordinates of the nuclei are, respectively, $n_A(-\sigma, 0, 0)$ and $n_B(\sigma, 0, 0)$ and their order number is equal to Z_A . The C_1 and C_2 curves, which correspond to the bond electrons are situated in the plane (x, y) , as shown in Fig. 1. In Subsection 3.1 we have shown that each curve is composed of two quasilinear ellipses, denoted by C_{aA} and C_{aB} . We assume that the kinetic energies of the electrons positioned at points $A_1(0, a, 0)$ and $A_2(0, -a, 0)$ are negligible as compared to the total energy. The electrons are situated in average positions in Fig. 1, and their coordinates are $e_1[-(1/4)\sigma, (3/4)a, 0]$ and $e_2[(1/4)\sigma, -(3/4)a, 0]$, in agreement with (12), for $e \cong 1$ and $r_M = \sqrt{a^2 + \sigma^2}$. In this case E_b has the significance of the total energy from which the energies of the $1s$ electrons are subtracted. The three quantities E_b , σ and a are calculated with the aid of the following three equations [23, 24].

1) The first relation. This relation results from the central field approximation. It results in a similar manner as in the case of atoms [27, 28]: we have to write the expression of the energy of the electron e_1 , denoted by E_1 , and to consider the approximation of the central field. We have $E_1 = T_1 + U_{e_1 n_A}$, where T_1 is the kinetic energy of the electron e_1 and $U_{e_1 n_A}$ is the electrostatic energy of interaction between the electron e_1 and the nucleus n_A , which includes the screening effect of the $1s$ electrons. Taking into account the symmetry of the system (from where we

have $T_1 = T_2$, $U_{e_1 n_A} = U_{e_2 n_B}$, $U_{e_1 n_B} = U_{e_2 n_A}$) and the expression of the energy E_b , we have

$$E_1 = T_1 + U_{e_1 n_A} = \frac{E_b}{2} - U_0 \quad \text{with } U_0 = U_{e_1 n_B} + \frac{1}{2} (U_{e_1 e_2} + U_{n_A n_B}) \quad (\text{A1})$$

The significance of the above electrostatic terms is specified by their notations (for example, $U_{e_1 n_B}$ is the potential energy of electrostatic interaction between the electron e_1 and nucleus n_B , and so on), and the screening effect of the $1s$ electrons is taken into account through the terms $U_{e_1 n_B}$ and $U_{n_A n_B}$. In these terms, which refer at the interaction at distance between electrons and nuclei, and, respectively, between nuclei, the screening coefficient due to the $1s$ electrons is equal to unity. The expressions of these terms are (see Fig. 1): $U_{e_1 n_B} = K_1 Z_{1M}/s'_1$ and $U_{n_A n_B} = K_1 Z_{nA}^2/(2\sigma)$, where the corresponding order numbers are

$$Z_{1M} = Z_A - 2 \quad \text{and} \quad Z_{nA} = Z_A - 2 \quad (\text{A2})$$

Since U_0 is a relatively small quantity, we consider its averaged value, denoted by U_{0m} , calculated for the average positions of the electrons. In this case the expression $E_1 = T_1 + U_{e_1 n_A} = \frac{E_b}{2} - U_{0m}$ represents the constant energy of a hydrogenoid system, resulting that the electron e_1 moves in the central field of the nucleus in an averaged field of the other electron. We apply the quantization relation from (2), which is $\Delta_{C_{1A}} S_{01} = n_1 h$, for the curve C_{1A} and, in virtue of the relations shown in Appendix A of Ref. [27], we have:

$$E_1 = \frac{E_b}{2} - U_{0m} = -\frac{Z_1^2 R_\infty}{n_1^2} \quad (\text{A3})$$

where

$$U_{0m} = -\frac{4K_1 Z_{1M}}{\sqrt{9a^2 + 25\sigma^2}} + \frac{K_1}{\sqrt{9a^2 + \sigma^2}} + \frac{K_1 Z_{nA}^2}{4\sigma} \quad (\text{A4})$$

and

$$Z_1 = Z_A - 2s_{1,A1} \quad (\text{A5})$$

From (A3), (A4) obtain

$$E_b = -2\frac{Z_1^2 R_\infty}{n_1^2} - \frac{8K_1 Z_{1M}}{\sqrt{9a^2 + 25\sigma^2}} + \frac{2K_1}{\sqrt{9a^2 + \sigma^2}} + \frac{K_1 Z_{nA}^2}{2\sigma} \quad (\text{A6})$$

2) The second relation. This relation results from the virial theorem. Taking into account that the curve C_1 is symmetrical, the virial theorem can be written

$$E_b = -\tilde{T} = -\frac{1}{\tau} \int_{\tau} m v_1^2 dt = -\frac{\Delta_{C_{1A}} S_{01}}{\tau} = -\frac{n_1 h}{\tau} \quad (\text{A7})$$

where \tilde{T} is the average value of the total kinetic energy and τ is the period corresponding to the curve C_{1A} . Since $\tau = 2 \int_0^{r_M} ds_1/v_1$ where $v_1 = 0$ and $T_1 = 0$ for $s_1 = r_M$, it results that the domain in the vicinity of the point A_1 , which is relatively far from nucleus, has a big weight in the calculation of the integral. In this case we have $U_{e_1 n_A} \cong -K_1 Z_{1M}/s_1$, and from (A1) we obtain

$E_b/2 - U_0 = T_1 - K_1 Z_{1M}/s_1 = -K_1 Z_{1M}/r_M$, or $T_1 = K_1 Z_{1M}/s_1 - K_1 Z_{1M}/r_M$.
The expression of τ becomes:

$$\tau = 2 \int_0^{r_M} \frac{ds_1}{\sqrt{\frac{2T_1}{m}}} = \sqrt{2m} \int_0^{r_M} \frac{ds_1}{\sqrt{\frac{K_1 Z_{1M}}{s_1} - \frac{K_1 Z_{1M}}{r_M}}} = \pi \sqrt{\frac{m}{2K_1 Z_{1M}}} r_M^{\frac{3}{2}} \quad (\text{A8})$$

Introducing the expression of r_M , and taking into account (A7), the above relation becomes

$$E_b = -\frac{n_1 h \sqrt{2K_1 Z_{1M}}}{\pi \sqrt{m} (\sigma^2 + a^2)^{\frac{3}{4}}} \quad (\text{A9})$$

3) The third relation. This relation results from the equation of the energy E_b , when the electrons are situated at maximum distance from the nuclei, respectively, in the points $A_1(0, a, 0)$ and $A_2(0, -a, 0)$, as follows:

$$E_b = 4U_{e_1 n_A} + U_{e_1 e_2} + U_{n_A n_B} = -\frac{4K_1 Z_{1M}}{\sqrt{\sigma^2 + a^2}} + \frac{K_1}{2a} + \frac{K_1 Z_{n_A}^2}{2\sigma} \quad (\text{A10})$$

The calculations of the geometric parameters of the bond in the cases of the double and triple covalent bonds of homonuclear molecules and in the cases of ionic and covalent bonds in heteronuclear molecules are similar to the calculation presented in this Appendix. These calculations are shown in details in the Supplementary Online Material.

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SUPPLEMENTARY ONLINE MATERIAL

for the paper

Unconventional semiclassical method for calculating the energetic values of diatomic molecules

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In this material we extend the calculation of the geometric parameters of the bond, which has been presented in the Appendix A of the paper, to the cases of the double and triple covalent bonds of homonuclear molecules and to the cases of ionic and covalent bonds in heteronuclear molecules. We present also detailed calculations of the molecules properties in the cases of B_2 , C_2 , LiH , BeH , BH and CH molecules, together with Mathematica 7 scripts containing the calculations necessary for all the molecules which have been analyzed in paper and in supplementary material. The references are those from the paper.

S1. Calculation of the geometric parameters in the particular cases of the double and triple covalent bonds of homonuclear molecules and of ionic and covalent bonds in heteronuclear molecules.

S1.1. Covalent double bond of homonuclear molecules

1) **The first relation.** The procedure is identical to that for simple bonds, which has been presented in Appendix A of the paper. We need, however, to take into account that four electrons participate in this case to the bond. Their average positions are $e_1[-(1/4)\sigma, (3/4)a, 0]$, $e_2[-(1/4)\sigma, -(3/4)a, 0]$, $e_3[(1/4)\sigma, 0, (3/4)a]$ and $e_4[(1/4)\sigma, 0, -(3/4)a]$, as shown in Fig.2(a) from the paper. In this case, taking into account the symmetry relations $T_1 = T_2 = T_3 = T_4$, $U_{e_1n_A} = U_{e_2n_A} = U_{e_3n_B} = U_{e_4n_B}$, $U_{e_1n_B} = U_{e_2n_B} = U_{e_3n_A} = U_{e_4n_A}$ and $U_{e_1e_3} = U_{e_1e_4} = U_{e_2e_3} = U_{e_2e_4}$, (A1) from paper becomes: $E_1 = T_1 + U_{e_1n_A} = \frac{E_b}{4} - U_0$ with $U_0 = U_{e_1n_B} + \frac{1}{4}(4U_{e_1e_3} + U_{n_An_B})$. A procedure identical to the one presented in Appendix A of the paper, while taking into account the quantization relation, leads to the equation $E_1 = -Z_1^2 R_\infty / n_1^2$ where

$$Z_1 = Z_A - 2s_{1,A1} - s_{1,2} \quad \text{and} \quad s_{1,2} = s_{2,1} = \frac{\sqrt{\sigma^2 + a^2}}{4a} \quad (S1)$$

The screening coefficient $s_{1,2}$ is calculated with (9) from paper. We have also

$$Z_{1M} = Z_A - 2 - s_{1,2} \quad (S2)$$

In virtue of the above relations, the second term of the second member of (A6) from paper corresponds to $U_{e_1n_B} + U_{e_2n_B} + U_{e_3n_A} + U_{e_4n_A} = 4U_{e_1n_B}$ instead of $2U_{e_1n_B}$ obtained in the case of the single bond. We can further write: $4U_{e_1n_B} = \frac{4K_1(Z_B - 2)}{\sqrt{(5\sigma/4)^2 + (3a/4)^2}} = \frac{16K_1(Z_{1M} + s_{1,2})}{\sqrt{25\sigma^2 + 9a^2}}$. The third term of the second member of (A6) from paper corresponds to the interactions between the bond electrons e_1 , e_2 and the bond electrons e_3 , e_4 , and, because of symmetry, it corresponds to $4U_{e_1e_3}$,

1 instead of $U_{e_1e_2}$ obtained in the case of simple bond. With these modifications, the
2 correspondent of (A6) from paper, in the case of double bond is:
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$$4 E_b = -4 \frac{Z_1^2 R_\infty}{n_1^2} - \frac{16K_1 (Z_{1M} + s_{1,2})}{\sqrt{9a^2 + 25\sigma^2}} + \frac{8K_1}{\sqrt{\sigma^2 + 4.5a^2}} + \frac{K_1 Z_{nA}^2}{2\sigma} \quad (S3)$$

8 **2) The second relation.** Since there are four bond electrons, the virial relation
9 must be modified, namely instead of (A7) from paper, we have $E_b = -2n_1 h/\tau$,
10 from which it follows that the second relation, i.e. (A9) from paper, becomes:
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$$12 E_b = -\frac{2n_1 h \sqrt{2K_1 Z_{1M}}}{\pi \sqrt{m} (\sigma^2 + a^2)^{\frac{3}{4}}} \quad (S4)$$

16 **3) The third relation.** This relation results directly, taking into account
17 that the first term from the second member represents the sum of the interac-
18 tions between the bond electrons e_1, e_2, e_3, e_4 , (situated, respectively, at points
19 A_1, A_2, A_3, A_4) and nuclei, and the second term represents the sum of the inter-
20 action between all the bond electrons, corresponding to these positions. The third
21 relation, (A10) from paper must be rewritten as follows:
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$$23 E_b = -\frac{8K_1 (Z_{1M} + s_{1,2})}{\sqrt{\sigma^2 + a^2}} + \frac{K_1}{a} + \frac{2\sqrt{2}K_1}{a} + \frac{K_1 Z_{nA}^2}{2\sigma} \quad (S5)$$

24 *S1.2. Covalent triple bond of homonuclear molecules*

25 The solution is similar to that for simple bonds. We have to take into account
26 that, in this case, six electrons participate to the bond. Their average positions are
27 $e_1[-\frac{1}{4}\sigma, \frac{3}{4}a, 0]$, $e_2[-\frac{1}{4}\sigma, -\frac{3}{4} \cdot \frac{1}{2}a, \frac{3}{4} \cdot \frac{\sqrt{3}}{2}a]$, $e_3[-\frac{1}{4}\sigma, -\frac{3}{4} \cdot \frac{1}{2}a, -\frac{3}{4} \cdot \frac{\sqrt{3}}{2}a]$, $e_4[\frac{1}{4}\sigma, -\frac{3}{4}a, 0]$,
28 $e_5[\frac{1}{4}\sigma, \frac{3}{4} \cdot \frac{1}{2}a, -\frac{3}{4} \cdot \frac{\sqrt{3}}{2}a]$ and $e_6[\frac{1}{4}\sigma, \frac{3}{4} \cdot \frac{1}{2}a, \frac{3}{4} \cdot \frac{\sqrt{3}}{2}a]$, as shown in Fig.2(b) from the
29 paper. The analysis in this case is analogous to the analysis of the simple and
30 double bonds. The difference from these two previous cases is that we have to
31 take into account that six bond electrons participate to the triple bond instead of
32 four (double bond) or two (simple bond) electrons. It easy to see that the three
33 relations, in the case of the triple bond, become:
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$$43 E_b = -6 \frac{Z_1^2 R_\infty}{n_1^2} - \frac{24K_1 (Z_{1M} + 2s_{1,2})}{\sqrt{9a^2 + 25\sigma^2}} + \frac{6K_1}{\sqrt{\sigma^2 + 9a^2}} + \frac{24K_1}{\sqrt{4\sigma^2 + 9a^2}} + \frac{K_1 Z_{nA}^2}{2\sigma} \quad (S6)$$

$$44 E_b = -\frac{3n_1 h \sqrt{2K_1 Z_{1M}}}{\pi \sqrt{m} (\sigma^2 + a^2)^{\frac{3}{4}}} \quad (S7)$$

$$45 E_b = -\frac{12K_1 (Z_{1M} + 2s_{1,2})}{\sqrt{\sigma^2 + a^2}} + \frac{6K_1}{\sqrt{3}a} + \frac{6K_1}{a} + \frac{3K_1}{2a} + \frac{K_1 Z_{nA}^2}{2\sigma} \quad (S8)$$

46 where

$$47 Z_1 = Z_A - 2s_{1,A1} - 2s_{1,2}, \quad Z_{1M} = Z_A - 2 - 2s_{1,2} \quad (S9)$$

and

$$s_{1,2} = \frac{\sqrt{2}}{4\sqrt{1 - \frac{\sigma^2 - \frac{1}{2}a^2}{\sigma^2 + a^2}}} \quad (\text{S10})$$

S1.3. Ionic bonds in heteronuclear molecules

We consider a heteronuclear molecule composed of two fixed different nuclei, denoted by n_A and n_B , two $1s$ electrons in the vicinity of the n_A nucleus, denoted by e_{A1} and e_{A2} , and two valence electrons which participate to the bond, denoted by e_1 and e_2 . In Subsection 3.2. we have shown that the curves C_1 and C_2 for this molecule are represented in Fig. 3(a) from the paper. These curves are situated in the plane xy , the Cartesian coordinates of the nuclei are $n_A(0, 0, 0)$ and $n_B(\sigma_1 + \sigma_2, 0, 0)$ and their order numbers are, respectively, equal to Z_A and Z_B , where $Z_A > Z_B$. The curve C_a , where $a = 1$ or $a = 2$, is composed of two quasilinear ellipses, denoted by C_{aA} and C_{aB} , which surround, respectively the nuclei n_A and n_B . We distinguish two phases, the phase A , when the electrons are situated on the curves C_{1A} and C_{2A} , in the vicinity of the nucleus n_A , and the phase B , when the electrons are situated on the curves C_{1B} and C_{2B} , in the vicinity of the nucleus n_B . The average positions of the electrons in the phase A are $e_1 [(3/4)\sigma_1, (3/4)a, 0]$ and $e_2 [(3/4)\sigma_1, -(3/4)a, 0]$, while in the phase B they are $e_1 [\sigma_1 + (1/4)\sigma_2, (3/4)a, 0]$ and $e_2 [\sigma_1 + (1/4)\sigma_2, -(3/4)a, 0]$. We note that the curves C_{1A} and C_{2A} , on one hand, and the curves C_{1B} and C_{2B} , on the other hand, are very similar to the curves C_1 and C_2 in the case of helium atom.

In the case of the heteronuclear diatomic molecules, the order number corresponding to the bond electron e_i is denoted by $Z_{i(A)}$ when e_i moves in the vicinity of the nucleus n_A and by $Z_{i(B)}$ when e_i moves in the vicinity of the nucleus n_B . The screening coefficients between the bond electrons e_1 and e_2 , which move in the vicinity of the nucleus n_A , are denoted by $s_{1,2(A)}$ and $s_{2,1(A)}$. The screening coefficients between the electrons e_{Ai} and e_j when e_j moves in the vicinity of the nucleus n_A have the same significance, as they do in the case of the homonuclear molecules, and therefore we keep the same notations for them, namely $s_{Ai,j}$ and $s_{j,Ai}$.

The treatment of this system is almost identical to that presented in Appendix A from the paper, for the simple bond, with the difference that, due to asymmetry, the order numbers are different, for the two phases, as follows

$$Z_{1(A)} = Z_A - 2s_{1,A1} - s_{1,2(A)}, \quad Z_{1M(A)} = Z_A - 2 - s_{1,2(A)} \quad \text{and} \quad Z_{nA} = Z_A - 2 \quad (\text{S11})$$

$$Z_{1(B)} = Z_B - s_{1,2(B)}, \quad Z_{1M(B)} = Z_B - s_{1,2(B)} \quad \text{and} \quad Z_{nB} = Z_B \quad (\text{S12})$$

where

$$s_{1,2(A)} = \frac{\sqrt{\sigma_1^2 + a^2}}{4a} \quad \text{and} \quad s_{1,2(B)} = \frac{\sqrt{\sigma_2^2 + a^2}}{4a} \quad (\text{S13})$$

Because of this difference between phases, the quantum numbers associated to the motion of the electron e_1 on curves C_{1A} and C_{2B} , denoted, respectively, by $n_{1(A)}$ and $n_{1(B)}$, and the corresponding periods, denoted by τ_A and τ_B , are different.

Due to the symmetry of the system, we have $Z_{1(A)} = Z_{2(A)}$, $Z_{1(B)} = Z_{2(B)}$, $Z_{1M(A)} = Z_{2M(A)}$, $Z_{1M(B)} = Z_{2M(B)}$, $n_{1(A)} = n_{2(A)}$ and $n_{1(B)} = n_{2(B)}$.

The kinetic energy of one electron, corresponding to the points A_1 or A_2 is denoted by T_m . Despite the fact that its value is very small, is it not neglected. The three types of equations from the previous subsection are derived in a similar manner, as follows.

1) The first type of relation. These relations result from the central field approximation, using the quantization condition. The energy of the electron e_1 , when the system is in the phase A , is

$$E_1 = T_1 + U_{e_1 n_A} = \frac{E_b}{2} - U_{0A} \quad \text{with } U_{0A} = U_{e_1 n_B} + \frac{1}{2} U_{n_A n_B} \quad (\text{S14})$$

Since the e_1 and e_2 electrons are situated in the vicinity of the nucleus n_A , their interaction energy is included in $U_{e_1 n_A}$ and $U_{e_2 n_A}$, by the term $s_{1,2(A)}$.

The quantization relation, applied for the curve C_{1A} , is $\Delta_{C_{1A}} S_{01} = n_{1(A)} h$. The processing of these relations is identical to the processing of relations (A1), (A3) and (A4) from paper. Thus, we approximate the quantity U_{0A} , with its value, denoted by U_{0Am} , calculated when the electrons are in average positions. In this case, the motions of the electrons reduces to that in a central field. An identical procedure to that presented in Appendix A from the paper leads to the following relation

$$E_b = -2 \frac{Z_{1(A)}^2 R_\infty}{n_{1(A)}^2} - \frac{8K_1 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{9a^2 + (\sigma_1 + 4\sigma_2)^2}} + \frac{K_1 Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2} \quad (\text{S15})$$

The same analysis, made for phase B , leads to the following relation

$$E_b = -2 \frac{Z_{1(B)}^2 R_\infty}{n_{1(B)}^2} - \frac{8K_1 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{9a^2 + (\sigma_2 + 4\sigma_1)^2}} + \frac{K_1 Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2} \quad (\text{S16})$$

2) The second type of relation. These relations result from the virial theorem. We show that this theorem can be written separately for phases A and B . We take into account the notations from Fig. 3(a) from the paper and write the following relation for the phase A : $d(m\bar{r} \cdot \bar{v}_1)/dt + d(m\bar{r}' \cdot \bar{v}_2)/dt = m\bar{r} \cdot d\bar{v}_1/dt + m\bar{r}' \cdot d\bar{v}_2/dt + mv_1^2 + mv_2^2$. The integration of this relation with respect to time, over the period τ_A , considering that $\bar{r} \cdot \bar{v}_1 \cong 0$ and $\bar{r}' \cdot \bar{v}_2 \cong 0$, respectively, at points A_1 and A_2 , leads to the following relation:

$$2\bar{T} = -\frac{1}{\tau_A} \int_{\tau_A} (\bar{r} \cdot \bar{F}_1 + \bar{r}' \cdot \bar{F}_2) dt \quad (\text{S17})$$

where \bar{F}_1 and \bar{F}_2 are the forces which act, respectively, on the electrons e_1 and e_2 . With the aid of their expressions [see Fig. 3(a) from the paper], and taking into account the symmetry of the system and the fact that $\bar{r} = -\sigma_1 \bar{i} + \bar{r}_1 = \sigma_2 \bar{i} + \bar{r}'_1$ and $\bar{r}' = -\sigma_1 \bar{i} + \bar{r}_2 = \sigma_2 \bar{i} + \bar{r}'_2$, we obtain

$$\begin{aligned} \bar{r} \cdot \bar{F}_1 + \bar{r}' \cdot \bar{F}_2 = & \left[-\frac{K_1 Z_{1(A)}}{r_1^3} \bar{r}_1 - \frac{K_1 Z_{1M(B)}}{r_1'^3} \bar{r}_1' + \frac{K_1}{|\bar{r}_1 - \bar{r}_2|^3} (\bar{r}_1 - \bar{r}_2) \right] \bar{r} + (S18) \\ & \left[-\frac{K_1 Z_{1(A)}}{r_2^3} \bar{r}_2 - \frac{K_1 Z_{1M(B)}}{r_2'^3} \bar{r}_2' + \frac{K_1}{|\bar{r}_2 - \bar{r}_1|^3} (\bar{r}_2 - \bar{r}_1) \right] \bar{r}' = \\ & 2\sigma_1 \frac{K_1 Z_{1(A)}}{r_1^2} \cos \alpha_1 + 2\sigma_2 \frac{K_1 Z_{1M(B)}}{r_1'^2} \cos \alpha_2 + U - \frac{K_1 Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2} \end{aligned}$$

where $U = -2K_1 Z_{1(A)}/r_1 - 2K_1 Z_{1M(B)}/r_1' + K_1/|\bar{r}_1 - \bar{r}_2| + K_1 Z_{nA} Z_{nB}/(\sigma_1 + \sigma_2)$. This is the potential energy of the system.

Introducing the above relation in (S17) and supposing that the average forces which act on the two nuclei are zero, we obtain $2\tilde{T} = -\tilde{U}$. Since $E_b = \tilde{U} + \tilde{T}$, we have:

$$E_b = -\tilde{T} = -\frac{1}{\tau_A} \int_{\tau} m v_1^2 dt = -\frac{\Delta_{C_{1A}} S_{01}}{\tau_A} = -\frac{n_{1(A)} h}{\tau_A} \quad (S19)$$

In this case $\tau_A = 2 \int_0^{r_{M(A)}} dr_1/v_1 = 2 \int_0^{r_{M(A)}} dr_1/\sqrt{2T_1/m}$ where $T_1 = T_m$ for $r_1 = r_{M(A)} = \sqrt{\sigma_1^2 + a^2}$. Since T_m is a very small quantity, we consider again that the domain in the vicinity of the point A_1 has a big weight in the calculation of the integral. We, thus, have $U_{e_1 n_A} \cong -K_1 Z_{1M(A)}/r_1$. The calculation of τ_A is performed similarly as in (A9) from paper. Using (S14) it follows that $E_b/2 - U_0 = T_1 - K_1 Z_{1M(A)}/r_1 = T_m - K_1 Z_{1M(A)}/r_{M(A)}$, or $T_1 = K_1 Z_{1M(A)}/r_1 - K_1 Z_{1M(A)}/r_{M(A)} + T_m$ and, instead of (A9) from paper, we write

$$\tau_A = \sqrt{2m} \int_0^{r_{M(A)}} \frac{dr_1}{\sqrt{\frac{K_1 Z_{1M(A)}}{r_1} - \frac{K_1 Z_{1M(A)}}{r_{M(A)}} + T_m}} = \pi \sqrt{\frac{m}{2K_1 Z_{1M(A)}}} r_{M(A)}^{\frac{3}{2}} t_{cA} \quad (S20)$$

where t_{cA} is a correction term, given by the relation

$$t_{cA} = \frac{2}{\pi a_{cA}^{3/2}} (\arcsin \sqrt{a_{cA}} - \sqrt{a_{cA}} \sqrt{1 - a_{cA}}) \quad (S21)$$

with

$$a_{cA} = 1 - \frac{T_m \sqrt{\sigma_1^2 + a^2}}{K_1 Z_{1M(A)}} \quad (S22)$$

Since $r_{M(A)} = \sqrt{\sigma_1^2 + a^2}$, from (S19) and (S20) we obtain

$$E_b = -\frac{n_{1(A)} h \sqrt{2K_1 Z_{1M(A)}}}{\pi \sqrt{m} (\sigma_1^2 + a^2)^{\frac{3}{4}} t_{cA}} \quad (S23)$$

An identical analysis, corresponding to phase B , leads to the following relations:

$$E_b = -\frac{n_{1(B)} h \sqrt{2K_1 Z_{1M(B)}}}{\pi \sqrt{m} (\sigma_2^2 + a^2)^{\frac{3}{4}} t_{cB}} \quad (S24)$$

where

$$t_{cB} = \frac{2}{\pi a_{cB}^{3/2}} \left(\arcsin \sqrt{a_{cB}} - \sqrt{a_{cB}} \sqrt{1 - a_{cB}} \right) \quad (\text{S25})$$

and

$$a_{cB} = 1 - \frac{T_m \sqrt{\sigma_2^2 + a^2}}{K_1 Z_{1M(B)}} \quad (\text{S26})$$

3) The third type of relation. This relation, which is the expression of the energy E_b , when the electrons are situated, respectively, at points $A_1(0, a, 0)$ and $A_2(0, -a, 0)$, results directly

$$E_b = -\frac{2K_1 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{\sigma_1^2 + a^2}} - \frac{2K_1 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{\sigma_2^2 + a^2}} + \frac{K_1}{2a} + \frac{K_1 Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2} + 2T_m \quad (\text{S27})$$

S1.4. Covalent bonds in heteronuclear diatomic molecules.

We consider the same heteronuclear covalent diatomic molecule as that presented in Subsection 3.2 from paper, having $n_A > n_B$, when the e_1 and e_2 electrons are situated in the vicinities of different nuclei, as shown in Fig. 3(b) from paper. The average positions of the electrons are $e_1 [(3/4)\sigma_1, (3/4)a, 0]$ and $e_2 [(\sigma_1 + (1/4)\sigma_2), -(3/4)a, 0]$. The curves C_1 and C_2 are asymmetrical, similar to those shown in Fig. 3(a) from paper. The treatment of this system is almost identical to that from Appendix A from paper for simple bond, with the difference that the order numbers are different. For the positions of the electrons shown in Fig. 3(b) from paper, we have

$$Z_{1(A)} = Z_A - 2s_{1,A1}, \quad Z_{1M(A)} = Z_A - 2, \quad \text{and} \quad Z_{nA} = Z_A - 2 \quad (\text{S28})$$

$$Z_{2(B)} = Z_B, \quad Z_{2M(B)} = Z_B \quad \text{and} \quad Z_{nB} = Z_B \quad (\text{S29})$$

The quantum numbers associated to the electrons e_1 and e_2 , for the positions shown in Fig. 3(b) from paper, are respectively, $n_{1(A)}$ and $n_{2(B)}$. Taking into account the symmetry of the curves C_1 and C_2 , we have $Z_{1(A)} = Z_{2(A)}$, $Z_{1(B)} = Z_{2(B)}$, $Z_{1M(A)} = Z_{2M(A)}$, $Z_{1M(B)} = Z_{2M(B)}$, $n_{1(A)} = n_{2(A)}$ and $n_{1(B)} = n_{2(B)}$.

Both electrons move alternatively in the fields of the two nuclei, on the curves C_{1A} , C_{1B} and C_{2A} , C_{2B} . We assume that the kinetic energies of the bond electrons in the points A_1 and A_2 are neglected, as in Appendix A from paper, and that the motion of the electrons is periodical. The periodicity leads to the following relation

$$\tau_A = \tau_B \quad (\text{S30})$$

In the case of the ionic bond, the electrons move together on helium type trajectories in the field of the same nucleus, and due to the nonsymmetry of the C_a trajectory, in the majority of the time, the electrons are in the vicinity of the nucleus whose order number is smaller. Unlike the ionic bond, in the present case, the electrons move alternatively in the fields of different nuclei, the two periods of

1 motion, τ_A and τ_B , are equal and their charge is disposed in the vicinities of both
 2 nuclei, from here resulting the covalent character of the bond.

3 The three types of equations from the previous subsection, result, similarly as in
 4 Appendix A from paper, as follows.

5 **1) The first type of relation.** This relation results from the central field
 6 approximation, using the quantization condition. In this case the expression of the
 7 energy E_b can be written:
 8

$$9 \quad E_b = E_1 + E_2 + U_{01} + U_{02} \quad \text{with} \quad E_1 = T_1 + U_{e_1 n_A} \quad \text{and} \quad E_2 = T_2 + U_{e_2 n_B} \quad (S31)$$

10 where

$$11 \quad U_{01} = U_{e_1 n_B} + \frac{1}{2} (U_{e_1 e_2} + U_{n_A n_B}) \quad \text{and} \quad U_{02} = U_{e_2 n_A} + \frac{1}{2} (U_{e_1 e_2} + U_{n_A n_B}) \quad (S32)$$

12 We consider that the motions of the e_1 and e_2 electrons are approximated by
 13 motions in the in central fields of the nuclei n_a and n_B . In this case E_1 and E_2 are
 14 constants and the quantities U_{01} and U_{02} are calculated for the average positions of
 15 the electrons. We apply quantization relations $\Delta_{C_{1A}} S_{01} = n_{1(A)} h$ and $\Delta_{C_{2B}} S_{02} =$
 16 $n_{2(B)} h$, respectively, for the curves C_{1A} and C_{2B} . We obtain $E_1 = -R_\infty Z_{1(A)}^2 / n_{1(A)}^2$
 17 and $E_2 = -R_\infty Z_{2(B)}^2 / n_{2(B)}^2$. Taking into account (S31) and (S32), we obtain:
 18

$$19 \quad E_b = -\frac{R_\infty Z_{1(A)}^2}{n_{1(A)}^2} - \frac{R_\infty Z_{2(B)}^2}{n_{2(B)}^2} - \frac{4K_1 Z_{1M(B)}}{\sqrt{9a^2 + (\sigma_1 + 4\sigma_2)^2}} - \quad (S33)$$

$$20 \quad \frac{4K_1 Z_{1M(A)}}{\sqrt{9a^2 + (\sigma_2 + 4\sigma_1)^2}} + \frac{4K_1}{\sqrt{36a^2 + (\sigma_1 + \sigma_2)^2}} + \frac{Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2}$$

21 **2) The second type of relation.** The virial theorem, written for the curve C_1 ,
 22 and taking into account the symmetry of the curves C_1 and C_2 , is

$$23 \quad E_b = -\frac{1}{\tau_A} \int_{\tau_A} \frac{mv_1^2}{2} dt - \frac{1}{\tau_B} \int_{\tau_B} \frac{mv_2^2}{2} dt = -\frac{\Delta S_{01}}{2\tau_A} - \frac{\Delta S_{02}}{2\tau_B} = \quad (S34)$$

$$24 \quad -\frac{n_{1(A)} h}{2\tau_A} - \frac{n_{2(B)} h}{2\tau_B}$$

25 which, in virtue of equation (S30), can be written:

$$26 \quad 2\tau_A E_b = 2\tau_B E_b = -[n_{1(A)} + n_{1(B)}] h \quad (S35)$$

27 A calculation similar to that presented in Appendix A from paper, which takes
 28 into account (S31), leads to the following relation:
 29

$$30 \quad \tau_A = \tau_B = \pi \sqrt{\frac{m}{2K_1 Z_{1M(A)}}} (\sigma_1^2 + a^2)^{\frac{3}{4}} = \pi \sqrt{\frac{m}{2K_1 Z_{1M(B)}}} (\sigma_2^2 + a^2)^{\frac{3}{4}} = \quad (S36)$$

$$31 \quad -\frac{[n_{1(A)} + n_{1(B)}] h}{2E_b}$$

32 **3) The third type of relation.** This relation, which is the expression of the
 33 energy E_B , when the electrons are situated, respectively, at points $A_1(0, a, 0)$ and
 34

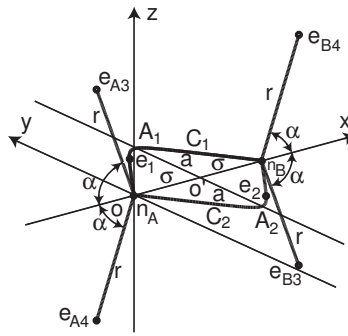


Figure S1. Structure of B_2 molecule.

Table S1. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of B_2 molecule.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|---|---|
| $n_A(0, 0, 0); n_B(2\sigma, 0, 0)$ | $s_{1,A1} = s_{A3,A1} = 0.862983$ [28] |
| $e_1(\frac{3}{4}\sigma, \frac{3}{4}a, 0); e_2(\frac{5}{4}\sigma, -\frac{3}{4}a, 0)$ | $s_{A1,1} = s_{A1,A3} = 0.00246735$ [28] |
| $e_{A3}(-d, 0, b); e_{A4}(-d, 0, -b)$ | $s_{A1,A2} = .25$ |
| $e_{B3}(2\sigma + d, 0, -b); e_{B4}(2\sigma + d, 0, b)$ | $s_{1,A3} = (\sqrt{2}/4)/\sqrt{1 + \frac{\sigma \cos \alpha}{\sqrt{\sigma^2 + a^2}}}$ |
| $n_1 = n_{A3} = n_{A4} = 2; n_{A1} = n_{A2} = 1$ | $s_{A3,A4} = (1/4)/\sin \alpha$ |
| $\underline{E}_b = -3.857$ | $Z_1 = Z_2 = Z_A - 2s_{1,A1} - 2s_{1,A3}$ |
| $\sigma = 0.844851; a = 1.07468$ | $Z_{1M} = Z_{2M} = Z_A - 2 - 2s_{1,A3}$ |
| $\alpha = 63^\circ$ | $Z_{A1} = Z_{A2} = Z_A - s_{A1,A2} - 3s_{A1,1}$ |
| $\underline{S}_{EiA} = 49.3177$ [35]; $D_0^0 = 0.221972$ [36] | $Z_{A3} = Z_A - 2s_{1,A1} - s_{1,A3} - s_{A3,A4}$ |
| $r_0 = 1.7883$ A; $r_e = 1.59$ A [29] | $Z_{A3} = Z_{A4} = Z_{B3} = Z_{B4}$ |
| | $r = r_{A3} = r_{A4}$ where $r_{A3} = 3/Z_{A3}$ |
| | $d = r \cos \alpha; b = r \sin \alpha$ |
| | $Z_{nA} = Z_A - 2 - \frac{2(2\sigma)^2(2\sigma + d)}{[(2\sigma + d)^2 + b^2]^{3/2}}$ |

$A_2(0, -a, 0)$, results directly

$$E_b = -\frac{2K_1 Z_{1M(A)}}{\sqrt{\sigma_1^2 + a^2}} - \frac{2K_1 Z_{1M(B)}}{\sqrt{\sigma_2^2 + a^2}} + \frac{K_1}{2a} + \frac{K_1 Z_{nA} Z_{nB}}{\sigma_1 + \sigma_2} \quad (S37)$$

S2. Details of the calculations for B_2, C_2, LiH, BeH, BH and CH molecules.

S2.1. B_2 molecule

The structure of this molecule is shown in Fig. S1. This molecule contains four electrons, denoted by e_{A3}, e_{A4}, e_{B3} and e_{B4} which do not participate to the bond. All the data necessary in calculations are given in Table S1.

The geometrical structure of the molecule results from the system (34)-(36) from paper, while the normalized value of the total energy is calculated with the aid of equation (41) from paper, and can be written, taking into account the symmetry of the system (namely $\underline{E}_1 = \underline{E}_2, \underline{E}_{A3} = \underline{E}_{A4} = \underline{E}_{B3} = \underline{E}_{B4}, \underline{E}_{A1} = \underline{E}_{A2} = \underline{E}_{B1} = \underline{E}_{B2}, \underline{U}_{e_1 n_B} = \underline{U}_{e_2 n_A}, \underline{U}_{e_{A3} e_2} = \underline{U}_{e_{A4} e_2} = \underline{U}_{e_{B3} e_1} = \underline{U}_{e_{B4} e_1}, \underline{U}_{e_{A3} n_B} = \underline{U}_{e_{A4} n_B} =$

$\underline{U}_{e_{B_3}n_A} = \underline{U}_{e_{B_4}n_A}$, $\underline{U}_{e_{A_3}e_{B_3}} = \underline{U}_{e_{A_4}e_{B_4}}$ and $\underline{U}_{e_{A_3}e_{B_4}} = \underline{U}_{e_{A_4}e_{B_3}}$), as follows:

$$\begin{aligned} \underline{E} &= 2\underline{E}_1 + 4\underline{E}_{A_3} + 4\underline{E}_{A_1} + \underline{U}_{e_1e_2} + 2\underline{U}_{e_1n_B} + 4\underline{U}_{e_{A_3}e_2} + 4\underline{U}_{e_{A_3}n_B} + \quad (S38) \\ &2\underline{U}_{e_{A_3}e_{B_3}} + 2\underline{U}_{e_{A_3}e_{B_4}} + \underline{U}_{n_An_B} + 2\underline{E}_{m1s} = -2\frac{Z_1^2}{n_1^2} - 4\frac{Z_{A_3}^2}{n_{A_3}^2} - 4\frac{Z_{A_1}^2}{n_{A_1}^2} + \\ &\frac{1}{2\sqrt{(\frac{1}{4}\underline{\sigma})^2 + (\frac{3}{4}\underline{a})^2}} - \frac{2(Z_A - 2)}{\sqrt{(\frac{5}{4}\underline{\sigma})^2 + (\frac{3}{4}\underline{a})^2}} + \frac{4}{\sqrt{(\underline{d} + \frac{5}{4}\underline{\sigma})^2 + (\frac{3}{4}\underline{a})^2 + \underline{b}^2}} - \\ &\frac{4(Z_A - 2)}{\sqrt{(\underline{d} + 2\underline{\sigma})^2 + \underline{b}^2}} + \frac{1}{\sqrt{(\underline{\sigma} + \underline{d})^2 + \underline{b}^2}} + \frac{1}{\underline{\sigma} + \underline{d}} + \frac{(Z_A - 2)^2}{2\underline{\sigma}} + 2\frac{Z_{A_1}^{3/2}}{8n_{A_1}^3} \end{aligned}$$

The angle α is a parameter. We perform the calculation for a lot of values of this angle and choose the value for which the total energy is minimum. This value is given in Table S1. This value is very easy to find because the value of 2α is close to the angle between the axes of the C_a curves for the valence electrons in the boron atom, that is equal to 120° .

In this case and in all the cases which follow, \underline{E}_{exp} is obtained with the aid of equation (45) from paper, where S_{EiA} and D_0^0 are taken, respectively, from Ref. [35] and Ref. [36]. As for the molecules analyzed in the paper, all the experimental and calculated data are given in Table S1, excepting the comparison of the energetic values \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} , which are given in Table 1 from paper. The relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, equal to 0.005 and 0.007.

S2.2. C_2 molecule

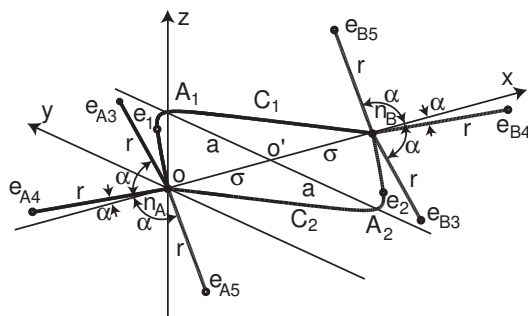
We analyze the C_2 molecule in three cases: when the bond is simple, double and triple. We calculate the total energy and choose the case having the lowest total energy. We consider that this case corresponds to the real C_2 molecule.

1) C_2 molecule with simple bond. The structure of this molecule is shown in Fig. S2(a). This molecule contains six electrons, denoted by e_{A_3} , e_{A_4} , e_{A_5} , e_{B_3} , e_{B_4} , and e_{B_5} which do not participate to the bond. The coordinates of these electrons are as follows: $e_{A_3}(-\underline{d}, 0, \underline{b})$, $e_{A_4}(-\underline{d}, \frac{\sqrt{3}}{2}\underline{b}, -\frac{1}{2}\underline{b})$, $e_{A_5}(-\underline{d}, -\frac{\sqrt{3}}{2}\underline{b}, -\frac{1}{2}\underline{b})$, $e_{B_3}(2\underline{\sigma} + \underline{d}, 0, -\underline{b})$, $e_{B_4}(2\underline{\sigma} + \underline{d}, -\frac{\sqrt{3}}{2}\underline{b}, \frac{1}{2}\underline{b})$ and $e_{B_5}(2\underline{\sigma} + \underline{d}, \frac{\sqrt{3}}{2}\underline{b}, \frac{1}{2}\underline{b})$. A calculation identical to that for the B_2 molecule leads to the following values: $\underline{E}_b = -5.69164$, $\underline{\sigma} = 0.751248$, $\underline{a} = 0.857921$, $r_0 = 1.59018A$ and $\underline{E} = -150.365$.

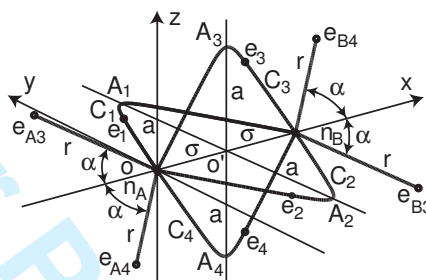
2) C_2 molecule with double bond. The structure of this molecule is shown in Fig. S2(b). This molecule contains four electrons, denoted by e_{A_3} , e_{A_4} , e_{B_3} and e_{B_4} , which do not participate to the bond. The geometrical structure of the molecule results from the system (S3)-(S5), which can be written in normalized form, as follows:

$$\underline{E}_b = -4\frac{Z_1^2}{n_1^2} - \frac{16(Z_{1M} + s_{1,2})}{\sqrt{9\underline{a}^2 + 25\underline{\sigma}^2}} + \frac{8}{\sqrt{\underline{\sigma}^2 + 4.5\underline{a}^2}} + \frac{Z_{nA}^2}{2\underline{\sigma}} \quad (S39)$$

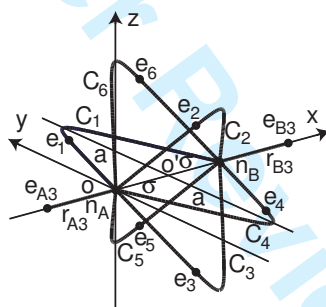
$$\underline{E}_b = -\frac{4n_1\sqrt{Z_{1M}}}{(\underline{a}^2 + \underline{\sigma}^2)^{3/4}} \quad (S40)$$



(a)



(b)



(c)

Figure S2. Structures of (a) simple, (b) double and (c) triple bonds in C_2 molecule.

$$E_b = -\frac{8(Z_{1M} + s_{1,2})}{\sqrt{\sigma^2 + a^2}} + \frac{1}{a} + \frac{2\sqrt{2}}{a} + \frac{Z_{nA}^2}{2\sigma} \quad (S41)$$

All the data necessary for calculations, together with the experimental data and the results of the calculations are given in Table S2. The angle α corresponds to the minimum value of the total energy. The normalized value of the total energy is calculated with the aid of equation (41) from paper. Taking into account the symmetry of the system (namely $\underline{E}_1 = \underline{E}_2 = \underline{E}_3 = \underline{E}_4$, $\underline{E}_{A3} = \underline{E}_{A4} = \underline{E}_{B3} = \underline{E}_{B4}$, $\underline{E}_{A1} = \underline{E}_{A2} = \underline{E}_{B1} = \underline{E}_{B2}$, $\underline{U}_{e_1e_3} = \underline{U}_{e_1e_4} = \underline{U}_{e_2e_3} = \underline{U}_{e_2e_4}$, $\underline{U}_{e_1n_B} = \underline{U}_{e_2n_B} = \underline{U}_{e_3n_A} = \underline{U}_{e_4n_A}$, $\underline{U}_{e_{A3}e_3} = \underline{U}_{e_{A4}e_4} = \underline{U}_{e_{B3}e_2} = \underline{U}_{e_{B4}e_1}$, $\underline{U}_{e_{A3}e_4} = \underline{U}_{e_{A4}e_3} = \underline{U}_{e_{B3}e_1} = \underline{U}_{e_{B4}e_2}$, $\underline{U}_{e_{A3}n_B} = \underline{U}_{e_{A4}n_B} = \underline{U}_{e_{B3}n_A} = \underline{U}_{e_{B4}n_A}$, $\underline{U}_{e_{A3}e_{B3}} = \underline{U}_{e_{A4}e_{B4}}$ and $\underline{U}_{e_{A3}e_{B4}} =$

Table S2. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of C_2 molecule in the case of double bond.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|---|---|
| $n_A(0, 0, 0, 0); n_B(2\sigma, 0, 0, 0)$ | $s_{1,A1} = s_{A3,A1} = s_{A4,A1} = 0.85505$ [28] |
| $e_1(\frac{3}{4}\sigma, \frac{3}{4}a, 0); e_2(\frac{3}{4}\sigma, -\frac{3}{4}a, 0)$ | $s_{A1,1} = s_{A1,A3} = s_{A1,A4} = 0.00269287$ [28] |
| $e_3(\frac{5}{4}\sigma, 0, \frac{3}{4}a); e_4(\frac{5}{4}\sigma, 0, -\frac{3}{4}a)$ | $s_{A1,A2} = .25$ |
| $e_{A3}(-d, \frac{\sqrt{2}}{2}b, \frac{\sqrt{2}}{2}b)$ | $s_{1,2} = \sqrt{\sigma^2 + a^2}/(4a)$ |
| $e_{A4}(-d, -\frac{\sqrt{2}}{2}b, -\frac{\sqrt{2}}{2}b)$ | $s_{1,A3} = s_{2,A4} = \frac{\sqrt{2}}{4\sqrt{1 + \frac{\sigma \cos \alpha - \frac{\sqrt{2}}{2}a \sin \alpha}{\sqrt{\sigma^2 + a^2}}}}$ |
| $e_{B3}(2\sigma + d, -\frac{\sqrt{2}}{2}b, -\frac{\sqrt{2}}{2}b)$ | $s_{1,A4} = s_{2,A3} = \frac{\sqrt{2}}{4\sqrt{1 + \frac{\sigma \cos \alpha + \frac{\sqrt{2}}{2}a \sin \alpha}{\sqrt{\sigma^2 + a^2}}}}$ |
| $e_{B4}(2\sigma + d, \frac{\sqrt{2}}{2}b, \frac{\sqrt{2}}{2}b)$ | $s_{A3,A4} = 1/(4 \sin \alpha)$ |
| $n_1 = n_{A3} = n_{A4} = 2$ | $Z_1 = Z_2 = Z_A - 2s_{1,A1} - s_{1,2} - s_{1,A3} - s_{1,A4}$ |
| $n_{A1} = n_{A2} = 1$ | $Z_{1M} = Z_{2M} = Z_A - 2 - s_{1,2} - s_{1,A3} - s_{1,A4}$ |
| $E_b = -12.1816$ | $Z_{A1} = Z_{A2} = Z_A - s_{A1,A2} - 4s_{A1,1}$ |
| $\sigma = 0.641059; a = 0.894043$ | $Z_{A3} = Z_A - 2s_{1,A1} - s_{1,A3} - s_{1,A4} - s_{A3,A4}$ |
| $\alpha = 41^\circ$ | $Z_{A3} = Z_{A4} = Z_{B3} = Z_{B4}$ |
| $S_{EiA} = 75.7133$ [35]; $D_0^0 = 0.45644$ [36] | $r = \frac{2}{Z_{A3}}(1 + \frac{e^2}{2})$ where $e = 0.98$ [28] |
| $r_0 = 1.35694$ A; $r_e = 1.243$ A [29] | $d = r \cos \alpha; \underline{d} = r \cos \alpha$ |
| | $Z_{nA} = Z_A - 2 - \frac{2(2\sigma)^2(2\sigma + d)}{[(2\sigma + d)^2 + b^2]^{3/2}}$ |
| | $Z_{nA} = Z_{nB}$ |

$U_{e_{A4}e_{B3}}$), this relation can be written for C_2 molecule with double bond, as follows:

$$\underline{E} = 4\underline{E}_1 + 4\underline{E}_{A3} + 4\underline{E}_{A1} + 4\underline{U}_{e_1e_3} + 4\underline{U}_{e_1n_B} + 4\underline{U}_{e_{A3}n_B} + 2\underline{U}_{e_{A3}e_{B3}} + \quad (S42)$$

$$2\underline{U}_{e_{A3}e_{B4}} + 4\underline{U}_{e_{A3}e_3} + 4\underline{U}_{e_{A3}e_4} + \underline{U}_{n_A n_B} + 2\underline{E}_{m1s} = -4\frac{Z_1^2}{n_1^2} - 4\frac{Z_{A3}^2}{n_{A3}^2} -$$

$$4\frac{Z_{A1}^2}{n_{A1}^2} + \frac{4}{\sqrt{(\frac{1}{2}\sigma)^2 + 2(\frac{3}{4}a)^2}} - \frac{4(Z_A - 2)}{\sqrt{(\frac{5}{4}\sigma)^2 + (\frac{3}{4}a)^2}} - \frac{4(Z_A - 2)}{\sqrt{(\underline{d} + 2\sigma)^2 + b^2}} +$$

$$\frac{1}{\sqrt{(\underline{d} + \sigma)^2 + b^2}} + \frac{1}{\underline{d} + \sigma} + \frac{4}{\sqrt{(\underline{d} + \frac{5}{4}\sigma)^2 + (\frac{\sqrt{2}}{2}b)^2 + (\frac{3}{4}a - \frac{\sqrt{2}}{2}b)^2}} +$$

$$\frac{4}{\sqrt{(\underline{d} + \frac{5}{4}\sigma)^2 + (\frac{\sqrt{2}}{2}b)^2 + (\frac{3}{4}a + \frac{\sqrt{2}}{2}b)^2}} + \frac{(Z_A - 2)^2}{2\sigma} + 2\frac{Z_{A1}^{3/2}}{8n_{A1}^3}$$

From this relation, we obtain $\underline{E} = -151.148$.

3) C_2 molecule with triple bond. The structure of this molecule is shown in Fig. S2(c). This molecule contains two electrons, denoted by e_{A3} and e_{B3} , which do not participate to the bond. The geometrical structure of the molecule results from the system (S6)-(S8), which can be written in normalized form, as follows:

$$\underline{E}_b = -6\frac{Z_1^2}{n_1^2} - \frac{24(Z_{1M} + 2s_{1,2})}{\sqrt{9a^2 + 25\sigma^2}} + \frac{6}{\sqrt{\sigma^2 + 9a^2}} + \frac{24}{\sqrt{4\sigma^2 + 9a^2}} + \frac{Z_{nA}^2}{2\sigma} \quad (S43)$$

$$\underline{E}_b = -\frac{6n_1\sqrt{Z_{1M}}}{(a^2 + \sigma^2)^{3/4}} \quad (S44)$$

Table S3. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of C_2 molecule in the case of triple bond.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|--|---|
| $n_A(0, 0, 0,); n_B(2\sigma, 0, 0,)$ | $s_{1,A1} = s_{A3,A1} = 0.85505$ [28] |
| $e_1\left(\frac{3}{4}\sigma, \frac{3}{4}a, 0\right)$ | $s_{A1,1} = s_{A1,A3} = 0.00269287$ [28] |
| $e_2\left(\frac{3}{4}\sigma, -\frac{3}{4}\cdot\frac{1}{2}a, \frac{3}{4}\cdot\frac{\sqrt{3}}{2}a\right)$ | $s_{A1,A2} = .25$ |
| $e_3\left(\frac{3}{4}\sigma, -\frac{3}{4}\cdot\frac{1}{2}a, -\frac{3}{4}\cdot\frac{\sqrt{3}}{2}a\right)$ | $s_{1,2} = s_{2,3} = s_{1,3} = \frac{\sqrt{2}}{4\sqrt{1-\frac{\sigma^2-\frac{1}{2}a^2}{\sigma^2+a^2}}}$ |
| $e_4\left(\frac{5}{4}\sigma, -\frac{3}{4}a, 0\right)$ | $s_{1,A3} = s_{2,A3} = s_{3,A3} = \frac{\sqrt{2}}{4\sqrt{1+\frac{\frac{5}{4}\sigma^2}{\sigma^2+a^2}}}$ |
| $e_5\left(\frac{5}{4}\sigma, \frac{3}{4}\cdot\frac{1}{2}a, -\frac{3}{4}\cdot\frac{\sqrt{3}}{2}a\right)$ | $Z_1 = Z_2 = Z_3 = Z_A - 2s_{1,A1} - 2s_{1,2} - s_{1,A3}$ |
| $e_6\left(\frac{5}{4}\sigma, \frac{3}{4}\cdot\frac{1}{2}a, \frac{3}{4}\cdot\frac{\sqrt{3}}{2}a\right)$ | $Z_{1M} = Z_{2M} = Z_{3M} = Z_A - 2 - 2s_{1,2} - s_{1,A3}$ |
| $e_{A3}(-r_{A3}, 0, 0); e_{B3}(2\sigma + r_{A3}, 0, 0)$ | $Z_{A1} = Z_{A2} = Z_A - s_{A1,A2} - 4s_{A1,1}$ |
| $n_1 = n_{A3} = 2; n_{A1} = n_{A2} = 1$ | $Z_{A3} = Z_{B3} = Z_A - 2s_{1,A1} - 3s_{1,A3}$ |
| $E_B = -17.1499$ | $r_{A3} = \frac{2}{Z_{A3}}\left(1 + \frac{e^2}{2}\right)$ where $e = 0.98$ [28] |
| $\sigma = 0.639379; a = 0.942817$ | $Z_{nA} = Z_{nB} = Z_A - 2 - \frac{(2\sigma)^2}{(2\sigma+r_{A3})^2}$ |
| $r_0 = 1.35339 \text{ \AA}$ | |

$$E_b = -\frac{12(Z_{1M} + 2s_{1,2})}{\sqrt{\sigma^2 + a^2}} + \frac{6}{\sqrt{3}a} + \frac{6}{a} + \frac{3}{2a} + \frac{Z_{nA}^2}{2\sigma} \quad (S45)$$

All the experimental and theoretical data, excepting the total energy, are given in Table S3. Taking into account the symmetry of the system (namely $E_1 = E_2 = \dots = E_6$, $E_{A3} = E_{B3}$, $E_{A1} = E_{A2} = E_{B1} = E_{B2}$, $U_{e_1e_4} = U_{e_2e_5} = U_{e_3e_6}$, $U_{e_1e_5} = U_{e_5e_3} = U_{e_3e_4} = U_{e_4e_2} = U_{e_2e_6} = U_{e_6e_1}$, $U_{e_{A3}n_B} = U_{e_{B3}n_A}$, $U_{e_in_B} = U_{e_jn_A}$, $U_{e_{A3}e_j} = U_{e_{B3}e_i}$, where $i = 1, 2, 3$ and $j = 3, 4, 5$), the total energy results from the following relation:

$$\begin{aligned} E = & 6E_1 + 2E_{A3} + 4E_{A1} + 3U_{e_1e_4} + 6U_{e_1e_5} + 6U_{e_1n_B} + 6U_{e_{A3}e_4} + (S46) \\ & 2U_{e_{A3}n_B} + U_{e_{A3}e_{B3}} + U_{n_An_B} + 2E_{m1s} = -6\frac{Z_1^2}{n_1^2} - 2\frac{Z_{A3}^2}{n_{A3}^2} - 4\frac{Z_{A1}^2}{n_{A1}^2} + \\ & \frac{3}{\sqrt{\left(\frac{1}{2}\sigma\right)^2 + \left(\frac{3}{4}a\right)^2}} + \frac{6}{\sqrt{\left(\frac{1}{2}\sigma\right)^2 + \left(\frac{3}{4}a\right)^2}} - \frac{6(Z_A - 2)}{\sqrt{\left(\frac{5}{4}\sigma\right)^2 + \left(\frac{3}{4}a\right)^2}} + \\ & \frac{6}{\sqrt{\left(r_{A3} + \frac{5}{4}\sigma\right)^2 + \left(\frac{3}{4}a\right)^2}} - \frac{2(Z_A - 2)}{r_{A3} + 2\sigma} + \frac{1}{2r_{A3} + 2\sigma} + \frac{(Z_A - 2)^2}{2\sigma} + 2\frac{Z_{A1}^3}{8n_{A1}^3} \end{aligned}$$

From this relation, we obtain $E = -150.923$.

If we compare the three above values of the total energy, we will see that the energy corresponding to the double bond is minimum, resulting that the real bond of the C_2 molecule is double. This result is identical to that obtained by pure quantum evaluations (see, for example pag. 97 of Ref. [31]). In Table 1 from paper it is shown the value of E corresponding to the C_2 molecule with double bond, together with E_{HF} and E_{exp} . The analysis of Table 1 from paper shows that the relative errors corresponding to E and E_{HF} are, respectively, equal to 0.005 and 0.007.

A comparison between, on one hand, the symmetry properties of the systems composed of the C atoms and the electrons which do not participate to the bond [see Figs. S2(a), S2(b) and S2(c)], and, on the other hand, the experimental sym-

metry properties of the ethane, ethylene and acetylene molecules, namely C_2H_6 , C_2H_4 and C_2H_2 (see Ref. [29]), shows that these properties are identical. For example, all these structures have a center of symmetry, the configurations of C_2H_4 and of $n_A, n_B, e_{A3}, e_{A4}, e_{B3}$ and e_{B4} , in the case of double bond, are plane, or the configurations of C_2H_2 and of n_A, n_B, e_{A3} and e_{B3} , in the case of triple bond, are linear. This explains why adding 6, 4 and, respectively, 2 hydrogen atoms to the structures of C_2 with simple, double and triple bonds leads to the formation of the C_2H_6 , C_2H_4 and, respectively, C_2H_2 molecules. Also, our calculations explain the property that the length of the bond decreases with the increasing of the bond order.

S2.3. LiH molecule

We analyze now the following molecules: LiH , BeH , BH and CH . The model of ionic bond is in agreement with the experimental data for LiH , BeH , while the model of covalent bond is in agreement with the experimental data only for BH and CH . For example, if we apply the covalent model in the case of LiH , it will lead to a symmetrical molecule, for which $\sigma_1 = \sigma_2$, which is in strong disagreement with the fact that this molecule has a big electrical dipole moment.

The structure of the LiH molecule molecule is shown in Fig. 3(a) from paper. This molecule contains only valence electrons that participate to the bond. The geometrical structure of the molecule results from the system (S15), (S16), (S23), (S24) and (S27), which can be written in normalized form as follows:

$$\underline{E}_b = -2 \frac{Z_{1(A)}^2}{n_{1(A)}^2} - \frac{8 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{9a^2 + (\sigma_1 + 4\sigma_2)^2}} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S47)$$

$$\underline{E}_b = -2 \frac{Z_{1(B)}^2}{n_{1(B)}^2} - \frac{8 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{9a^2 + (\sigma_2 + 4\sigma_1)^2}} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S48)$$

$$\underline{E}_b = - \frac{2n_{1(A)} \sqrt{Z_{1M(A)}}}{(\sigma_1^2 + a^2)^{\frac{3}{4}} t_{cA}} \quad (S49)$$

$$\underline{E}_b = - \frac{2n_{1(B)} \sqrt{Z_{1M(B)}}}{(\sigma_2^2 + a^2)^{\frac{3}{4}} t_{cB}} \quad (S50)$$

$$\underline{E}_b = - \frac{2 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{\sigma_1^2 + a^2}} - \frac{2 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{\sigma_2^2 + a^2}} + \frac{1}{2a} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} + 2T_m \quad (S51)$$

where

$$t_{cA} = \frac{2}{\pi a_{cA}^{3/2}} (\arcsin \sqrt{a_{cA}} - \sqrt{a_{cA}} \sqrt{1 - a_{cA}}) \quad (S52)$$

Table S4. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of *LiH* molecule.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|---|---|
| $n_A(0, 0, 0,); n_B(\sigma_1 + \sigma_2, 0, 0,)$ | $s_{1,A1} = 0.854942$ [27] |
| Phase A: | $s_{A1,1} = 0.0013792$ [27] |
| $e_1 [\frac{3}{4}\sigma_1, \frac{3}{4}a, 0]; e_2 [\frac{3}{4}\sigma_1, -\frac{3}{4}a, 0]$ | $s_{A1,A2} = 0.25$ |
| Phase B: | $s_{1,2(A)} = \sqrt{\sigma_1^2 + a^2}/(4a)$ |
| $e_1 [\sigma_1 + \frac{1}{4}\sigma_2, \frac{3}{4}a, 0]; e_2 [\sigma_1 + \frac{1}{4}\sigma_2, -\frac{3}{4}a, 0]$ | $s_{1,2(B)} = \sqrt{\sigma_2^2 + a^2}/(4a)$ |
| $n_{1(A)} = n_{2(A)} = 2; n_{1(B)} = n_{2(B)} = 1$ | $Z_{1(A)} = Z_A - 2s_{1,A1} - s_{1,2(A)}$ |
| $n_{A1} = n_{A2} = 1$ | $Z_{1M(A)} = Z_A - 2 - s_{1,2(A)}$ |
| $E_b = -1.65659$ | $Z_{A1} = Z_A - s_{A1,A2} - 2s_{A1,1}$ |
| $\sigma_1 = 1.47713; \sigma_2 = 0.267425$ | $Z_{1(B)} = Z_B - s_{1,2(B)}$ |
| $a = 1.18038; T_m = 0.0284159$ | $Z_{1M(B)} = Z_B - s_{1,2(B)}$ |
| $S_{EiA} = 14.9563$ [35]; $S_{EiB} = 1$ | $Z_{nA} = Z_A - 2$ |
| $D_0^0 = 0.178511$ [36] | $Z_{nB} = Z_B$ |
| $r_0 = 1.84635$ A; $r_e = 1.5957$ A [29] | |
| $\mu_e = 6.1491$ D | |
| $\mu_{eHF} = (4.839, 6.083)$ D [29] | |

with

$$a_{cA} = 1 - \frac{T_m \sqrt{\sigma_1^2 + a^2}}{Z_{1M(A)}} \tag{S53}$$

and

$$t_{cB} = \frac{2}{\pi a_{cB}^{3/2}} (\arcsin \sqrt{a_{cB}} - \sqrt{a_{cB}} \sqrt{1 - a_{cB}}) \tag{S54}$$

with

$$a_{cB} = 1 - \frac{T_m \sqrt{\sigma_2^2 + a^2}}{Z_{1M(B)}} \tag{S55}$$

The system (S47)-(S51) has 5 equations with 5 unknowns, which are E_b , σ_1 , σ_2 , a and T_m .

We follow again the algorithm presented in Section 4 from paper and calculate the screening coefficients, order numbers and solve the system (S47)-(S51). All these values are given in Table S4. The screening coefficients between the 1s electrons and the e_1 and e_2 electrons, namely $s_{1,A1}$ and $s_{A1,1}$, when the system is in the phase *A* are identical, respectively to s_{31e} and s_{13e} , which have been calculated in Ref. [27] for the $1s^2 2s$ state of lithium atom. The coefficients $s_{A1,A2}$, $s_{1,2(A)}$ and $s_{1,2(B)}$ are calculated with equation (9). Since 2s and 1s valence electrons participate to the bond, respectively, in phases *A* and *B*, we have $n_{1(A)} = n_{1(B)} = 2$ and $n_{2(A)} = n_{2(B)} = 1$.

Since in this case E_b has the significance of the total energy from which the energies of the 1s electrons are subtracted, we have:

$$E = E_b + 2E_{A1} + E_{m1s} = E_b - 2 \frac{Z_{A1}^2}{n_{A1}^2} + \frac{Z_{A1}^{3/2}}{8n_{A1}^3} \tag{S56}$$

The normalized value of the total energy, together with the best two values of E_{HF} ,

obtained from Ref. [29], and the experimental value, \underline{E}_{exp} , given by

$$\underline{E}_{exp} = -\underline{S}_{EiA} - \underline{S}_{EiB} - \underline{D}_0^0 \quad (S57)$$

are presented in Table 1 of the paper. The values of S_{EiA} and S_{EiB} , which are the sum of the ionization energies of the two atoms, are taken from Ref. [35], while D_0^0 is taken from Ref. [36]. The analysis of Table 1 from paper shows that the relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, equal to 0.003 and 0.010.

In this case we have

$$r_0 = \sigma_1 + \sigma_2 \quad (S58)$$

The values of r_0 and r_e , which is taken from Ref. [29], are given in angstroms in Table S4.

The electric dipole moment of the molecule is denoted by $\bar{\mu}_e$. It is calculated when the electrons are situated at the points A_1 and A_2 , which are the average positions on the molecular C_a curves taking into account the convention that the positive sense of the vector $\bar{\mu}_e$ is from the negative charge to the positive charge. In this case, the sign convention is the same as that from Ref. [29]. The expression of μ_e in the case of the LiH molecule, when the result is given in debyes (D), is

$$\mu_e = -5.08315[-2\sigma_1 + Z_B(\sigma_1 + \sigma_2)] \quad (S59)$$

The theoretical value, calculated with equation (S59), and the experimental value, taken from CCCBDB [29], are equal, respectively, to 6.1491 D and 5.88 D. The CCCBDB does not contain experimental values of the electric dipole moment in the cases of the molecules BeH , BH and CH . In Table S4 we compare our theoretical values with the theoretical values of the electric dipole moment, calculated using the Hartree-Fock method, which are taken from Ref. [29]. The analysis of the data from Ref. [29] shows that the dispersion of the theoretical values of the electric dipole moments, in the case of a given system, is very high. For this reason, in Table S4 we give the domain of the theoretical values of the dipole moments, taken from Ref. [29], and computed using the Hartree-Fock method. These values are denoted by μ_{eHF} .

S2.4. BeH molecule

The structure of this molecule is shown in Fig. S3(a). This molecule contains one electron, denoted by e_{A3} which do not participate to the bond. The distance r_{A3} varies slightly when the bond electrons move in the phases A and B . Since the bond electrons are in the majority of the time far from nucleus, we consider an average value, approximately equal to that in the case of the isolated atom, which is given by the relation $\tilde{r}_{A3} = 3/(Z_A - 2s_{A3,A1})$. In this case the value of E_b is slightly different in the two phases, being equal, respectively, to E_{b1} and E_{b2} , in the phases A and B . The system (S47)-(S51) becomes

$$\underline{E}_{b1} = -2 \frac{Z_{1(A)}^2}{n_{1(A)}^2} - \frac{8 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{9a^2 + (\sigma_1 + 4\sigma_2)^2}} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S60)$$

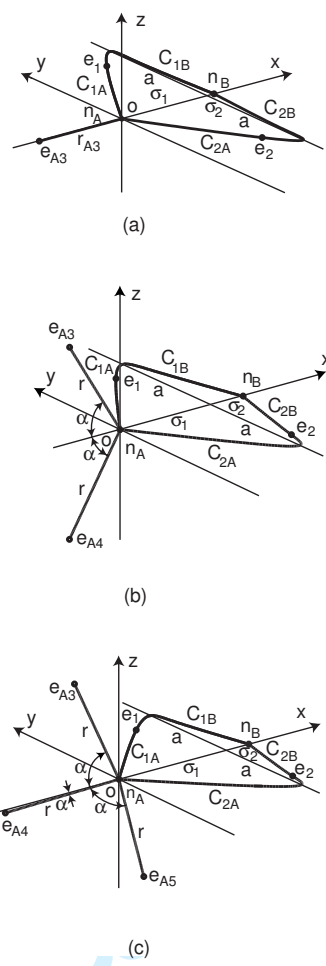


Figure S3. Structures of (a) *BeH*, (b) *BH* and (c) *CH* molecules.

$$\underline{E}_{b2} = -2 \frac{Z_{1(B)}^2}{n_{1(B)}^2} - \frac{8 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{9a^2 + (\sigma_2 + 4\sigma_1)^2}} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S61)$$

$$\underline{E}_{b1} = - \frac{2n_{1(A)}\sqrt{Z_{1M(A)}}}{(\sigma_1^2 + a^2)^{\frac{3}{4}} t_{cA}} \quad (S62)$$

$$\underline{E}_{b2} = - \frac{2n_{1(B)}\sqrt{Z_{1M(B)}}}{(\sigma_2^2 + a^2)^{\frac{3}{4}} t_{cB}} \quad (S63)$$

$$\frac{1}{2} (\underline{E}_{b1} + \underline{E}_{b2}) = - \frac{2 [Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{\sigma_1^2 + a^2}} - \frac{2 [Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{\sigma_2^2 + a^2}} + \frac{1}{2a} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} + 2T_m \quad (S64)$$

where t_{cA} and t_{cB} are calculated, respectively, with the equations (S52) and (S54). This system has 5 equations with 5 unknowns, which are E_{b1} , E_{b2} , σ_1 , σ_2 and a . The value of T_m is very small; it is chosen from the condition of minimum value of the total energy. All the parameters and expressions which are used in calculations

Table S5. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of *BeH* molecule.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|---|---|
| $n_A(0, 0, 0); n_B(\underline{\sigma}_1 + \underline{\sigma}_2, 0, 0)$ | $s_{1,A1} = s_{A3,A1} = 0.83882$ [27] |
| Phase A: | $s_{A1,1} = s_{A1,A3} = 0.00221203$ [27] |
| $e_1 [\frac{3}{4}\underline{\sigma}_1, \frac{3}{4}\underline{a}, 0]; e_2 [\frac{3}{4}\underline{\sigma}_1, -\frac{3}{4}\underline{a}, 0]$ | $s_{A1,A2} = 0.25$ |
| Phase B: | $s_{1,2(A)} = \sqrt{\underline{\sigma}_1^2 + \underline{a}^2}/(4\underline{a})$ |
| $e_1 [\underline{\sigma}_1 + \frac{1}{4}\underline{\sigma}_1, \frac{3}{4}\underline{a}, 0]; e_2 [\underline{\sigma}_1 + \frac{1}{4}\underline{\sigma}_1, -\frac{3}{4}\underline{a}, 0]$ | $s_{1,A3} = (\sqrt{2}/4)/\sqrt{1 + \frac{\underline{\sigma}_1}{\sqrt{\underline{\sigma}_1^2 + \underline{a}^2}}}$ |
| $e_3 (-\tilde{r}_{A3}, 0, 0)$ | $s_{1,2(B)} = \sqrt{\underline{\sigma}_2^2 + \underline{a}^2}/(4\underline{a})$ |
| $n_{1(A)} = n_{2(A)} = 2; n_{1(B)} = n_{2(B)} = 1$ | $Z_{1(A)} = Z_A - 2s_{1,A1} - s_{1,2(A)} - s_{1,A3}$ |
| $n_{A1} = n_{A2} = 1; n_{A3} = 2$ | $Z_{1M(A)} = Z_A - 2 - s_{1,2(A)} - s_{1,A3}$ |
| $\underline{E}_{b1} = -2.51578; \underline{E}_{b2} = 2.11007$ | $Z_{A1} = Z_A - s_{A1,A2} - 3s_{A1,1}$ |
| $\underline{\sigma}_1 = 1.34462; \underline{\sigma}_2 = 0.0149424$ | $Z_{A3} = Z_A - 2s_{1,A1} - 2s_{1,A3}$ |
| $\underline{a} = 0.979054; \underline{T}_m = .015$ | $Z_{1(B)} = Z_B - s_{1,2(B)}$ |
| $\underline{S}_{EiA} = 29.3377$ [35]; $\underline{S}_{EiB} = 1$ | $Z_{1M(B)} = Z_B - s_{1,2(B)}$ |
| $\underline{D}_0^0 = 0.1495$ [36] | $\tilde{r}_{A3} = \frac{3}{Z_A - 2s_{A3,A1}}$ |
| $r_0 = 1.4389$ A; $r_e = 1.3426$ A [29] | $Z_{nA} = Z_A - 2 - \frac{(\underline{\sigma}_1 + \underline{\sigma}_2)^2}{(\underline{\sigma}_1 + \underline{\sigma}_2 + \tilde{r}_{A3})^2}$ |
| $\mu_e = 0.192613$ D | $Z_{nB} = Z_B$ |
| $\mu_{eHF} = (0.232, 0.595)$ D | |

are shown in Table S5. The screening coefficients between the 1s electrons and the e_1, e_2 and e_{A3} electrons are identical to s_{31e} and s_{13e} , which have been calculated in Ref. [27] for the $1s^2 2s^2$ state of beryllium atom. In the case of heteronuclear molecules, the values of Z_{nA} and Z_{nB} are calculated with equation (39) from paper in which, instead of $(2\sigma)^2$, we consider the expression $(\sigma_1 + \sigma_2)^2$.

The normalized value of the total energy is calculated with the aid of equation (41) from paper, which can be written for *BeH* molecule, when the electrons are situated at points A_1 and A_2 , taking into account the symmetry of the system (namely $\underline{U}_{e_1 n_A} = \underline{U}_{e_2 n_A}$ and $\underline{U}_{e_1 n_B} = \underline{U}_{e_2 n_B}$), as follows:

$$\underline{E} = \underline{E}_{A3} + 2\underline{E}_{A1} + 2\underline{U}_{e_1 n_A} + 2\underline{U}_{e_1 n_B} + \underline{U}_{e_1 e_2} + \underline{U}_{e_{A3} n_B} + \underline{U}_{n_A n_B} + \underline{E}_{m1s} = (S65)$$

$$- \frac{Z_{A3}^2}{n_{A3}^2} - 2 \frac{Z_{A1}^2}{n_{A1}^2} - \frac{2[Z_{1M(A)} + s_{1,2(A)}]}{\sqrt{\underline{\sigma}_1^2 + \underline{a}^2}} - \frac{2[Z_{1M(B)} + s_{1,2(B)}]}{\sqrt{\underline{\sigma}_2^2 + \underline{a}^2}} + \frac{1}{2\underline{a}} -$$

$$\frac{Z_B}{\underline{\sigma}_1 + \underline{\sigma}_2 + \tilde{r}_{A3}} + \frac{(Z_A - 2) Z_B}{\underline{\sigma}_1 + \underline{\sigma}_2} + \frac{Z_{A1}^{3/2}}{8n_{A1}^3} + 2\underline{T}_m$$

The values of \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} are given in Table 1 of paper. The relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, equal to 0.002 and 0.006. The electric dipole moment is given by the following relation:

$$\mu_e = -5.08315[-2\underline{\sigma}_1 + Z_B(\underline{\sigma}_1 + \underline{\sigma}_2) + \tilde{r}_{A3}] \quad (S66)$$

The values of r_0, r_e, μ_e and the domain of the values of μ_{eHF} [29] are shown in Table S5.

S2.5. BH molecule

The structure of this molecule is shown in Fig. S3(b). This molecule contains two electrons, denoted by e_{A3} and e_{A4} which do not participate to the bond. The geometrical structure of the molecule results from the system (S33), (S36) and

Table S6. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of *BH* molecule.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|--|--|
| $n_A(0, 0, 0); n_B(\sigma_1 + \sigma_2, 0, 0)$ | $s_{1,A1} = s_{A3,A1} = 0.862983$ [28] |
| $e_1[\frac{3}{4}\sigma_1, \frac{3}{4}a, 0]; e_2[\frac{\sigma_1}{4} + \frac{1}{4}\sigma_2, -\frac{3}{4}a, 0]$ | $s_{A1,1} = s_{A1,A3} = .00246735$ [28] |
| $e_{A3}(-d, 0, b); e_{A4}(-d, 0, -b)$ | $s_{A1,A2} = 0.25$ |
| $n_{1(A)} = n_{2(A)} = 2; n_{1(B)} = n_{2(B)} = 1$ | $s_{1,A3} = (\sqrt{2}/4) / \sqrt{1 + \frac{\sigma_1 \cos \alpha}{\sqrt{\sigma_1^2 + a^2}}}$ |
| $n_{A1} = n_{A2} = 1; n_{A3} = n_{A4} = 2$ | $s_{A3,A4} = 1 / (4 \sin \alpha)$ |
| $E_b = -3.19537$ | $Z_{1(A)} = Z_{2(A)} = Z_A - 2s_{1,A1} - 2s_{1,A3}$ |
| $\sigma_1 = 0.888324; \sigma_2 = 0.261022$ | $Z_{1M(A)} = Z_{2M(A)} = Z_A - 2 - 2s_{1,A3}$ |
| $a = 0.922599$ | $Z_{A1} = Z_A - s_{A1,A2} - 3s_{A1,1}$ |
| $\alpha = 63^\circ$ | $Z_{A3} = Z_A - 2s_{1,A1} - s_{1,A3} - s_{A3,A4}$ |
| $S_{EiA} = 49.3177$ [35]; $S_{EiB} = 1$ | $Z_{A4} = Z_{A3}$ |
| $D_0^0 = 0.251372$ [36] | $Z_{1(B)} = Z_{2(B)} = Z_B$ |
| $r_0 = 1.21642 \text{ \AA}; r_e = 1.2324 \text{ \AA}$ [29] | $Z_{1M(B)} = Z_{2M(B)} = Z_B$ |
| $\mu_e = -1.86638 \text{ D}$ | $r_{A3} = \frac{2}{Z_{A3}}(1 + \frac{e^2}{2})$ where $e = 0.97$ [28] |
| $\mu_{eHF} = (-0.994, -1.814) \text{ D}$ [29] | $d = r_{A3} \cos \alpha; b = r_{A3} \sin \alpha$ |
| | $Z_{nA} = Z_A - 2 - \frac{2(\sigma_1 + \sigma_2)^2(\sigma_1 + \sigma_2 + d)}{[(\sigma_1 + \sigma_2)^2 + b^2]^{3/2}}$ |
| | $Z_{nB} = Z_B$ |

(S37), which can be written in normalized form, as follows:

$$E_b = -\frac{Z_{1(A)}^2}{n_{1(A)}^2} - \frac{Z_{2(B)}^2}{n_{2(B)}^2} - \frac{4Z_{1M(B)}}{\sqrt{9a^2 + (\sigma_1 + 4\sigma_2)^2}} - \frac{4Z_{1M(A)}}{\sqrt{9a^2 + (\sigma_2 + 4\sigma_1)^2}} + \frac{4}{\sqrt{36a^2 + (\sigma_1 + \sigma_2)^2}} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S67)$$

$$E_b = -\frac{[n_{1(A)} + n_{1(B)}] \sqrt{Z_{1M(A)}}}{(a^2 + \sigma_1^2)^{3/4}} \quad (S68)$$

$$E_b = -\frac{[n_{1(A)} + n_{1(B)}] \sqrt{Z_{1M(B)}}}{(a^2 + \sigma_2^2)^{3/4}} \quad (S69)$$

$$E_b = -\frac{2Z_{1M(A)}}{\sqrt{\sigma_1^2 + a^2}} - \frac{2Z_{1M(B)}}{\sqrt{\sigma_2^2 + a^2}} + \frac{1}{2a} + \frac{Z_{nA}Z_{nB}}{\sigma_1 + \sigma_2} \quad (S70)$$

The system (S67)-(S70) has 4 equations with 4 unknowns, which are E_b , σ_1 , σ_2 and a . The expressions of the screening coefficients, order numbers and quantum numbers are given in Table S6. The screening coefficients between the 1s electrons and the e_1 , e_2 , e_{A3} and e_{A4} electrons, namely $s_{1,A1}$, $s_{A1,1}$, $s_{A3,A1}$, $s_{A1,A3}$, and so on, are identical, respectively to s_{31e} and s_{13e} , which have been calculated in Ref. [28] for the boron atom. The angle α is a parameter. We perform the calculation for a lot of values of this angle and choose the value for which the total energy is minimum. This value is given in Table S6.

Taking into account the symmetry of the system, the total energy results from

the following relation [see Fig. S3(b)]:

$$\underline{E} = \underline{E}_1 + \underline{E}_2 + 2\underline{E}_{A3} + 2\underline{E}_{A1} + \underline{U}_{e_1e_2} + \underline{U}_{e_1n_B} + \underline{U}_{e_2n_A} + 2\underline{U}_{e_{A3}e_2} + \quad (S71)$$

$$2\underline{U}_{e_{A3}n_B} + \underline{U}_{n_An_B} + 2\underline{E}_{m1s} = -\frac{Z_{1(A)}^2}{n_{1(A)}^2} - \frac{Z_{2(B)}^2}{n_{2(B)}^2} - 2\frac{Z_{A3}^2}{n_{A3}^2} - 2\frac{Z_{A1}^2}{n_{A1}^2} +$$

$$\frac{1}{\sqrt{(\frac{1}{4}\sigma_1 + \frac{1}{4}\sigma_2)^2 + (\frac{3}{2}a)^2}} - \frac{Z_B}{\sqrt{(\frac{1}{4}\sigma_1 + \sigma_2)^2 + (\frac{3}{4}a)^2}} -$$

$$\frac{Z_A - 2}{\sqrt{(\frac{1}{4}\sigma_2 + \sigma_1)^2 + (\frac{3}{4}a)^2}} + \frac{2}{\sqrt{(\sigma_1 + \frac{1}{4}\sigma_2 + d)^2 + (\frac{3}{4}a)^2 + b^2}} -$$

$$\frac{2Z_B}{\sqrt{(\sigma_1 + \sigma_2 + d)^2 + b^2}} + \frac{(Z_A - 2)Z_B}{\sigma_1 + \sigma_2} + \frac{Z_{A1}^{3/2}}{8n_{A1}^3}$$

The values of \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} are given in Table 1 of paper. The relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, equal to 0.002 and 0.006. The electric dipole moment is given by the following relation:

$$\mu_e = -5.08315[-2\sigma_1 + Z_B(\sigma_1 + \sigma_2) + 2d] \quad (S72)$$

The values of r_0 , r_e , μ_e and the domain of the values of μ_{eHF} [29] are shown in Table S6.

S2.6. CH molecule

The structure of this molecule is shown in Fig. S3(c). This molecule contains three electrons, denoted by e_{A3} , e_{A4} and e_{A5} which do not participate to the bond. The geometrical structure of the molecule results from the system (S67)-(S70). All the data necessary in calculations, together with the results of the calculations, are given in Table S7.

The normalized value of the total energy is calculated with the aid of equation

Table S7. Coordinates of average positions of particles, effective screening coefficients, effective order numbers and solutions of the equations describing the behavior of *CH* molecule.

| Particle coordinates; quantum numbers Calculated and experimental values | Screening coefficients; order numbers |
|--|--|
| $n_A(0, 0, 0); n_B(\sigma_1 + \sigma_2, 0, 0)$ | $s_{1,A1} = 0.85505$ [28] |
| $e_1 [\frac{3}{4}\sigma_1, \frac{3}{4}a, 0]; e_2 [\sigma_1 + \frac{1}{4}\sigma_2, -\frac{3}{4}a, 0]$ | $s_{A1,1} = 0.00269287$ [28] |
| $e_{A3}(-d, 0, b)$ | $s_{1,A1} = s_{A3,A1} = s_{A4,A1} = s_{A5,A1}$ |
| $e_{A4}(-d, \frac{\sqrt{3}}{2}b, -\frac{1}{2}b)$ | $s_{A1,1} = s_{A1,A3} = s_{A1,A4} = s_{A1,A5}$ |
| $e_{A5}(-d, -\frac{\sqrt{3}}{2}b, -\frac{1}{2}b)$ | $s_{A1,A2} = 0.25$ |
| $n_{1(A)} = n_{2(A)} = 2; n_{1(B)} = n_{2(B)} = 1$ | $s_{1,A3} = \frac{\sqrt{2}}{4\sqrt{1 + \frac{\sigma_1 \cos \alpha}{\sqrt{\sigma_1^2 + a^2}}}}$ |
| $n_{A1} = n_{A2} = 1; n_{A3} = n_{A4} = n_{A5} = 2$ | $s_{1,A4} = \frac{\sqrt{2}}{4\sqrt{1 + \frac{\sigma_1 \cos \alpha - \frac{\sqrt{3}}{2}a \sin \alpha}{\sqrt{\sigma_1^2 + a^2}}}}$ |
| $\underline{E}_b = -4.29182$ | $s_{1,A5} = \frac{\sqrt{2}}{4\sqrt{1 + \frac{\sigma_1 \cos \alpha + \frac{\sqrt{3}}{2}a \sin \alpha}{\sqrt{\sigma_1^2 + a^2}}}}$ |
| $\sigma_1 = 0.840475; \sigma_2 = 0.175936$ | $s_{A3,A4} = \frac{1}{2\sqrt{3} \sin \alpha}$ |
| $a = 0.767725$ | $Z_{1(A)} = Z_A - 2s_{1,A1} - s_{1,A3} - s_{1,A4} - s_{1,A5}$ |
| $\alpha = 67^\circ$ | $Z_{1M(A)} = Z_A - 2 - s_{1,A3} - s_{1,A4} - s_{1,A5}$ |
| $\underline{S}_{EiA} = 75.7133$ [35]; $\underline{S}_{EiB} = 1$ | $Z_{1(A)} = Z_{2(A)}; Z_{1M(A)} = Z_{2M(A)}$ |
| $\underline{D}_0^0 = 0.254679$ [36] | $Z_{A1} = Z_A - s_{A1,A2} - 4s_{A1,1}$ |
| $r_0 = 1.07572$ A; $r_e = 1.1199$ A [29] | $Z_{A3} = Z_A - 2s_{1,A1} - s_{1,A3} - 2s_{A3,A4}$ |
| $\mu_e = -1.91195$ D | $Z_{A4} = Z_A - 2s_{1,A1} - s_{1,A4} - 2s_{A3,A4}$ |
| $\mu_{eHF} = (-1.069, -1.666)$ D [29] | $Z_{A5} = Z_A - 2s_{1,A1} - s_{1,A5} - 2s_{A3,A4}$ |
| | $Z_{1(B)} = Z_{2(B)} = Z_B; Z_{1M(B)} = Z_{2M(B)} = Z_B$ |
| | $e = .98$ [28] |
| | $r = \left(\frac{1}{Z_{A3}} + \frac{1}{Z_{A4}} + \frac{1}{Z_{A5}}\right) \frac{2}{3} \left(1 + \frac{e^2}{2}\right)$ |
| | $d = r \cos \alpha; b = r \sin \alpha$ |
| | $Z_{nA} = Z_A - 2 - \frac{3(\sigma_1 + \sigma_2)^2(\sigma_1 + \sigma_2 + d)}{[(\sigma_1 + \sigma_2 + d)^2 + b^2]^{3/2}}$ |
| | $Z_{nB} = Z_B$ |

(41), which can be written as follows:

$$\underline{E} = \underline{E}_1 + \underline{E}_2 + \underline{E}_{A3} + \underline{E}_{A4} + \underline{E}_{A5} + 2\underline{E}_{A1} + \underline{U}_{e_1 e_2} + \underline{U}_{e_1 n_B} + \underline{U}_{e_2 n_A} + \quad (S73)$$

$$\begin{aligned} & \underline{U}_{e_{A3} e_2} + \underline{U}_{e_{A4} e_2} + \underline{U}_{e_{A5} e_2} + 3\underline{U}_{e_{A3} n_B} + \underline{U}_{n_A n_B} + 2\underline{E}_{m1s} = -\frac{Z_{1(A)}^2}{n_{1(A)}^2} - \\ & \frac{Z_{2(B)}^2}{n_{2(B)}^2} - \frac{Z_{A3}^2}{n_{A3}^2} - \frac{Z_{A4}^2}{n_{A3}^2} - \frac{Z_{A5}^2}{n_{A3}^2} - 2\frac{Z_{A1}^2}{n_{A1}^2} + \frac{1}{\sqrt{\left(\frac{1}{4}\sigma_1 + \frac{1}{4}\sigma_2\right)^2 + \left(\frac{3}{2}a\right)^2}} - \\ & \frac{Z_B}{\sqrt{\left(\frac{1}{4}\sigma_1 + \sigma_2\right)^2 + \left(\frac{3}{4}a\right)^2}} - \frac{Z_A - 2}{\sqrt{\left(\frac{1}{4}\sigma_2 + \sigma_1\right)^2 + \left(\frac{3}{4}a\right)^2}} + \\ & \frac{1}{\sqrt{\left(\sigma_1 + \frac{1}{4}\sigma_2 + d\right)^2 + \left(\frac{3}{4}a\right)^2 + b^2}} + \\ & \frac{1}{\sqrt{\left(\sigma_1 + \frac{1}{4}\sigma_2 + d\right)^2 + \left(\frac{3}{4}a + \frac{\sqrt{3}}{2}b\right)^2 + \left(\frac{1}{2}b\right)^2}} + \\ & \frac{1}{\sqrt{\left(\sigma_1 + \frac{1}{4}\sigma_2 + d\right)^2 + \left(\frac{3}{4}a - \frac{\sqrt{3}}{2}b\right)^2 + \left(\frac{1}{2}b\right)^2}} - \\ & \frac{3Z_B}{\sqrt{\left(\sigma_1 + \sigma_2 + d\right)^2 + b^2}} + \frac{(Z_A - 2) Z_B}{\sigma_1 + \sigma_2} + \frac{Z_{A1}^{3/2}}{8n_{A1}^3} \end{aligned}$$

The values of \underline{E} , \underline{E}_{HF} and \underline{E}_{exp} are given in Table 1 of paper. The relative errors corresponding to \underline{E} and \underline{E}_{HF} are, respectively, equal to 0.004 and 0.005. The electric dipole moment is given by the following relation:

$$\mu_e = -5.08315[-2\sigma_1 + Z_B(\sigma_1 + \sigma_2) + 3d] \quad (S74)$$

The values of α , corresponding to the minimum value of \underline{E} , r_0 , r_e , μ_e and the domain of the values of μ_{eHF} are shown in Table S7.

The analysis of the Table 1 from paper shows that the relative error of our calculations, in the most unfavorable cases, is, as in the case of atoms [27, 28], of the order 0.005. In Section 6 of Ref. [27] we presented a brief error analysis of our calculation method, arriving to the conclusion that the main source of error comes from the approximations made when calculating the correction term E_{m1s} . This analysis is valid also for the present paper.

S3. MATHEMATICA 7 scripts for the calculation of the Li_2 , Be_2 , B_2 , C_2 , LiH , BeH , BH and CH molecules.

This material contains all the numerical calculations, necessary in the paper.

S3.1. Mathematica 7 script for the calculation of Li_2 .

The calculation algorithm is described in Section 4. We have the following equivalences between the notations from paper and the symbols which are used in program: $Z_A \equiv ZA$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $Z_1 \equiv Z1$, $Z_{1M} \equiv Z1M$, $Z_{nA} \equiv ZnA$, $\underline{E} \equiv Etotal$, $\underline{E}_b \equiv EB$, $r_0 \equiv r0$, $\underline{D}_0^0 \equiv D00$, $\underline{S}_{EiA} \equiv SEiA$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{a} \equiv a$, $\underline{\sigma} \equiv s$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , r_0 and r_e .

Input data.

ZA = 3;

s1A1 = 0.854942;

sA11 = 0.0013792;

sA1A2 = .25;

Z1 = ZA - 2 * s1A1;

Z1M = ZA - 2;

ZnA = ZA - 2;

Etotal = EB - 4 * (ZA - sA1A2 - sA11)² + $\frac{(ZA - sA1A2 - sA11)^{\frac{3}{2}}}{4}$;

r0 = 2 * s * 2 * .529177A;

Experimental data.

D00 = $\frac{1.046}{13.60535}$;

SEiA = $\frac{5.39172 + 75.64018 + 122.45429}{13.60535}$;

Eexp = -2 * SEiA - D00;

re = 2.673A;

System of equations

Eq1 = EB + $\frac{Z1^2}{2}$ + $\frac{8 * Z1M}{\sqrt{9 * a^2 + 25 * s^2}}$ - $\frac{2}{\sqrt{9 * a^2 + s^2}}$ - $\frac{ZnA^2}{2 * s}$;

Eq2 = EB + $\frac{4 * \sqrt{Z1M}}{(s^2 + a^2)^{\frac{3}{4}}}$;

Eq3 = EB + $\frac{4 * Z1M}{\sqrt{s^2 + a^2}}$ - $\frac{ZnA^2}{2 * s}$ - $\frac{1}{2a}$;

The solution of the system of equations

```

1 Sol = FindRoot[{Eq1 == 0, Eq2 == 0, Eq3 == 0}, {{EB, 1}, {s, 1.2}, {a, 2.5}}]
2 {EB → -1.0115, s → 1.46474, a → 2.02683}
3 Verification.
4 N[Eq1]/.Sol
5 N[Eq2]/.Sol
6 N[Eq3]/.Sol
7 0.
8 2.220446049250313*^-16
9 4.440892098500626*^-16
10 Calculation of other quantities.
11 Etotal/.Sol
12 Eexp/.Sol
13 r0/.Sol
14 re/.Sol
15 -30.0919
16 -29.9896
17 3.10043A
18 2.673A
19
20
21
22

```

S3.2. Mathematica 7 script for the calculation of Be₂.

We have the following equivalences between the notations from paper and the symbols which are used in program: $Z_A \equiv ZA$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{1,A3} \equiv s1A3$, $s_{A1,A2} \equiv sA1A2$, $Z_1 \equiv Z1$, $Z_{1M} \equiv Z1M$, $Z_{A3} \equiv ZA3$, $Z_{A1} \equiv ZA1$, $r_{A3} \equiv rA3$, $Z_{nA} \equiv ZnA$, $\underline{E} \equiv Etotal$, $\underline{E}_b \equiv EB$, $r_0 \equiv r0$, $\underline{D}_0^0 \equiv D00$, $\underline{S}_{EiA} \equiv SEiA$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{a} \equiv a$, $\underline{\sigma} \equiv s$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , r_0 and r_e .

Input data.

```

34 ZA = 4;
35 s1A1 = 0.83882;
36 sA11 = .00221203;
37 s1A3 =  $\frac{\sqrt{2}}{4 \cdot \sqrt{1 + \frac{s}{\sqrt{s^2 + a^2}}}}$ ;
38 sA1A2 = .25;
39 Z1 = ZA - 2s1A1 - s1A3;
40 Z1M = ZA - 2 - s1A3;
41 ZA3 = Z1;
42 ZA1 = ZA - sA1A2 - 2 * sA11;
43 rA3 =  $\frac{3}{ZA3}$ ;
44 ZnA = ZA - 2 -  $\frac{(2s)^2}{(2s+rA3)^2}$ ;
45 Etotal =  $-\frac{Z1^2}{2} - \frac{ZA3^2}{2} - 4 * ZA1^2 + \frac{1}{2\sqrt{(\frac{1}{4}s)^2 + (\frac{3}{4}a)^2}} - \frac{2*(ZA-2)}{\sqrt{(\frac{5}{4}s)^2 + (\frac{3}{4}a)^2}} + \frac{2}{\sqrt{(\frac{5}{4}s+rA3)^2 + (\frac{3}{4}a)^2}} -$ 
46  $\frac{2*(ZA-2)}{2*s+rA3} + \frac{1}{2*s+2*rA3} + \frac{(ZA-2)^2}{2*s} + \frac{ZA1^{\frac{3}{2}}}{4}$ ;
47 r0 = 2 * s * 2 * .529177A;
48
49

```

Experimental data.

```

54 D00 = .1643;
55 SEiA =  $\frac{9.3227+18.21116+153.89661+217.71865}{13.60535}$ ;
56 Eexp = -2 * SEiA - D00;
57 re = 2.460A;
58

```

System of equations.

$$\text{Eq1} = EB + \frac{Z1^2}{2} + \frac{8*Z1M}{\sqrt{9*a^2+25*s^2}} - \frac{2}{\sqrt{9*a^2+s^2}} - \frac{ZnA^2}{2*s};$$

$$\text{Eq2} = EB + \frac{4\sqrt{Z1M}}{(s^2+a^2)^{\frac{3}{4}}};$$

$$\text{Eq3} = EB + \frac{4*Z1M}{\sqrt{s^2+a^2}} - \frac{ZnA^2}{2*s} - \frac{1}{2a};$$

The solution of the system of equations.

$$\text{Sol} = \text{FindRoot}\{\{\text{Eq1} == 0, \text{Eq2} == 0, \text{Eq3} == 0\}, \{\{EB, -2\}, \{s, 1\}, \{a, 1\}\}\}$$

$$\{EB \rightarrow -2.39104, s \rightarrow 1.04502, a \rightarrow 1.32709\}$$

Verification.

$$N[\text{Eq1}]/.\text{Sol}$$

$$N[\text{Eq2}]/.\text{Sol}$$

$$N[\text{Eq3}]/.\text{Sol}$$

$$2.220446049250313*^{-16}$$

$$-4.440892098500626*^{-16}$$

$$-4.440892098500626*^{-16}$$

Calculation of other quantities.

$$\text{Etotal}/.\text{Sol}$$

$$\text{Eexp}/.\text{Sol}$$

$$r0/.\text{Sol}$$

$$re/.\text{Sol}$$

$$-58.7676$$

$$-58.8396$$

$$2.212A$$

$$2.46A$$

S3.3. Mathematica 7 script for the calculation of B_2 .

The equivalences between the notations from paper and the symbols which are used in program are $Z_A \equiv ZA$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $\alpha \equiv \text{alpha}$, $s_{1,A3} \equiv s1A3$, $s_{A3,A4} \equiv sA3A4$, $Z_1 \equiv Z1$, $Z_{1M} \equiv Z1M$, $Z_{A3} \equiv ZA3$, $Z_{A1} \equiv ZA1$, $r \equiv r$, $d \equiv d$, $b \equiv b$, $Z_{nA} \equiv ZnA$, $\underline{E} \equiv \text{Etotal}$, $\underline{E}_b \equiv EB$, $r_0 \equiv r0$, $\underline{D}_0^0 \equiv D00$, $\underline{S}_{EiA} \equiv SEiA$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{a} \equiv a$, $\underline{\sigma} \equiv s$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , r_0 and r_e .

Input data.

$$\text{ZA} = 5;$$

$$\text{s1A1} = 0.862983;$$

$$\text{sA11} = .00246735;$$

$$\text{sA1A2} = .25;$$

$$\text{alpha} = 63;$$

$$\text{al} = \text{alpha} * \frac{\pi}{180};$$

$$\text{s1A3} = \frac{1}{4 * \sqrt{\frac{1}{2} + \frac{s * \text{Cos}[\text{al}]}{2 * \sqrt{s^2 + a^2}}}};$$

$$\text{sA3A4} = \frac{1}{4 * \text{Sin}[\text{al}]};$$

$$\text{Z1} = \text{ZA} - 2 * \text{s1A1} - 2 * \text{s1A3};$$

$$\text{Z1M} = \text{ZA} - 2 - 2 * \text{s1A3};$$

$$\text{ZA1} = \text{ZA} - \text{sA1A2} - 3 * \text{sA11};$$

$$\text{ZA3} = \text{ZA} - 2 * \text{s1A1} - \text{s1A3} - \text{sA3A4};$$

$$r = \frac{3}{\text{ZA3}};$$

$$d = r * \text{Cos}[\text{al}];$$

$$b = r * \text{Sin}[\text{al}];$$

$$\begin{aligned} \text{ZnA} &= \text{ZA} - 2 - \frac{2*(2s)^2*(2*s+d)}{((2*s+d)^2+b^2)^{\frac{3}{2}}}; \\ \text{Etotal} &= -\frac{\text{Z1}^2}{2} - \text{ZA}^3 - 4 * \text{ZA}^2 + \frac{1}{2*\sqrt{(\frac{1}{4}*s)^2+(\frac{3}{4}*a)^2}} - \frac{2*(\text{ZA}-2)}{\sqrt{(\frac{5}{4}*s)^2+(\frac{3}{4}*a)^2}} + \\ &\frac{4}{\sqrt{(\frac{5}{4}*s+d)^2+(\frac{3}{4}*a)^2+b^2}} - \frac{4*(\text{ZA}-2)}{\sqrt{(d+2*s)^2+b^2}} + \frac{1}{\sqrt{(s+d)^2+b^2}} + \frac{1}{s+d} + \frac{(\text{ZA}-2)^2}{2*s} + \frac{\text{ZA1}^{\frac{3}{2}}}{4}; \\ r_0 &= 2 * s * 2 * .529177A; \end{aligned}$$

Experimental data.

$$\begin{aligned} \text{D00} &= \frac{3.02}{13.60535}; \\ \text{SEiA} &= \frac{8.29803+25.15484+37.93064+259.37521+340.22580}{13.60535}; \\ \text{Eexp} &= -2 * \text{SEiA} - \text{D00}; \\ r_e &= 1.5900A; \end{aligned}$$

System of equations.

$$\begin{aligned} \text{Eq1} &= \text{EB} + \frac{\text{Z1}^2}{2} + \frac{8*\text{Z1M}}{\sqrt{9*a^2+25*s^2}} - \frac{2}{\sqrt{9*a^2+s^2}} - \frac{\text{ZnA}^2}{2*s}; \\ \text{Eq2} &= \text{EB} + \frac{4*\sqrt{\text{Z1M}}}{(s^2+a^2)^{\frac{3}{4}}}; \\ \text{Eq3} &= \text{EB} + \frac{4*\text{Z1M}}{\sqrt{s^2+a^2}} - \frac{\text{ZnA}^2}{2*s} - \frac{1}{2a}; \end{aligned}$$

The solution of the system of equations.

$$\begin{aligned} \text{Sol} &= \text{FindRoot}\{\{\text{Eq1} == 0, \text{Eq2} == 0, \text{Eq3} == 0\}, \{\{\text{EB}, 1\}, \{s, 1\}, \{a, 1\}\}\} \\ &\{\text{EB} \rightarrow -3.857, s \rightarrow 0.844851, a \rightarrow 1.07468\} \end{aligned}$$

Verification.

$$\begin{aligned} &N[\text{Eq1}]/.\text{Sol} \\ &N[\text{Eq2}]/.\text{Sol} \\ &N[\text{Eq3}]/.\text{Sol} \\ &1.3322676295501878*^{-15} \\ &4.440892098500626*^{-16} \\ &0. \end{aligned}$$

Calculation of other quantities.

$$\begin{aligned} &\text{Etotal}/.\text{Sol} \\ &\text{Eexp}/.\text{Sol} \\ &r_0/.\text{Sol} \\ &r_e/.\text{Sol} \\ &-98.3341 \\ &-98.8574 \\ &1.7883A \\ &1.59A \end{aligned}$$

53.4. Mathematica 7 script for the calculation of C_2 with double bond.

The equivalences between the notations from paper and the symbols which are used in program are $Z_A \equiv ZA$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $\alpha \equiv alpha$, $s_{1,2} \equiv s12$, $s_{1,A3} \equiv s1A3$, $s_{1,A4} \equiv s1A4$, $s_{A3,A4} \equiv sA3A4$, $Z_1 \equiv Z1$, $Z_{1M} \equiv Z1M$, $Z_{A1} \equiv ZA1$, $Z_{A3} \equiv ZA3$, $Z_{A4} \equiv ZA4$, $e \equiv excen$, $r \equiv r$, $\underline{d} \equiv d$, $\underline{b} \equiv b$, $Z_{nA} \equiv ZnA$, $\underline{E} \equiv Etotal$, $\underline{E}_b \equiv EB$, $r_0 \equiv r_0$, $\underline{D}_0^0 \equiv D00$, $\underline{S}_{EiA} \equiv SEiA$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv r_e$, $\underline{a} \equiv a$, $\underline{\sigma} \equiv s$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , r_0 and r_e .

Input data.

$$\begin{aligned} \text{ZA} &= 6; \\ \text{s1A1} &= 0.85505; \\ \text{sA11} &= .00269287; \end{aligned}$$

$$sA1A2 = .25;$$

$$\text{alpha} = 41;$$

$$\text{al} = \text{alpha} * \frac{\pi}{180};$$

$$s12 = \frac{\sqrt{s^2+a^2}}{4*a};$$

$$s1A3 = \frac{\sqrt{2}}{4*\sqrt{1+\frac{s*\text{Cos}[\text{al}]-\frac{\sqrt{2}}{4}*a*\text{Sin}[\text{al}]}{\sqrt{s^2+a^2}}}};$$

$$s1A4 = \frac{\sqrt{2}}{4*\sqrt{1+\frac{s*\text{Cos}[\text{al}]+\frac{\sqrt{2}}{4}*a*\text{Sin}[\text{al}]}{\sqrt{s^2+a^2}}}};$$

$$sA3A4 = \frac{1}{4*\text{Sin}[\text{al}]};$$

$$Z1 = ZA - 2 * s1A1 - s12 - s1A3 - s1A4;$$

$$Z1M = ZA - 2 - s12 - s1A3 - s1A4;$$

$$ZA1 = ZA - sA1A2 - 4 * sA11;$$

$$ZA3 = ZA - 2 * s1A1 - sA3A4 - s1A3 - s1A4;$$

$$ZA4 = ZA3;$$

$$\text{excen} = .98;$$

$$r = \frac{2}{ZA3} * \left(1 + \frac{\text{excen}^2}{2}\right);$$

$$d = r * \text{Cos}[\text{al}];$$

$$b = r * \text{Sin}[\text{al}];$$

$$ZnA = ZA - 2 - \frac{2*(2*s)^2*(2*s+d)}{((2*s+d)^2+b^2)^{\frac{3}{2}}};$$

$$\text{Etotal} = -Z1^2 - ZA3^2 - 4 * ZA1^2 + \frac{4}{\sqrt{\left(\frac{s}{2}\right)^2+2*\left(\frac{3*a}{4}\right)^2}} - \frac{4*(ZA-2)}{\sqrt{\left(\frac{5*s}{4}\right)^2+\left(\frac{3*a}{4}\right)^2}} +$$

$$\frac{4}{\sqrt{\left(\frac{5*s}{4}+d\right)^2+\left(\frac{\sqrt{2}}{2}*b\right)^2+\left(\frac{3*a}{4}-\frac{\sqrt{2}}{2}*b\right)^2}} + \frac{4}{\sqrt{\left(\frac{5*s}{4}+d\right)^2+\left(\frac{\sqrt{2}}{2}*b\right)^2+\left(\frac{3*a}{4}+\frac{\sqrt{2}}{2}*b\right)^2}} -$$

$$\frac{4*(ZA-2)}{\sqrt{(2*s+d)^2+b^2}} + \frac{1}{\sqrt{(s+d)^2+b^2}} + \frac{1}{s+d} + \frac{(ZA-2)^2}{2*s} + \frac{ZA1^{\frac{3}{2}}}{4};$$

$$r0 = 2 * s * 2 * .52918A;$$

Experimental data

$$D00 = \frac{6.21}{13.60535};$$

$$\text{SEiA} = \frac{11.2603+24.38332+47.8878+64.4939+392.087+489.99334}{13.60535};$$

$$\text{Eexp} = -2 * \text{SEiA} - D00;$$

$$\text{re} = 1.243A;$$

System of equations.

$$\text{Eq1} = \text{EB} + Z1^2 + \frac{16*(Z1M+s12)}{\sqrt{25s^2+9a^2}} - \frac{8}{\sqrt{s^2+4.5*a^2}} - \frac{ZnA^2}{2*s};$$

$$\text{Eq2} = \text{EB} + \frac{8*\sqrt{Z1M}}{(s^2+a^2)^{3/4}};$$

$$\text{Eq3} = \text{EB} + \frac{8*(Z1M+s12)}{\sqrt{s^2+a^2}} - \frac{1}{a} - \frac{2*\sqrt{2}}{a} - \frac{ZnA^2}{2*s};$$

The solution of the system of equations.

$$\text{Sol} = \text{FindRoot}\{\{\text{Eq1} == 0, \text{Eq2} == 0, \text{Eq3} == 0\}, \{\{\text{EB}, -12\}, \{s, .6\}, \{a, .9\}\}\}$$

$$\{\text{EB} \rightarrow -12.1816, s \rightarrow 0.641059, a \rightarrow 0.894043\}$$

Verification.

$$N[\text{Eq1}]/.\text{Sol}$$

$$N[\text{Eq2}]/.\text{Sol}$$

$$N[\text{Eq3}]/.\text{Sol}$$

$$0.$$

$$3.552713678800501*^{-15}$$

$$5.329070518200751*^{-15}$$

Calculation of other quantities.

$$\text{Etotal}/.\text{Sol}$$

$$\text{Eexp}/.\text{Sol}$$

1 r0/.Sol
 2 re/.Sol
 3 -151.148
 4 -151.883
 5 1.35694A
 6 1.243A
 7
 8
 9
 10

11 **S3.5. Mathematica 7 script for the calculation of C₂ with triple bond.**

12 The equivalences between the notations from paper and the symbols which are
 13 used in program are $Z_A \equiv ZA$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$,
 14 $s_{1,2} \equiv s12$, $s_{1,A3} \equiv s1A3$, $Z_1 \equiv Z1$, $Z_{1M} \equiv Z1M$, $Z_{A1} \equiv ZA1$, $Z_{A3} \equiv ZA3$, $e \equiv$
 15 $excen$, $r_{A3} \equiv rA3$, $Z_{nA} \equiv ZnA$, $\underline{E} \equiv Etotal$, $\underline{E}_b \equiv EB$, $r_0 \equiv r0$, $\underline{D}_0^0 \equiv D00$,
 16 $\underline{S}_{EiA} \equiv SEiA$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{a} \equiv a$, $\underline{\sigma} \equiv s$.

17 The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , r_0 and
 18 r_e .

19 Input data.

20
 21
 22 **ZA = 6;**
 23 **s1A1 = 0.85505;**
 24 **sA11 = .00269287;**
 25 **sA1A2 = .25;**
 26 **s12 = $\frac{\sqrt{2}}{4} / \sqrt{1 - \frac{s^2 - \frac{1}{2} * a^2}{s^2 + a^2}}$;**
 27 **s1A3 = $\frac{\sqrt{2}}{4} / \sqrt{1 + \frac{s}{\sqrt{s^2 + a^2}}}$;**
 28 **Z1 = ZA - 2 * s1A1 - 2 * s12 - s1A3;**
 29 **Z1M = ZA - 2 - 2 * s12 - s1A3;**
 30 **ZA1 = ZA - sA1A2 - 4 * sA11;**
 31 **ZA3 = ZA - 2 * s1A1 - 3 * s1A3;**
 32 **excen = .98;**
 33 **rA3 = $\frac{2}{ZA3} * \left(1 + \frac{excen^2}{2}\right)$;**
 34 **ZnA = ZA - 2 - $\frac{(2*s)^2}{(2*s+rA3)^2}$;**
 35 **Etotal = $-6 * \frac{Z1^2}{4} - 2 * \frac{ZA3^2}{4} - 4 * ZA1^2 + \frac{3}{\sqrt{(\frac{1}{2}*s)^2 + (\frac{3}{2}*a)^2}} +$**
 36 **$\frac{6}{\sqrt{(\frac{1}{2}*s)^2 + (\frac{3}{4}*a)^2}} - \frac{6*(ZA-2)}{\sqrt{(\frac{5}{4}*s)^2 + (\frac{3}{4}*a)^2}} + \frac{6}{\sqrt{(\frac{5*s}{4} + rA3)^2 + (\frac{3*a}{4})^2}}$**
 37 **$\frac{2*(ZA-2)}{2*s+rA3} + \frac{1}{2*s+2*rA3} + \frac{(ZA-2)^2}{2*s} + \frac{ZA1^{\frac{3}{2}}}{4}$;**
 38 **r0 = 2 * s * 2 * .52918A;**

39 Experimental data

40 **D00 = $\frac{6.21}{13.60535}$;**
 41 **SEiA = $\frac{11.2603+24.38332+47.8878+64.4939+392.087+489.99334}{13.60535}$;**
 42 **Eexp = -2 * SEiA - D00;**
 43 **re = 1.243A;**

44 System of equations.

45 **Eq1 = EB + $6 * \frac{Z1^2}{4} + \frac{24*(Z1M+2*s12)}{\sqrt{9*a^2+25*s^2}} - \frac{6}{\sqrt{s^2+9*a^2}} - \frac{24}{\sqrt{4*s^2+9*a^2}} - \frac{ZnA^2}{2*s}$;**
 46 **Eq2 = EB + $\frac{12*\sqrt{Z1M}}{(s^2+a^2)^{3/4}}$;**
 47 **Eq3 = EB + $\frac{12*(Z1M+2*s12)}{\sqrt{s^2+a^2}} - \frac{6}{a*\sqrt{3}} - \frac{6}{a} - \frac{3}{2*a} - \frac{ZnA^2}{2*s}$;**

48 The solution of the system of equations.

49 **Sol = FindRoot[{Eq1 == 0, Eq2 == 0, Eq3 == 0}, {{EB, 12}, {s, .6}, {a, .9}}]**

{EB \rightarrow -17.1499, $s \rightarrow$ 0.639379, $a \rightarrow$ 0.942817}

Verification.

N[Eq1]/.Sol

N[Eq2]/.Sol

N[Eq3]/.Sol

-3.552713678800501^{*^-15}

0.

1.7763568394002505^{*^-14}

Calculation of other quantities.

Ettotal/.Sol

Eexp/.Sol

r0/.Sol

re/.Sol

-150.923

-151.883

1.35339A

1.243A

S3.6. Mathematica 7 script for the calculation of LiH.

The equivalences between the notations from paper and the symbols which are used in program are $Z_A \equiv ZA$, $Z_B \equiv ZB$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $s_{1,2(A)} \equiv s12A$, $s_{1,2(B)} \equiv s12B$, $Z_{1(A)} \equiv Z1A$, $Z_{1M(A)} \equiv Z1MA$, $Z_{A1} \equiv ZA1$, $Z_{1(B)} \equiv Z1B$, $Z_{1M(B)} \equiv Z1MB$, $Z_{nA} \equiv ZnA$, $Z_{nB} \equiv ZnB$, $a_{cA} \equiv acA$, $a_{cB} \equiv acB$, $I_A \equiv IA$, $I_B \equiv IB$, $t_{cA} \equiv tcA$, $t_{cB} \equiv tcB$, $\underline{E} \equiv Ettotal$, $r_0 \equiv r0$, $\mu_e \equiv \mu e$, $D_0^0 \equiv D00$, $S_{EiA} \equiv SEiA$, $S_{EiB} \equiv SEiB$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{E}_b \equiv EB$, $\underline{a} \equiv a$, $\underline{\sigma}_1 \equiv s1$, $\underline{\sigma}_2 \equiv s2$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , μ_e , r_0 and r_e .

Input data.

ZA = 3;

ZB = 1;

s1A1 = 0.854942;

sA11 = .0013792;

sA1A2 = .25;

s12A = $\frac{\sqrt{s1^2+a^2}}{4a}$;

s12B = $\frac{\sqrt{s2^2+a^2}}{4a}$;

Z1A = ZA - 2 * s1A1 - s12A;

Z1MA = ZA - 2 - s12A;

ZA1 = ZA - sA1A2 - 2 * sA11;

Z1B = ZB - s12B;

Z1MB = ZB - s12B;

ZnA = 1;

ZnB = 1;

acA = $1 - \frac{T\sqrt{s1^2+a^2}}{Z1MA}$;

acB = $1 - \frac{T\sqrt{s2^2+a^2}}{Z1MB}$;

IA = ArcSin $\left[\sqrt{acA} \right] - \sqrt{acA}\sqrt{1 - acA}$;

IB = ArcSin $\left[\sqrt{acB} \right] - \sqrt{acB}\sqrt{1 - acB}$;

tcA = $\frac{2IA}{\pi acA^{\frac{3}{2}}}$;

$$tcB = \frac{2IB}{\pi acB^{\frac{3}{2}}};$$

$$E_{total} = EB - 2 * ZA1^2 + \frac{ZA1^{\frac{3}{2}}}{8};$$

$$r0 = (s1 + s2) * .529177 * 2A;$$

$$\mu e = -5.08315 * (-2 * s1 + ZB * (s1 + s2))D;$$

Experimental data.

$$D00 = \frac{2.42871}{13.60535};$$

$$SEiA = \frac{5.39172 + 75.64018 + 122.45429}{13.60535};$$

$$SEiB = 1;$$

$$E_{exp} = -SEiA - SEiB - D00;$$

$$re = 1.5957A;$$

System of equations.

$$Eq1 = EB + \frac{Z1A^2}{2} + \frac{2(Z1MB+s12B)}{\sqrt{(\frac{3}{4}a)^2 + (\frac{s1}{4}+s2)^2}} - \frac{ZnAZnB}{s1+s2};$$

$$Eq2 = EB + 2Z1B^2 + \frac{2(Z1MA+s12A)}{\sqrt{(\frac{3}{4}a)^2 + (\frac{s2}{4}+s1)^2}} - \frac{ZnAZnB}{s1+s2};$$

$$Eq3 = EB + \frac{4\sqrt{Z1MA}}{tcA(s1^2+a^2)^{\frac{3}{4}}};$$

$$Eq4 = EB + \frac{2\sqrt{Z1MB}}{tcB(s2^2+a^2)^{\frac{3}{4}}};$$

$$Eq5 = EB + \frac{2(Z1MA+s12A)}{\sqrt{s1^2+a^2}} + \frac{2(Z1MB+s12B)}{\sqrt{s2^2+a^2}} - \frac{1}{2a} - \frac{ZnAZnB}{s1+s2} - 2T;$$

The solution of the system of equations.

$$\text{Sol} = \text{FindRoot}\{\{Eq1 == 0, Eq2 == 0, Eq3 == 0, Eq4 == 0, Eq5 == 0\},$$

$$\{\{EB, 1.6\}, \{s1, 1.5\}, \{s2, .25\}, \{a, 1.2\}, \{T, .04\}\}\}$$

$$\{EB \rightarrow -1.65659, s1 \rightarrow 1.47713, s2 \rightarrow 0.267425, a \rightarrow 1.18038, T \rightarrow 0.0284159\}$$

Verification.

$$N[Eq1]/.\text{Sol}$$

$$N[Eq2]/.\text{Sol}$$

$$N[Eq3]/.\text{Sol}$$

$$N[Eq4]/.\text{Sol}$$

$$N[Eq5]/.\text{Sol}$$

0.

$$-1.1102230246251565^{*-16}$$

$$-6.661338147750939^{*-16}$$

$$-2.220446049250313^{*-16}$$

$$-4.440892098500626^{*-16}$$

Calculation of other quantities.

$$E_{total}/.\text{Sol}$$

$$E_{exp}/.\text{Sol}$$

$$\mu e/.\text{Sol}$$

$$r0/.\text{Sol}$$

$$re/.\text{Sol}$$

$$-16.1821$$

$$-16.1348$$

$$6.1491D$$

$$1.84635A$$

$$1.5957A$$

S3.7. Mathematica 7 script for the calculation of BeH.

The equivalences between the notations from paper and the symbols which are used in program are $Z_A \equiv ZA$, $Z_B \equiv ZB$, $T_m \equiv T$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $s_{1,2(A)} \equiv s12A$, $s_{1,2(B)} \equiv s12B$, $s_{1,A3} \equiv s1A3$, $Z_{1(A)} \equiv Z1A$,

$Z_{1M(A)} \equiv Z1MA$, $Z_{A1} \equiv ZA1$, $Z_{A3} \equiv ZA3$, $Z_{1(B)} \equiv Z1B$, $Z_{1M(B)} \equiv Z1MB$,
 $\tilde{r}_{A3} \equiv rA3$, $Z_{nA} \equiv ZnA$, $Z_{nB} \equiv ZnB$, $a_{cA} \equiv acA$, $a_{cB} \equiv acB$, $I_A \equiv IA$, $I_B \equiv IB$,
 $t_{cA} \equiv tcA$, $t_{cB} \equiv tcB$, $E \equiv Etotal$, $r_0 \equiv r0$, $\mu_e \equiv \mu_e$, $D_0^0 \equiv D00$, $\underline{S}_{EiA} \equiv SEiA$,
 $\underline{S}_{EiB} \equiv SEiB$, $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{E}_{b1} \equiv EB1$, $\underline{E}_{b2} \equiv EB2$, $\underline{a} \equiv a$, $\sigma_1 \equiv s1$,
 $\sigma_2 \equiv s2$.

The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , μ_e , r_0 and r_e .

Input data.

$$ZA = 4;$$

$$ZB = 1;$$

$$T = .015;$$

$$s1A1 = 0.83882;$$

$$sA11 = .00221203;$$

$$sA1A2 = .25;$$

$$s12A = \frac{\sqrt{s1^2+a^2}}{4a};$$

$$s12B = \frac{\sqrt{s2^2+a^2}}{4a};$$

$$s1A3 = \frac{\sqrt{2}}{4 * \sqrt{1 + \frac{s1}{\sqrt{s1^2+a^2}}}};$$

$$Z1A = ZA - 2 * s1A1 - s12A - s1A3;$$

$$Z1MA = ZA - 2 - s12A - s1A3;$$

$$ZA1 = ZA - sA1A2 - 3 * sA11;$$

$$ZA3 = ZA - 2 * s1A1 - 2 * s1A3;$$

$$Z1B = ZB - s12B;$$

$$Z1MB = ZB - s12B;$$

$$rA3 = \frac{3}{ZA - 2 * s1A1};$$

$$ZnA = ZA - 2 - \frac{(s1+s2)^2}{(s1+s2+rA3)^2};$$

$$ZnB = 1;$$

$$acA = 1 - \frac{T\sqrt{s1^2+a^2}}{Z1MA};$$

$$acB = 1 - \frac{T\sqrt{s2^2+a^2}}{Z1MB};$$

$$IA = \text{ArcSin} \left[\sqrt{acA} \right] - \sqrt{acA} \sqrt{1 - acA};$$

$$IB = \text{ArcSin} \left[\sqrt{acB} \right] - \sqrt{acB} \sqrt{1 - acB};$$

$$tcA = \frac{2IA}{\pi acA^{\frac{3}{2}}};$$

$$tcB = \frac{2IB}{\pi acB^{\frac{3}{2}}};$$

$$Etotal = -\frac{ZA3^2}{4} - 2 * ZA1^2 - \frac{2*(Z1MA+s12A)}{\sqrt{s1^2+a^2}} - \frac{2*(Z1MB+s12B)}{\sqrt{s2^2+a^2}} + \frac{1}{2*a} -$$

$$\frac{1}{rA3+s1+s2} + \frac{(ZA-2)*ZB}{s1+s2} + \frac{ZA1^{\frac{3}{2}}}{8} + 2 * T;$$

$$r0 = (s1 + s2) * .529177 * 2A;$$

$$\mu_e = -5.08315 * (-2 * s1 + ZB * (s1 + s2) + rA3)D;$$

Experimental data.

$$D00 = \frac{2.034}{13.60535};$$

$$SEiA = \frac{9.3227+18.21116+153.89661+217.71865}{13.60535};$$

$$SEiB = 1;$$

$$Eexp = -SEiA - SEiB - D00;$$

$$re = 1.3426A;$$

System of equations.

$$Eq1 = EB1 + \frac{Z1A^2}{2} + \frac{2*(Z1MB+s12B)}{\sqrt{(\frac{3}{4}a)^2 + (\frac{s1}{4}+s2)^2}} - \frac{ZnAZnB}{s1+s2};$$

$$\text{Eq2} = \text{EB2} + 2\text{Z1B}^2 + \frac{2(\text{Z1MA} + \text{s12A})}{\sqrt{\left(\frac{3}{4}a\right)^2 + \left(\frac{s2}{4} + \text{s1}\right)^2}} - \frac{\text{ZnAZnB}}{\text{s1} + \text{s2}};$$

$$\text{Eq3} = \text{EB1} + \frac{4\sqrt{\text{Z1MA}}}{\text{tcA}(\text{s1}^2 + a^2)^{\frac{3}{4}}};$$

$$\text{Eq4} = \text{EB2} + \frac{2\sqrt{\text{Z1MB}}}{\text{tcB}(\text{s2}^2 + a^2)^{\frac{3}{4}}};$$

$$\text{Eq5} = 0.5 * (\text{EB1} + \text{EB2}) + \frac{2(\text{Z1MA} + \text{s12A})}{\sqrt{\text{s1}^2 + a^2}} + \frac{2(\text{Z1MB} + \text{s12B})}{\sqrt{\text{s2}^2 + a^2}} - \frac{1}{2a} - \frac{\text{ZnAZnB}}{\text{s1} + \text{s2}} - 2T;$$

The solution of the system of equations.

Sol = FindRoot{**{Eq1 == 0, Eq2 == 0, Eq3 == 0, Eq4 == 0, Eq5 == 0}**,

{{EB1, -2.3}, {EB2, -2}, {s1, 1.35}, {s2, .01}, {a, 1}}}

{EB1 → -2.51578, EB2 → -2.11007, s1 → 1.34462, s2 → 0.0149424, a → 0.979054}

Verification.

N[Eq1]/.Sol

N[Eq2]/.Sol

N[Eq3]/.Sol

N[Eq4]/.Sol

N[Eq5]/.Sol

1.1102230246251565*^-15

-2.220446049250313*^-16

0.

1.3322676295501878*^-15

0.

Calculation of other quantities.

Ettotal/.Sol

Eexp/.Sol

μe/.Sol

r0/.Sol

re/.Sol

-30.4238

-30.4872

0.192613D

1.4389A

1.3426A

S3.8. Mathematica 7 script for the calculation of BH.

The equivalences between the notations from paper and the symbols which are used in program are $Z_A \equiv ZA$, $Z_B \equiv ZB$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$, $\alpha \equiv alpha$, $s_{1,A3} \equiv s1A3$, $s_{A3,A4} \equiv sA3A4$, $Z_{1(A)} \equiv Z1A$, $Z_{1M(A)} \equiv Z1MA$, $Z_{A1} \equiv ZA1$, $Z_{A3} \equiv ZA3$, $Z_{A4} \equiv ZA4$, $Z_{2(B)} \equiv Z2B$, $Z_{2M(B)} \equiv Z2MB$, $e \equiv excen$, $r \equiv r$, $d \equiv d$, $b \equiv b$, $Z_{nA} \equiv ZnA$, $Z_{nB} \equiv ZnB$, $E \equiv Ettotal$, $E_b \equiv EB$, $r_0 \equiv r0$, $\mu_e \equiv \mu e$, $D_0^0 \equiv D00$, $S_{EiA} \equiv SEiA$, $S_{EiB} \equiv SEiB$, $E_{exp} \equiv Eexp$, $r_e \equiv re$, $a \equiv a$, $\sigma_1 \equiv s1$, $\sigma_2 \equiv s2$.

The output data, given at the end of the script are, respectively, E , E_{exp} , μ_e , r_0 and r_e .

Input data.

ZA = 5;

ZB = 1;

s1A1 = 0.862983;

sA11 = .00246735;

sA1A2 = .25;

1 **alpha = 63;**

2 **al = alpha * $\frac{\pi}{180}$;**

3 **s1A3 = $\frac{1}{4 * \sqrt{\frac{1}{2} + \frac{s1 * \text{Cos}[al]}{2 * \sqrt{s1^2 + a^2}}}}$;**

4 **sA3A4 = $\frac{1}{4 * \text{Sin}[al]}$;**

5 **Z1A = ZA - 2 * s1A1 - 2 * s1A3;**

6 **Z1MA = ZA - 2 - 2 * s1A3;**

7 **Z1MB = 1;**

8 **ZA1 = ZA - sA1A2 - 3 * sA11;**

9 **ZA3 = ZA - 2 * s1A1 - s1A3 - sA3A4;**

10 **ZA4 = ZA3;**

11 **Z2B = ZB;**

12 **Z2MB = ZB;**

13 **excen = .97;**

14 **r = $\frac{2}{ZA3} * \left(1 + \frac{\text{excen}^2}{2}\right)$;**

15 **d = r * Cos[al];**

16 **b = r * Sin[al];**

17 **ZnA = ZA - 2 - $\frac{2 * (s1 + s2)^2 * (s1 + s2 + d)}{((s1 + s2 + d)^2 + b^2)^{\frac{3}{2}}}$;**

18 **ZnB = 1;**

19 **Ettotal = $-\frac{Z1A^2}{4} - 1 - \frac{ZA3^2}{2} - 2 * ZA1^2 + \frac{1}{\sqrt{\left(\frac{s1}{4} + \frac{s2}{4}\right)^2 + \left(\frac{3}{2} * a\right)^2}} - \frac{1}{\sqrt{\left(\frac{s1}{4} + s2\right)^2 + \left(\frac{3}{4} a\right)^2}} -$**

20 **$\frac{ZA - 2}{\sqrt{\left(\frac{s2}{4} + s1\right)^2 + \left(\frac{3}{4} a\right)^2}} + \frac{2}{\sqrt{\left(\frac{s2}{4} + s1 + d\right)^2 + \left(\frac{3}{4} a\right)^2 + b^2}} - \frac{2}{\sqrt{(s1 + s2 + d)^2 + b^2}} + \frac{ZA - 2}{s1 + s2} + \frac{ZA1^{\frac{3}{2}}}{8}$;**

21 **r0 = (s1 + s2) * .529177 * 2A;**

22 **$\mu e = -5.08315 * (-2 * s1 + ZB * (s1 + s2) + 2 * d)D$;**

23 **Experimental data**

24 **D00 = $\frac{3.42}{13.60535}$;**

25 **SEiA = $\frac{8.29803 + 25.15484 + 37.93064 + 259.37521 + 340.22580}{13.60535}$;**

26 **SEiB = 1;**

27 **Eexp = -SEiA - SEiB - D00;**

28 **re = 1.2324A;**

29 **System of equations.**

30 **Eq1 = EB + $\frac{Z1A^2}{4} + Z2B^2 + \frac{Z1MB}{\sqrt{\left(\frac{3}{4} a\right)^2 + \left(\frac{s1}{4} + s2\right)^2}} + \frac{Z1MA}{\sqrt{\left(\frac{3}{4} a\right)^2 + \left(\frac{s2}{4} + s1\right)^2}} -$**

31 **$\frac{1}{\sqrt{\left(2 * \frac{3}{4} a\right)^2 + \left(\frac{s1}{4} + \frac{s2}{4}\right)^2}} - \frac{ZnAZnB}{s1 + s2}$;**

32 **Eq2 = EB + $\frac{3\sqrt{Z1MA}}{(s1^2 + a^2)^{\frac{3}{4}}}$;**

33 **Eq3 = EB + $\frac{3\sqrt{Z1MB}}{(s2^2 + a^2)^{\frac{3}{4}}}$;**

34 **Eq4 = EB + $\frac{2 * Z1MA}{\sqrt{s1^2 + a^2}} + \frac{2 * Z1MB}{\sqrt{s2^2 + a^2}} - \frac{1}{2a} - \frac{ZnAZnB}{s1 + s2}$;**

35 **The solution of the system of equations.**

36 **Sol = FindRoot[{Eq1 == 0, Eq2 == 0, Eq3 == 0, Eq4 == 0}, {{EB, 3.25},**

37 **{s1, .876}, {s2, .254}, {a, .911}}]**

38 **{EB → -3.19537, s1 → 0.888324, s2 → 0.261022, a → 0.922599}**

39 **Verification.**

40 **N[Eq1]/.Sol**

41 **N[Eq2]/.Sol**

42 **N[Eq3]/.Sol**

43 **N[Eq4]/.Sol**

44 **6.661338147750939*^-16**

1 4.440892098500626*^-16
 2 -8.881784197001252*^-16
 3 4.440892098500626*^-16
 4 Calculation of other quantities.

5 **Etotal/.Sol**

6 **Eexp**

7 **μe/.Sol**

8 **r0/.Sol**

9 **re/.Sol**

10 -50.4587

11 -50.5691

12 -1.86638D

13 1.21642A

14 1.2324A

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 16
 17
 18
 19
 20 **S3.9. Mathematica 7 script for the calculation of CH.**

21 The equivalences between the notations from paper and the symbols which are used
 22 in program are $Z_A \equiv ZA$, $Z_B \equiv ZB$, $s_{1,A1} \equiv s1A1$, $s_{A1,1} \equiv sA11$, $s_{A1,A2} \equiv sA1A2$,
 23 $\alpha \equiv \text{alpha}$, $s_{1,A3} \equiv s1A3$, $s_{1,A4} \equiv s1A4$, $s_{1,A5} \equiv s1A5$, $s_{A3,A4} \equiv sA3A4$, $Z_{1(A)} \equiv Z1A$,
 24 $Z_{1M(A)} \equiv Z1MA$, $Z_{A1} \equiv ZA1$, $Z_{A3} \equiv ZA3$, $Z_{A4} \equiv ZA4$, $Z_{A5} \equiv ZA5$, $Z_{2(B)} \equiv$
 25 $Z2B$, $Z_{2M(B)} \equiv Z2MB$, $e \equiv \text{excen}$ $r \equiv r$, $d \equiv d$, $b \equiv b$, $Z_{nA} \equiv ZnA$, $Z_{nB} \equiv ZnB$,
 26 $\underline{E} \equiv Etotal$, $\underline{E}_b \equiv EB$, $r_0 \equiv r0$, $\mu_e \equiv \mu e$, $\underline{D}_0^0 \equiv D00$, $\underline{SE}_{iA} \equiv SEiA$, $\underline{SE}_{iB} \equiv SEiB$,
 27 $\underline{E}_{exp} \equiv Eexp$, $r_e \equiv re$, $\underline{a} \equiv A$, $\underline{\sigma}_1 \equiv s1$, $\underline{\sigma}_2 \equiv s2$.

28 The output data, given at the end of the script are, respectively, \underline{E} , \underline{E}_{exp} , μ_e , r_0
 29 and r_e .

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 31
 32 Input data.

33 **ZA = 6;**

34 **ZB = 1;**

35 **s1A1 = 0.85505;**

36 **sA11 = .00269287;**

37 **sA1A2 = .25;**

38 **alpha = 67;**

39 **al = alpha * $\frac{\pi}{180}$;**

40 **s1A3 = $\frac{1}{4 * \sqrt{\frac{1}{2} + \frac{s1 * \text{Cos}[al]}{2 * \sqrt{s1^2 + a^2}}}}$;**

41 **s1A4 = $\frac{\sqrt{2}}{4 * \sqrt{1 + \frac{s1 * \text{Cos}[al] - \frac{\sqrt{3}}{2} * a * \text{Sin}[al]}{\sqrt{s1^2 + a^2}}}}$;**

42 **s1A5 = $\frac{\sqrt{2}}{4 * \sqrt{1 + \frac{s1 * \text{Cos}[al] + \frac{\sqrt{3}}{2} * a * \text{Sin}[al]}{\sqrt{s1^2 + a^2}}}}$;**

43 **sA3A4 = $\frac{1}{2 * \sqrt{3} * \text{Sin}[al]}$;**

44 **Z1A = ZA - 2s1A1 - s1A3 - s1A4 - s1A5;**

45 **Z1MA = ZA - 2 - s1A3 - s1A4 - s1A5;**

46 **Z1MB = 1;**

47 **ZA1 = ZA - sA1A2 - 4 * sA11;**

48 **ZA3 = ZA - 2 * s1A1 - 2 * sA3A4 - s1A3;**

49 **ZA4 = ZA - 2 * s1A1 - 2 * sA3A4 - s1A4;**

50 **ZA5 = ZA - 2 * s1A1 - 2 * sA3A4 - s1A5;**

51 **Z2B = ZB;**

$$Z2MB = ZB;$$

$$\text{excen} = .98;$$

$$r = \left(\frac{1}{ZA3} + \frac{1}{ZA4} + \frac{1}{ZA5} \right) * \frac{2}{3} * \left(1 + \frac{\text{excen}^2}{2} \right);$$

$$d = r * \text{Cos}[al];$$

$$b = r * \text{Sin}[al];$$

$$ZnA = ZA - 2 - \frac{3*(s1+s2)^2*(s1+s2+d)}{((s1+s2+d)^2+b^2)^{\frac{3}{2}}};$$

$$ZnB = 1;$$

$$\text{Etotal} = -\frac{Z1A^2}{4} - \frac{ZA3^2}{4} - \frac{ZA4^2}{4} - \frac{ZA5^2}{4} - 1 - 2 * ZA1^2 + \frac{1}{\sqrt{\left(\frac{s1}{4} + \frac{s2}{4}\right)^2 + \left(\frac{3}{2} * a\right)^2}} -$$

$$\frac{1}{\sqrt{\left(\frac{s1}{4} + s2\right)^2 + \left(\frac{3}{4} * a\right)^2}} - \frac{ZA-2}{\sqrt{\left(\frac{s2}{4} + s1\right)^2 + \left(\frac{3}{4} * a\right)^2}} + \frac{1}{\sqrt{\left(\frac{3}{4} * a\right)^2 + b^2 + \left(\frac{s2}{4} + s1 + d\right)^2}} +$$

$$\frac{1}{\sqrt{\left(\frac{3}{4} * a - \frac{\sqrt{3}}{2} * b\right)^2 + \left(\frac{b}{2}\right)^2 + \left(\frac{s2}{4} + s1 + d\right)^2}} + \frac{1}{\sqrt{\left(\frac{3}{4} * a + \frac{\sqrt{3}}{2} * b\right)^2 + \left(\frac{b}{2}\right)^2 + \left(\frac{s2}{4} + s1 + d\right)^2}} -$$

$$\frac{3}{\sqrt{b^2 + (s1+s2+d)^2}} + \frac{(ZA-2)*ZB}{s1+s2} + \frac{ZA1^{\frac{3}{2}}}{8};$$

$$r0 = (s1 + s2) * .529177 * 2A;$$

$$\mu e = -5.08315 * (-2 * s1 + ZB * (s1 + s2) + 3 * d)D;$$

Experimental data.

$$D00 = \frac{3.465}{13.60535};$$

$$\text{SEiA} = \frac{11.26030 + 24.38332 + 47.8878 + 64.4939 + 392.087 + 489.99334}{13.60535};$$

$$\text{SEiB} = 1;$$

$$\text{Eexp} = -\text{SEiA} - \text{SEiB} - D00;$$

$$\text{re} = 1.1199A;$$

System of equations.

$$\text{Eq1} = \text{EB} + \frac{Z1A^2}{4} + Z2B^2 + \frac{Z1MB}{\sqrt{\left(\frac{3}{4} * a\right)^2 + \left(\frac{s1}{4} + s2\right)^2}} + \frac{Z1MA}{\sqrt{\left(\frac{3}{4} * a\right)^2 + \left(\frac{s2}{4} + s1\right)^2}} -$$

$$\frac{1}{\sqrt{\left(2 * \frac{3}{4} * a\right)^2 + \left(\frac{s1}{4} + \frac{s2}{4}\right)^2}} - \frac{ZnAZnB}{s1+s2};$$

$$\text{Eq2} = \text{EB} + \frac{3\sqrt{Z1MA}}{(s1^2+a^2)^{\frac{3}{4}}};$$

$$\text{Eq3} = \text{EB} + \frac{3\sqrt{Z2MB}}{(s2^2+a^2)^{\frac{3}{4}}};$$

$$\text{Eq4} = \text{EB} + \frac{2*Z1MA}{\sqrt{s1^2+a^2}} + \frac{2*Z1MB}{\sqrt{s2^2+a^2}} - \frac{1}{2a} - \frac{ZnAZnB}{s1+s2};$$

Solutia sistemului de ecuatii

$$\text{Sol} = \text{FindRoot}\{\{\text{Eq1} == 0, \text{Eq2} == 0, \text{Eq3} == 0, \text{Eq4} == 0\},$$

$$\{\{\text{EB}, 4.3\}, \{s1, .796\}, \{s2, .190\}, \{a, .808\}\}\}$$

$$\{\text{EB} \rightarrow -4.29182, s1 \rightarrow 0.840475, s2 \rightarrow 0.175936, a \rightarrow 0.767725\}$$

Verification.

$$N[\text{Eq1}]/.\text{Sol}$$

$$N[\text{Eq2}]/.\text{Sol}$$

$$N[\text{Eq3}]/.\text{Sol}$$

$$N[\text{Eq4}]/.\text{Sol}$$

$$4.440892098500626 * 10^{-16}$$

$$0.$$

$$-8.881784197001252 * 10^{-16}$$

$$8.881784197001252 * 10^{-16}$$

Calculation of other quantities.

$$\text{Etotal}/.\text{Sol}$$

$$\text{Eexp}$$

$$\mu e / .\text{Sol}$$

$$r0 / .\text{Sol}$$

$$\text{re} / .\text{Sol}$$

$$-76.6349$$

1 -76.968
2 -1.91195D
3 1.07572A
4 1.1199A
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For Peer Review Only

Dear Professor Head-Gordon,

Please receive the revised form of my manuscript TMPH-2010-0364, entitled “Unconventional semiclassical method for calculating the energetic values of diatomic molecules.”

Below is the cover letter containing the response to the referee comments and the changes I have made in the revised manuscript.

Thank you very much,
Alexandru Popa

Cover letter containing the response to the referee comments and the changes in the revised manuscript of manuscript TMPH-2010-0364, entitled “Unconventional semiclassical method for calculating the energetic values of diatomic molecules,” author Alexandru Popa

I would like to thank the referee for the analysis of my paper and for the suggestions and issues raised, which are very useful in order to improve the clarity of my presentation.

Below is my response to the issues raised by the referee, together with the changes I have made in the revised manuscript.

a) On the comment which refers to the central field method.

Since the behavior of stationary systems is described by the Schrodinger equation, the method to calculate the systems’ energetic values presented in this paper is based on the general wave properties, which are synthesized in our paper [26]. The main property of these systems is that the geometric elements of the wave described by the Schrodinger equation in the space R^{3N} of the electron coordinates, namely the Σ wave surfaces and their C normal curves, are solutions of the Hamilton-Jacobi equation written for the same system. The motion of the Σ surfaces is periodical and the C curves are closed. A. Luis proved the same property in a completely different way [32], by showing that the discontinuities of the second derivatives of the wave function propagate on trajectories that result from the Hamilton-Jacobi equation, written for the same system. On the other hand, according to the theory of differential equations, these discontinuities occur across characteristic surfaces of the wave equation, which are the wave surfaces of the system. It results the perfect equivalence between the properties which have been proven in [26] and [32].

From here it follows the idea of our approach: instead of finding the wave function ψ , we use the properties of the curve C , in order to calculate the energetic values, because ψ and C belong to the same physical system. To accomplish this, we calculate exactly the projections of the C curve from the space R^{3N} of the electron coordinates to the tridimensional spaces of the coordinates of the electrons of the systems, denoted by C_a in the cases of simple systems. For complex systems, a very good approximation of the C_a curves results using the central field approximation. More simply, we have to calculate or to approximate the classical periodic solutions of the system.

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The main mathematical problem, which is the calculation of the electrostatic energy between two electrons that move in the field of the same nucleus, is strongly simplified by the symmetry property of the system, which makes possible the calculation of the reciprocal screening coefficients between electrons. The expression of this electrostatic energy is given by relation (10). In this case, the motions of the electrons are separated, and each electron moves in the central field of the nucleus, having an effective order number, in the averaged field of the other electrons. These last two properties are the attributes of the central field method. At this point, the parallelism between the central field method in the case of the quantum calculation and in the case of semiclassical calculation is perfect.

This parallelism remains valid in the case of molecules because we proved that the C_1 curve corresponding to a molecular bond is composed of two atomic curves, which are denoted by C_{1A} and C_{1B} . In this case, in virtue of relation (A3), the motion of the e_1 bond electron on the curve C_{1A} is reduced to that in a central field, and e_1 moves in the averaged field of the electron e_2 and of the nucleus n_B . Similar properties are valid when the electron moves on the C_{1B} curve.

Revision: In Section 2, I introduced the following paragraph after Eq. (11):

“The model represented by equations (3)-(10) has two properties which are both attributes of a central field type solution. The first is that the motion of an arbitrary electron is similar to that in a hydrogenoid system, and it takes place in the averaged field of the other electrons. The effect of the interaction with these electrons is included in the effective order number of the nucleus. The second property, which is useful in applications, is that adding a supplementary electron to the system leads only to the modification of the effective order numbers corresponding to the other electrons, while their equations remain unchanged.”

A second revision, which refers to the central field method applied in the case of the calculation of the C_a curves of the bond electrons is made in the paragraph which has been introduced at the end of the Section 3, which refers also to the modeling of the lone pair electrons. See the revisions made at the point d).

b) On the comment which refers to the calculation of the bond length.

Our calculations take into account all the components of the total energy of the system, with one exception, which results from the hypothesis (h5), namely kinetic energies of the nuclei are zero. On the other hand, the potential energy of the interaction between nuclei is taken into account in our calculations. It follows that the distance between nuclei, which is denoted by r_0 in the manuscript, corresponds to values of the nuclei velocities of zero. The experimental value of the distance between nuclei, which is denoted by r_e in [34], corresponds to the minimum of the Morse curve, which stands for the maximum velocities of the nuclei. This explains the differences between the values of r_0 and r_e : the former corresponds to zero velocities of the nuclei, while the latter corresponds to maximum velocities of the nuclei.

Revisions:

- In the revised manuscript we introduced Table 3 which contains a comparison between the values of r_0 and r_e , which is taken from [29]. The table contains also the domains of the values of the distances between nuclei, calculated by the Hartree-Fock method, which are taken from [29] as well.
- The paragraphs before and after Eq. (44) in Section 4 are changed as follows:

“In virtue of hypothesis (h5), the kinetic energy of the nuclei is zero. It follows that the distance between nuclei, denoted by r_0 and calculated with the relation

$$\dots\dots\dots (44)$$

corresponds to values of the nuclei velocities of zero. On the other hand, the experimental value of the distance between nuclei, denoted by r_e , corresponds to the minimum of the Morse curve [34]. The theory of the harmonic oscillation of the nuclei shows that this minimum corresponds to maximum velocities of the nuclei. It follows that r_0 is different from r_e because the first corresponds to zero velocities of the nuclei, while the last corresponds to the maximum velocities of the nuclei.”

- In Section 5, I changed the paragraph following Eq. (46). It now reads:

“The values of r_0 , calculated from (44), and the experimental value of the distance between nuclei, denoted by r_e and taken from Ref. [29], are given in angstroms in Table 3. Table 3 also gives the range of values for the distances between nuclei, denoted by r_{eHF} , calculated with the Hartree-Fock method and taken from [29].”

- c) On the comment which refers to the shape of the curve C_{1A} from Fig. 1.

The C_a curves for s states and those resulting from the exact solutions in the cases of boron or carbon atoms [28] are elliptic quasilinear curves (sometimes called pendular curves). These ellipses have $b \gg a$, where b and a are the ellipse semiaxes. Consequently, the upper and lower parts of each ellipse are very close, and, for simplicity the ellipse is drawn as a straight line. This is why the curve C_{1a} in Fig. 1 is drawn as a straight line in the vicinity of the nucleus n_a . However, we have to imagine it as a very thin ellipse which surrounds the nucleus.

Revision: The second paragraph after Eqs. (16) and (17), in Section 3, is modified to read as follows

“..... For this reason, in this paper we restrict ourselves to the case in which the molecular C_1 curve is composed of two atomic curves, denoted by C_{1A} and C_{1B} which are ellipses with eccentricities very close to unity, as shown in Fig. 1. At the scale of the figure, these ellipses are drawn as straight lines in the vicinities of the nuclei, in spite of

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3 the fact that the curve C_{1A} surrounds the nucleus n_A while the curve C_{1B} surrounds the
4 nucleus n_B . The curves C_1 and C_2 depend on three parameters:

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8 d) On the comment which refers to the lone pair electrons.
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10 The interaction between the electrons that move in the field of the same nucleus, in the
11 case of the central field approach, is reflected by the reciprocal screening coefficient that
12 enters in the expression of the effective order number of the nucleus. A general property
13 results: the addition of a new electron to the system modifies only the expression of the
14 effective order number of the nucleus, but leaves unchanged the equations of motion of
15 the electrons.
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17 In view of this property, the calculation of the C_a curves of the bond electrons is done
18 in an identical manner regardless of whether there are valence electrons that do not
19 participate in the bond or there are no such valence electrons. More specifically, in
20 Section 3.1 we analyzed the case of no non-bonding electrons as a general recipe that
21 allows the calculation of C_a curves. Subsequently, we showed that, adding a non-bonding
22 valence electron does not change the system of equations that leads to the curve C_a .
23 Instead the only modification is in the expression of the effective order number.
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27 Revision: At the end of the Section 3 we have introduced the following paragraph in
28 order to explain these points better:
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31 “In this section we have calculated the C_a curves when the bond electrons move in the
32 fields of two nuclei and the system contains only valence electrons which participate to
33 the bond. In Appendix we proved that the motion of a bond electron in the case of
34 homonuclear molecules with simple bond is similar to that in a central field. An example
35 of such an electron is e_1 which moves on curves C_{1A} and C_{1B} . This property results from
36 relation (A3). Identical properties are proved in the Supplementary Online Material for
37 other types of bonds. It follows from Section 2 that, in virtue of the second property of
38 motion in the central field, adding a supplementary electron that does not participate to
39 the bond in the field of the nucleus n_A does not change the equation of motion of the
40 electron e_1 . The only change is the fact that the expression of Z_1 contains a supplementary
41 screening coefficient corresponding to the interaction between e_1 and the supplementary
42 electron. In the next section we will see that for the general case of the molecules which
43 contains electrons which do not participate to the bond, the relations from Appendix
44 remain valid, with the only difference that the expressions of the order numbers are
45 changed.”
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50 e) On the comment referring to the sigma and pi nature of the double bond.
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52 The parallelism between the central field approaches in quantum and classical
53 calculations goes far in the cases of the hybrid solutions which appear when the number
54 of the electrons is increased. The hybrid solutions are imposed by the symmetry
55 properties of the system. For example, in the case of the carbon atom, the wave function
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of the valence electrons is invariant under the symmetry operations of the regular tetrahedron (RTH) configuration [33], and leads to symmetrical orbitals, having identical shapes. We have shown that this property results rigorously from the classical equations [28], because the C_a curves have a tetrahedron configuration in the case of the carbon atom. These curves are hybrid ones, of sp type, because they have identical shapes and their angular momentum is between a negligible value and $\sqrt{2}\hbar$, which correspond, respectively, to the 2s and 2p curves [28].

As we have shown in Section 3, the molecular curves corresponding to the simple, double and triple bonds are combinations of the sp hybrid atomic curves. As a consequence, the C_a curves of the double bond have a sigma and pi nature, because they are combinations of sp atomic curves. The hybrid character of these curves is reflected, as in the case of the atomic curves, by the fact that they are symmetrical and their shapes are identical.

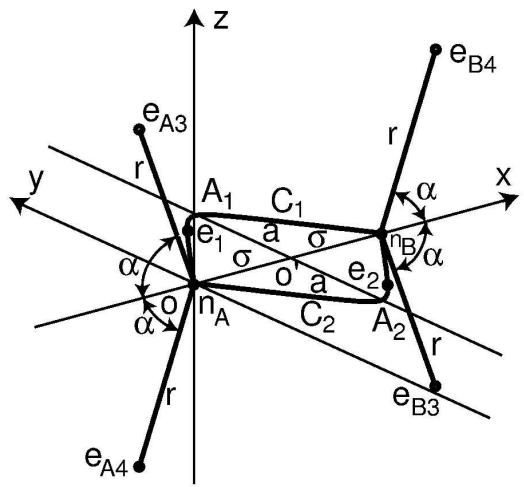
f) On the comment which refers to the references.

Answer and revisions: In response to the referee's comment I introduced 16 new references. In addition I have modified the first paragraph of the Introduction, as follows:

“Over the last few years, a large number of semiclassical approaches were published in the field of atomic and molecular systems [1]-[5]. The semiclassical methods lead to solutions which are relatively easy to calculate, using the information obtained from the study of classical trajectories. In numerous papers the semiclassical eigenvalues of the bond states are related to the periodic trajectories [6]-[12], in others they are related to the phase manifolds generated by quasiperiodic trajectories [13]-[15]. In this family of topics we can consider also the study of the semiclassical trajectories with the aid of the propagator functions [16]-[20] or the application of a generalized semiclassical theory to multidimensional dynamical systems [21]. In this paper we present a multidimensional semiclassical analysis which applies to a wide class of atoms and molecules.”

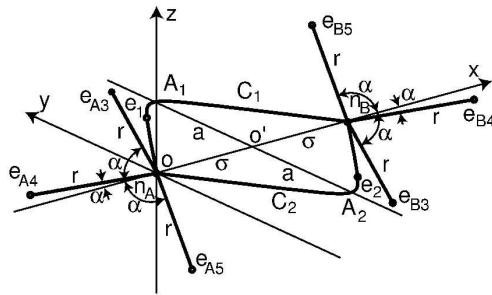
Thank you very much,
Alexandru Popa

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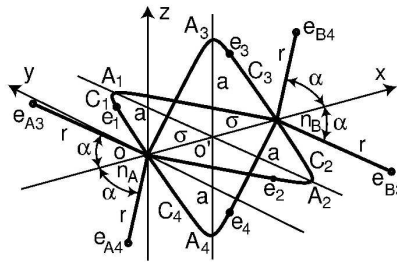


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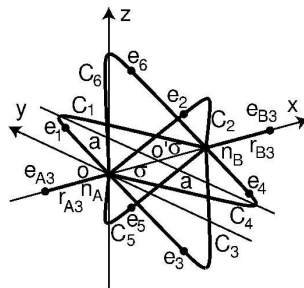
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(a)



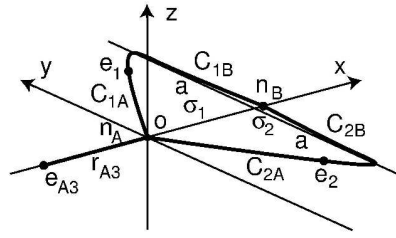
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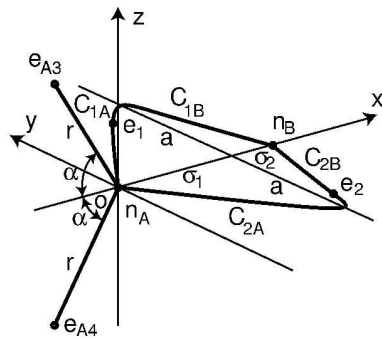
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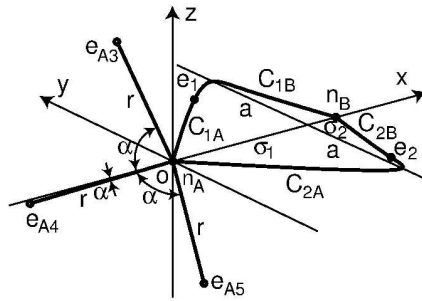
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