Chemical bond, de Broglie waves and bond multiplicity.

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Abstract: It is shown that the chemical bond is a purely quantum effect: when bonds are formed, the nuclei of atoms are inside the de Broglie waves of valence electrons. Moreover, the distance between chemically bound nuclei is always and for all types of bonding less than the de Broglie waves of valence electrons. Therefore, a chemical bond is a quantum mechanical effect. The physical substantiation of the multiplicity of the bond, which is the linear energy density of the chemical bond, is also given.

Keywords: Chemical bond, quantum effect, de Broglie wave, standing wave, bond multiplicity, complementarity principle.

INTRODUCTION.

Quantum mechanics is the science that describes our reality. More precisely, quantum mechanics describes our microcosm: the world of molecules, atoms, nuclei and elementary particles. That is, without quantum mechanics, we would not be able to correctly describe reality, as well as create modern electronic devices.

The world of quantum mechanics is described by the laws of nature, which are fundamentally different from the laws of the macrocosm in which we exist. Therefore, if we use classical physics (classical mechanics, thermodynamics, statistical physics and classical electrodynamics) to describe the microworld, then it is impossible to rationally explain and describe our reality. Misunderstanding of quantum mechanics is a consequence of the fact that people are trying to apply laws that, by definition, cannot describe the microcosm.

For example, Bohr in his doctoral dissertation (1911) on the classical electronic theory of metals proved a theorem according to which the magnetic moment of any set of elementary electric charges moving according to the laws of classical mechanics in a constant magnetic field is equal to zero in a stationary state.

"...In 1919, this theorem was independently rediscovered by Hendrik van Leeuwen and is called the Bohr-van Leeuwen theorem. It directly follows from it that it is impossible to explain the magnetic properties of matter (in particular, diamagnetism), while remaining within the framework of classical physics. This, apparently, was the first Bohr's collision with the limitations of the classical description, which led him to questions of quantum theory…" [1].

That is, if we want to correctly describe the real magnetic properties of substances, we need to abandon the classical laws.

Similarly, with electromagnetic radiation - for a correct description of the ultraviolet catastrophe we just need to accept that radiation represents certain portions of energy (quanta, 1901, M. Planck). Recall that the classical description considers electromagnetic radiation as an infinitely long wave.

The world of molecules (on the order of several angstroms) is also described by quantum mechanics. That is why the chemical bond is a purely quantum effect, which we will strictly show below. Consequently, the representation of a chemical bond as an electromagnetic interaction of nuclei and moving electrons is fundamentally wrong (this is a typically classical approach). Naturally, such a description will not be successful, and as a result, there is no physical justification, no predictive power, but only highly simplified, approximate and non-rigorous calculation methods. So, let's proceed to the proof that the chemical bond is a purely quantum effect.

RESULTS AND DISCUSSION.

Recall that quantum effects begin to manifest themselves significantly when the distance between interacting particles becomes smaller than the de Broglie wave.

$$\Lambda = h / (m * v)$$

Since particles in the microcosm are in constant specific motion, then, according to de Broglie, each such particle will correspond to a wave of a certain length. If the particles are inside such a wave, then the interaction between them will be of a quantum mechanical nature, that is, it will be quantum. The laws of classical physics no longer play a decisive role.

From here, the mechanism of formation of a chemical bond strictly follows: for the formation of a bond, it is necessary that the nuclei of atoms be inside the de Broglie waves of valence electrons, only under this condition is quantum mechanical interaction between atoms possible. Further, we will show that the distance between chemically bound nuclei is always and in all types of bonding less than the de Broglie waves of valence electrons. This is irrefutable proof that the chemical bond is a quantum mechanical effect. So let's get to the proof.

Using Bohr's principle of complementarity, we can legitimately consider the valence electrons of an atom and the electrons of a chemical bond as point particles that move at a certain speed. For example, in a Bohr hydrogen atom, an electron moves along an orbit of radius r = 0.5292 Å, with a speed v = 2.1877 * 10^6 m/s. Then, the length of the standing wave in the Bohr orbit will be equal to:

$$\lambda = 2 * \pi * r = 3.3249 \text{ Å}$$

Given that the chemical bond is formed by the valence electrons of the atom, and knowing the length of the de Broglie wave of the valence electron, we can easily determine the length of the chemical bond.

Here it is necessary to clarify that the chemical bond can be represented as the vibrations of a string. Moreover, in our consideration, the string will be a standing de Broglie wave between the nuclei. The nuclei of atoms are the nodes of a standing wave. Such a representation follows from the fact that the vibrations of an ordinary string are determined by the linear density of the string and the force of the string tension.

The chemical bond also has a certain linear density (energy), which is strictly correlated with the bond multiplicity. For more details, see: Note 2. The multiplicity of the chemical bond. In addition, the linear density of a chemical bond from a physical point of view can be interpreted as a force holding the nuclei of atoms ($F = E / L$).

Therefore, based on the multiplicity of the bond, it follows that the chemical bond is a standing wave with a certain linear energy density. That is, a chemical bond can be viewed as an oscillating string with a certain frequency (a standing wave). It is clear that this vibrational frequency will determine the energy of a given chemical bond. Therefore, a chemical bond is a kind of energy quantum, since the standing waves of a string are ideally quantized. Naturally, the de Broglie wave of an electron will form a standing wave.

Since the standing wave of the string is quantized, an integer number of half-waves ($\lambda/2$) will fit along the length of the string:
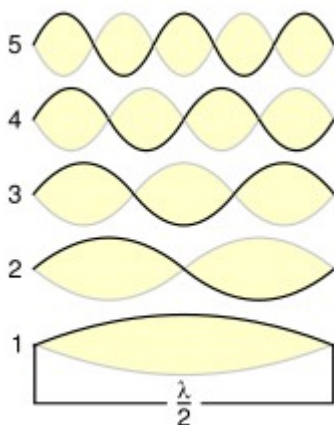
$$L = (\lambda / 2) * n$$

where L is the length of the chemical bond (the distance between the nuclei of atoms),

λ is the de Broglie wavelength of the valence electron,

$n = 1, 2, 3\ldots$

Look at the picture that shows the vibrations of a string attached to the ends [2].

In the ground state ($n = 1$), the standing wave of the string will be an ordinary chemical bond. Then, the length of the chemical bond will be equal to the de Broglie half-wave length ($\lambda/2$).

$$L = \lambda / 2$$

Given that the de Broglie wavelength in the Bohr orbit is 3.3249 Å ($\approx$ 3.33 Å), we can easily obtain the theoretical length of a chemical bond that a hydrogen atom can form.

$$L = \lambda / 2 = 3.3249 \text{ Å} / 2 = 1.6625 \text{ Å} \approx 1.66 \text{ Å}.$$

But, since during the transition of a valence electron from the Bohr orbit to a chemical bond, additional energy is released, due to taking into account the "longitudinal mass" [3], the length of a real chemical bond will always be less than the theoretical value calculated by us (than more energy, the shorter the wavelength). For example, in a molecular hydrogen ion and in a hydrogen molecule, the length of a chemical bond formed from one and, respectively, two valence electrons is:

$$L(H2+) = 1.06 \text{ Å}$$

$$L(H\text{-}H) = 0.7416 \text{ Å}$$

That is, the length of both bonds is less than 1.66 Å, which was to be expected based on our assumptions.

In fact, the "maximum" bond length obtained by us for the Bohr electron of hydrogen (1.66 Å) limits the length of "strong" chemical bonds in which a hydrogen atom can participate.

But, since the length of the de Broglie wave for a hydrogen electron is 3.33 Å, then "weak" chemical bonds involving a hydrogen atom can have a length of up to 3.33 Å. Theoretically, an even greater increase in the bond length, that is, more than 3.33 Å, is possible due to a change in the characteristics of the valence electron, and, consequently, an increase in the length of the de Broglie wave. But, such an increase will lead to a very strong decrease in the binding energy - these will already be "ultra-weak" bonds with the participation of a hydrogen atom.

The above is confirmed by real hydrogen bonds, which are divided into "weak" (energy of the order of 20 - 50 kJ/mol) and "strong" hydrogen bonds with an energy of 100 kJ/mol or more. Moreover, the length of "weak" hydrogen bonds is indeed more than 1.66 Å (up to 3 Å and more), and the length of "strong" bonds is less than 1.66 Å (hydrogen and ordinary covalent bonds involving a hydrogen atom).

It is also commonly believed that atoms can be linked by a hydrogen bond if the distance between them is up to 3.6 Å, which fully confirms what has been said.

Let us clarify that when calculating the bond length, another atom must also be taken into account, because valence electrons of different atoms participate in the classical covalent two-electron bond. Therefore, for a more accurate analysis of bonds involving hydrogen, we calculate the length of the de Broglie wave of the valence electron for oxygen and fluorine atoms.

For calculations, we assume that the valence electron rotates in a circular "Bohr" orbit of the corresponding atom. Then, the real radius of the atom will be the "Bohr" radius for a particular atom. In this case, the calculations are completely similar to those given above.

The radius of the oxygen atom, according to Enrico Clementi is 0.48 Å [4].

Calculate the wavelength and half-wave.

$$r(O) = 0.48 \text{ Å}$$

$$\lambda = 2 * \pi * r = 3.0159 \text{ Å} \approx 3 \text{ Å}$$

$$L = \lambda / 2 = 3.0159 \text{ Å} / 2 = 1.5080 \text{ Å} \approx 1.5 \text{ Å}.$$

According to the calculation, "strong" bonds involving hydrogen and oxygen atoms will be less than 1.5 Å, and "weak" bonds will be more than 1.5 Å, but less than 3 Å. Then, "ultra-weak" bonds (OH) will have a length of more than 3 Å.

The radius of the fluorine atom according to Clementi is 0.42 Å [4]. Calculate the wavelength and half-wave.

$$r(F) = 0.42 \text{ Å}$$

$$\lambda = 2 * \pi * r = 2.6389 \text{ Å} \approx 2.64 \text{ Å}$$

$$L = \lambda / 2 = 2.6389 \text{ Å} / 2 = 1.3195 \text{ Å} \approx 1.32 \text{ Å}.$$

That is, "strong" bonds involving hydrogen and fluorine atoms will be less than 1.32 Å, and "weak" bonds will be more than 1.32 Å, but less than 2.64 Å.

To confirm the results obtained, we consider the energy and length of bonds involving hydrogen in the water dimer, in the difluoride anion, and in hydrogen fluoride [5].

In the water dimer $(H_2O)_2$, the hydrogen bond length is 1.77 Å and the energy is 21.5 kJ/mol. The length of an ordinary O-H covalent bond is 0.96 Å.

$$(H_2O)_2$$
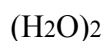
Hydrogen bond (O…H).   L = 1.77 Å,   E = 21.5 kJ/mol

O-H,   L = 0.96 Å

That is, in the water dimer, the "weak" hydrogen bond has a length of more than 1.5 Å, as we predicted (greater than the half-wave length of oxygen and hydrogen atoms, 1.5 Å, 1.66 Å). And the usual covalent O-H bond has a length less than the indicated values.

In the difluoride anion $[F…H…F]^-$ both hydrogen bonds are equal. The length of one such bond is 1.13 Å, and the energy is 150 kJ/mol.

$$[FHF]^-$$

Hydrogen bond (F…H).   L = 1.13 Å,   E = 150 kJ/mol

As you can see, the "strong" hydrogen bond in the difluoride anion has a length of 1.13 Å, that is, less than the half-wave length of the fluorine atom (1.32 Å), and naturally less than the hydrogen half-wave (1.66 Å). This is indeed a "strong" hydrogen bond, since its energy is 150 kJ/mol.

The usual H-F covalent bond in hydrogen fluoride has a length of 0.92 Å, which is also less than the half-wave of the fluorine atom (1.32 Å).

$$H\text{-}F, \quad L = 0.92 \text{ Å}$$

It is interesting to note that the single bond in the fluorine molecule has a length of 1.404 Å, which is slightly longer than the half-wavelength of the valence electron for the fluorine atom (1.32 Å).

$$L(F\text{-}F) = 1.404 \text{ Å}$$

$$\lambda / 2 = 1.32 \text{ Å}$$

Such an increase in the length of a chemical bond is due to the repulsion of electron pairs of different fluorine atoms (each atom has three pairs). Therefore, it can be strictly stated that the multiplicity of bond in a fluorine molecule will be less than unity.

Next, we will analyze the carbon atom, since the chemistry of carbon is the basis of our life.

The radius of the carbon atom according to Clementi is 0.67 Å [4]. Calculate the wavelength and half-wave for the valence electron.

$$r(C) = 0.67 \text{ Å}$$

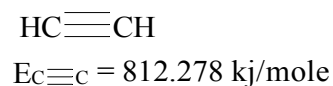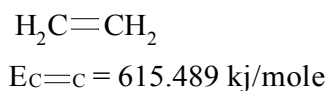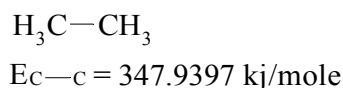$$\lambda = 2 * \pi * r = 4.2097 \text{ Å} \approx 4.21 \text{ Å}$$

$$L = \lambda / 2 = 4.2097 \text{ Å} / 2 = 2.1049 \text{ Å} \approx 2.11 \text{ Å}.$$

Therefore, "strong" C-C bonds will have a length of less than 2.11 Å, and "weak" C-C bonds will be greater than 2.11 Å, but less than 4.21 Å. "Ultra-weak" C-C bonds will have a length greater than 4.21 Å.

This is true. Here are the data on the length and energy of C-C bonds in ethane, ethylene and acetylene [6].

$$H_3C-CH_3 \qquad\qquad H_2C=CH_2 \qquad\qquad HC\equiv CH$$
$$L_{C-C} = 1.543 \text{ Å} \qquad L_{C=C} = 1.338 \text{ Å} \qquad L_{C\equiv C} = 1.205 \text{ Å}$$

$$H_3C-CH_3 \qquad\qquad H_2C=CH_2 \qquad\qquad HC\equiv CH$$
$$E_{C-C} = 347.9397 \text{ kj/mole} \qquad E_{C=C} = 615.489 \text{ kj/mole} \qquad E_{C\equiv C} = 812.278 \text{ kj/mole}$$

It is clear that these covalent bonds are "strong" bonds.

Another thing is interesting, in benzene and other aromatic compounds there are also "weak" C-C bonds - this is an interaction through a cycle. This type of interaction in condensed aromatic compounds such as naphthalene, anthracene, phenanthrene, coronene, benzpyrene, etc. are typical "weak" and "ultra-weak" C-C bonds. Here is the molecular structure of naphthalene and phenanthrene [7]:
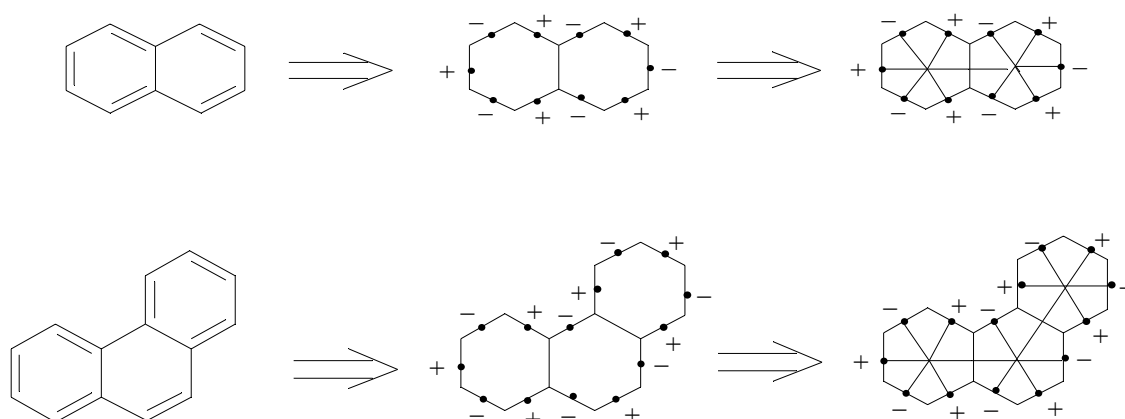
In benzene, the interaction through the cycle is formally a "weak" C-C bond, but in energy it is very close to "strong" chemical bonds: the length of such a bond is 2.42 Å, and the energy is 81.5252 kJ/mol. In fact, a bond with an energy greater than 80 kJ/mol can be considered a "strong" bond - it's just a matter of classification [7, p. 4-5].
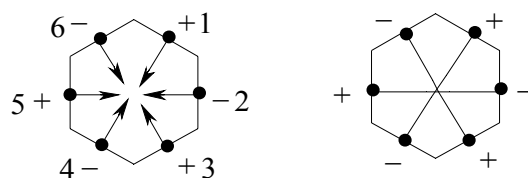

figure 3   figure 4

$$L_{1-2} = L_{1-6} = 1.210 \text{ Å}$$
$$L_{1-4} = 2.420 \text{ Å}$$
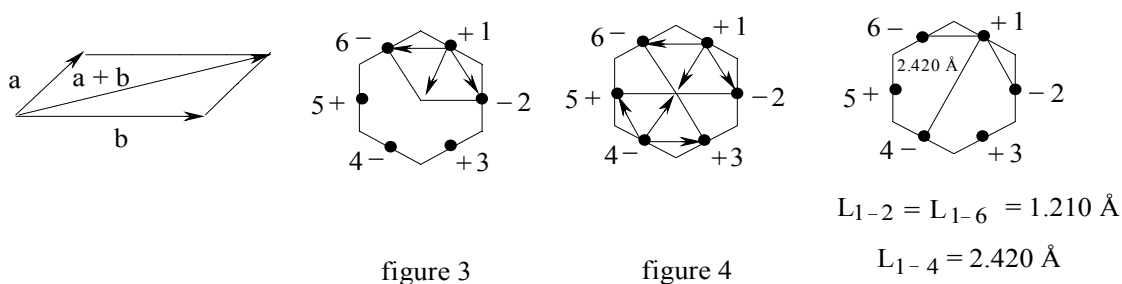
figure 5

L(1-4, 2-5, 3-6) = 2.42 Å

As we can see from the scheme of the benzene molecule, when interacting through the cycle, the electrons (or three-electron bonds) are at a distance of 2.42 Å, which is more than the half-wavelength for the valence electron of carbon (2.11 Å), but less than the wavelength (4.21 Å). The energy of one such interaction is 81.5252 kJ/mol [7, p. 10-11].

The three interactions through the cycle represent the delocalization energy of benzene [7, p. 11]:

$3 \cdot E = 244.5756$ kj/mole
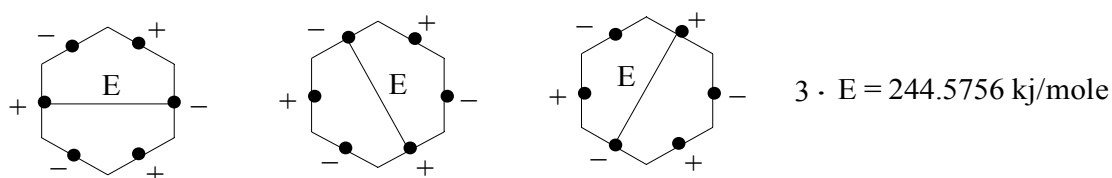
The interaction between graphite layers is also a typical "weak" chemical bond: the distance between the layers is 3.35 Å, which is greater than the half-wavelength (2.11 Å), but less than the wavelength (4.21 Å) of the carbon valence electron.

This approach to the explanation of the chemical bond easily describes the metallic bond. Consider alkali metals.

Recall that a metallic bond becomes covalent upon evaporation of alkali metals - metal vapors consist of diatomic Me-Me molecules and free atoms (during the condensation of vapors, we again obtain a metallic bond). The energy and length of the Me-Me covalent bond in the corresponding dimers are shown [8]:

Li_2,   L(Li-Li) = 2.67 Å,   E(Li-Li) = 102 kJ/mol

Na_2,   L(Na-Na) = 3.08 Å,   E(Na-Na) = 73 kJ/mol

K_2,   L(K-K) = 3.92 Å,   E(K-K) = 57 kJ/mol

Rb_2,   L(Rb-Rb) = 4.10 Å,   E(Rb-Rb) = 49 kJ/mol

8

Cs2,　　　L(Cs-Cs) = 4.30 Å,　　　E(Cs-Cs) = 42 kJ/mol

That is, a single bond in Me-Me diatomic alkali metal molecules is a typical covalent bond, the energy of which is slightly underestimated due to the large bond length, which is absolutely normal, since the energy and chemical bond length are strictly correlated (the longer the length, the less energy).

We especially note that in metals (metal bond), the nuclei of atoms are located at a distance that is much greater than the corresponding Me–Me single bond. For example, the translational lattice constant of a lithium crystal is a = 3.502 Å, and the Li-Li covalent bond length in a dimer is 2.67 Å. Similarly for other metals [9].

$$Li \rightarrow \quad a = 3.502 \text{ Å}, \quad L(Li-Li) = 2.67 \text{ Å}$$

$$Na \rightarrow \quad a = 4.282 \text{ Å}, \quad L(Na-Na) = 3.08 \text{ Å}$$

$$K \rightarrow \quad a = 5.247 \text{ Å}, \quad L(K-K) = 3.92 \text{ Å}$$

$$Rb \rightarrow \quad a = 5.69 \text{ Å}, \quad L(Rb-Rb) = 4.10 \text{ Å}$$

$$Cs \rightarrow \quad a = 6.084 \text{ Å}, \quad L(Cs-Cs) = 4.30 \text{ Å}$$

Therefore, it seems logical that it is impossible to extend the covalent bond to metals. But, it's not.

If we assume that the radius of the metal is the radius of the "Bohr" orbit of the valence electron, and then calculate the half-wave length of the electron, we will see that even the allowable length of a typical "strong" covalent bond (metal) is always greater than the constant translational lattice. The de Broglie (electron) wavelength will be much larger than the lattice constant. Therefore, "weak" bonds can span several atoms (~3).

Further, to demonstrate what has been said, based on the Clementi radii of alkali metals [4], we calculate the wavelength and half-wave of the valence electron, and compare with the lattice constant.

Lithium:

$$Li, \quad r = 1.67 \text{ Å}, \quad \lambda(Li) = 10.493 \text{ Å}$$

$$a = 3.502 \text{ Å}, \quad \lambda/2 = 5.247 \text{ Å}.$$

Sodium:

$$Na, \quad r = 1.90 \text{ Å}, \quad \lambda(Na) = 11.938 \text{ Å}$$

$$a = 4.282 \text{ Å}, \quad \lambda/2 = 5.969 \text{ Å}.$$

Potassium:

$$K, \quad r = 2.43 \text{ Å}, \quad \lambda(K) = 15.268 \text{ Å}$$

$$a = 5.247 \text{ Å}, \quad \lambda/2 = 7.634 \text{ Å}.$$

Rubidium:

$$Rb, \quad r = 2.65 \text{ Å}, \quad \lambda(Rb) = 16.650 \text{ Å}$$

$$a = 5.69 \text{ Å}, \quad \lambda/2 = 8.325 \text{ Å}.$$

Cesium:

$$Cs, \quad r = 2.98 \text{ Å}, \quad \lambda(Rb) = 18.724 \text{ Å}$$

$$a = 6.084 \text{ Å}, \quad \lambda/2 = 9.362 \text{ Å}.$$

As you can see, the half-wavelength of the valence electron of an alkali metal is about 1.5 times longer than the lattice constant, naturally, the wavelength will be 3 times longer.

From the calculated data, it is obvious that between the nuclei of metals (metallic bond), due to the de Broglie half-wave (or wave) of valence electrons, a chemical bond can form, which is essentially similar to a covalent bond. But, since the valence electrons of the metal are socialized, the "metal covalent" bond must cover many atoms (ions). This is possible if the wavelength is increased to the required value.

Therefore, at the optimal wavelength, we will get a stable crystalline structure of the metal (the longer the wavelength, the lower the energy, but a large number of atoms are involved in the bond).

CONCLUSION.

Thus, a chemical bond is a purely quantum effect that is formed between the nuclei of atoms due to de Broglie waves of valence electrons. This mechanism of bond formation can be considered universal, since from a unified theoretical standpoint it makes it possible to explain different types of chemical bonds up to intermolecular interaction.

Moreover, the physical essence of the chemical bond is simple and understandable - it is a standing wave (or half-wave) de Broglie of valence electrons between nuclei. With this approach, it is obvious that the electrons of a chemical bond are absolutely equivalent and make the same contribution to the bond.

When a chemical bond is formed from different atoms, valence electrons will have different "input" characteristics (velocity, momentum, energy, etc.), therefore, there will be a certain averaging of the characteristics of the socialized electrons that form a chemical bond.

It should also be noted that the idea of a chemical bond as a standing de Broglie wave between nuclei makes it possible to clearly explain the mechanism of formation of a three-center two-electron bond, for example, in diborane (BH3)2. Recall that a three-center two-electron bond is such a chemical bond when a pair of electrons is localized in the space between three atoms. A classic example is the structure of diborane B – H – B. Look at figure [10].
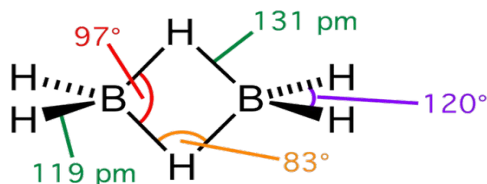
Note that the B-H-B bond angle is 83° and the single B-H bond length (half) is 1.31 Å. The usual, "normal" two-electron bond is localized between two nuclei. Therefore, from a classical point of view, it is not easy to explain why a pair of electrons "serves" three nuclei at once. Moreover, the nuclei form a triangle.

But everything changes if we remember that the chemical bond is a standing de Broglie wave between nuclei. In this case, the nuclei of atoms are the nodes of a standing wave. Recall that a standing wave is an oscillatory process characterized by a spatially stable distribution of alternating maxima (antinodes) and minima (nodes) of the oscillation amplitude. Moreover, the number of nodes for a standing wave is theoretically unlimited.

Therefore, for one chemical bond, the number of nodes can be two (then it is a "normal" two-center bond), or it can be three (then it is a three-center bond). Therefore, it is easy to imagine a three-center two-electron chemical bond. Look at the picture that explains everything.
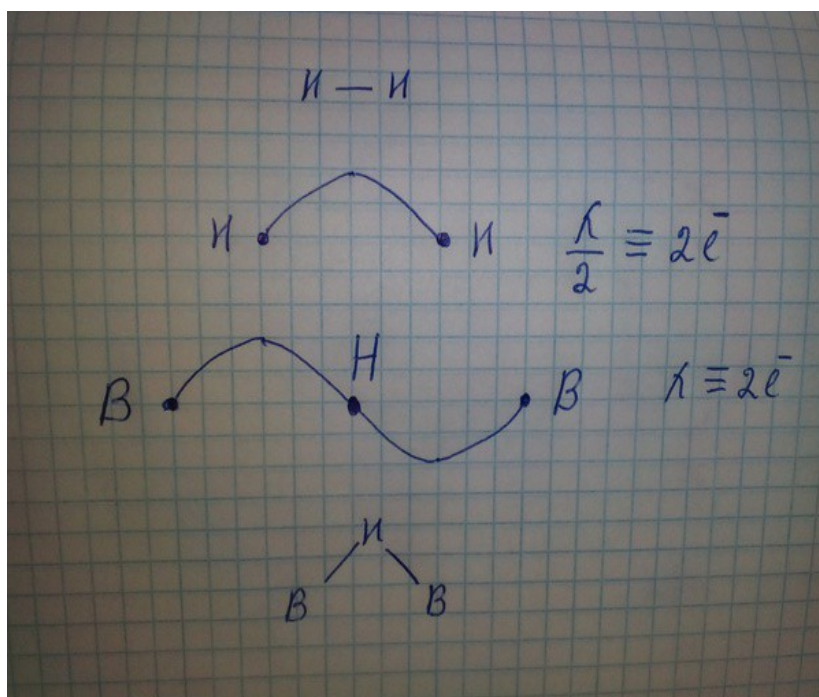
Naturally, this approach can be used with different numbers of electrons and with different numbers of nuclei.

Note 1. Some information about Bohr's complementarity principle.

"The principle of complementarity... formulated in 1927 by Niels Bohr. According to this principle, in order to fully describe quantum mechanical phenomena, it is necessary to apply two mutually exclusive ("additional") sets of classical concepts, the totality of which provides comprehensive information about these phenomena as holistic.

For example, additional in quantum mechanics are space-time and energy-momentum patterns.

Descriptions of any physical object as particles and as waves complement each other, one without the other is meaningless, the corpuscular and wave aspects of the description must necessarily be included in the description of physical reality...
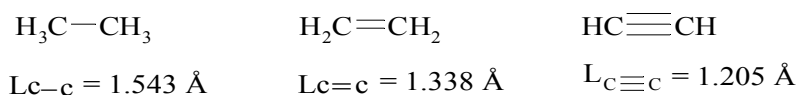
The principle of complementarity formed the basis of the so-called Copenhagen interpretation of quantum mechanics...

According to this interpretation, borrowed from classical physics, the dynamic characteristics of a microparticle (its coordinate, momentum, energy, etc.) are not at all inherent in the particle itself. The meaning and certain value of one or another characteristic of an electron, for example, its momentum, are revealed in connection with classical objects, for which these quantities have a certain meaning and all at the same time can have a certain value...

The role of the principle of complementarity turned out to be so significant that Wolfgang Pauli even suggested calling quantum mechanics the "theory of complementarity", by analogy with the theory of relativity..." [11].

Note 2. The multiplicity of the chemical bond.

It can be shown that from a physical point of view, the multiplicity of a chemical bond (or in MO theory - bond order) is literally the linear energy density of a chemical bond. But first, let's remember what the multiplicity of a bond is in the classical sense. The easiest way to demonstrate this is with the example of ethane, ethylene and acetylene.

$$H_3C-CH_3 \qquad H_2C=CH_2 \qquad HC\equiv CH$$
$$L_{C-C} = 1.543 \text{ Å} \qquad L_{C=C} = 1.338 \text{ Å} \qquad L_{C\equiv C} = 1.205 \text{ Å}$$

In ethane, the multiplicity of the C – C bond is 1,

in ethylene, the bond multiplicity C = C is 2,

in acetylene, the bond multiplicity C≡C is 3.

Thus, a chemical bond formed by two electrons has a bond multiplicity equal to one. Such a bond exists, for example, in an ethane molecule (C-C bond), or in a hydrogen molecule (H-H bond), or in a water molecule (O-H bond), or in an alcohol molecule (C-O bond).

A chemical bond formed by four electrons has a bond multiplicity of two. Such a bond is present in the ethylene molecule (C=C bond) or in the molecules of formaldehyde and acetone (C=O bond).

A chemical bond formed by six electrons has a bond multiplicity of three. Such a bond is present in the acetylene molecule (C≡C bond), as well as in the molecules of hydrocyanic acid (C≡N bond) and nitrogen (N≡N bond).

The multiplicity of chemical bonds can be fractional. For example, in benzene the C–C bond is 1.66, and in graphite the C–C bond is 1.54 [7, p. 10]. In general, looking at the structural formula of a molecule, one can immediately determine the multiplicity of chemical bonds. But still, difficulties arise, since there are bonds with fractional multiplicity, and then, the classical formulas cannot correctly convey the structure of the molecule. Look at the urea molecule and compare the classical and real structures [7, p. 31].

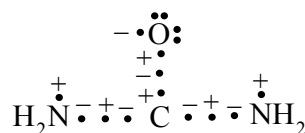| Classic structure	Real structure
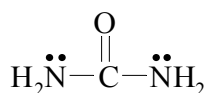
	$L_{C-N} = 1.33$ Å, $L_{C-O} = 1.27$ Å
Multiplicity C−N = 1	Multiplicity C−N (L=1.33 Å) = 1.686
Multiplicity C−O = 2	Multiplicity C−O (L=1.27 Å) = 1.486
E_{C-N} = 291.834 kJ/mol	E_{C-N} (L = 1.33 Å) = 523.790 kJ/mol
E_{C-O} = 728.538 kJ/mol (for $R_2C=O$)	E_{C-O} (L = 1.27 Å) = 496.940 kJ/mol
$E_1 = E_{C-O} + 2E_{C-N}$ = 1312.206 kJ/mol	$E_2 = E_{C-O} + 2E_{C-N}$ = 1544.520 kJ/mol

$\Delta E = E_2 - E_1 = 1544.520$ kJ/mol - 1312.206 kJ/mol = 232.314 kJ/mol

As we can see, the difference in the energy balance of the real structure and the classical structure is more than 230 kJ/mol. That is, the classical structure does not quite correctly convey the properties of the molecule.

Moreover, using the classical approach, one can assign a multiplicity equal to one, for example, to all C – H bonds, or all O – H bonds, or all N – H bonds. In principle, this is how it is done - but this is not true. Since all of the above chemical bonds in different chemicals have completely different properties. But, the classical approach does not make any distinction between the above bonds (all have the same multiplicity).
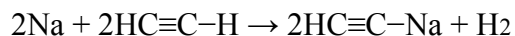
Consider C – H bonds, which from the classical point of view have a multiplicity equal to one, but have different chemical properties. To do this, we analyze the C - H bonds in the molecules of ethane, ethylene and acetylene [length - 6, p. 143; energy - 12]:

$$CH_3–CH_2−H, \quad L_{C-H} = 1.0914 \text{ Å}, \quad E_{C-H} = 405.848 \text{ kJ/mol}$$

$$H_2C=CH−H, \quad L_{C-H} = 1.085 \text{ Å}, \quad E_{C-H} = 435.136 \text{ kJ/mol}$$

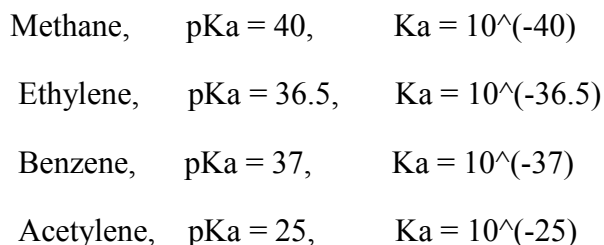$$HC≡C−H, \quad L_{C-H} = 1.059 \text{ Å}, \quad E_{C-H} = 476.976 \text{ kJ/mol}$$
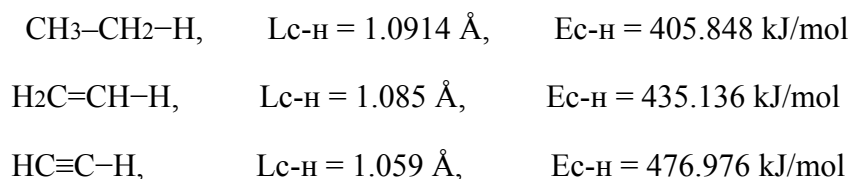
As you can see, the lengths of C – H bonds and their energies are very close. But these are completely different chemical bonds with different chemical properties. This is especially true for the C–H bond in the acetylene molecule. It is this chemical bond that is radically different from the other two bonds.

In terms of properties, the C - H bond in ethylene practically does not differ from the C - H bond in ethane (say, it does not radically differ). But if we go to the C-H bond in acetylene, we get a bond that is radically different from the other two. The fact is that the C - H bond in acetylene is a normal acid bond, which, upon dissociation, gives a hydrogen cation. Simply put, from a chemical point of view, acetylene is a typical acid. And it is the C-H bond of acetylene that gives it its acidic properties.

For example, the C–H bond of acetylene reacts with sodium to form hydrogen and sodium hydroacetylenide (or acetylenide, depending on the amount of sodium). This is a trivial reaction of a metal with an acid - similar to zinc reacting with hydrochloric acid.

$$2Na + 2HC≡C−H → 2HC≡C−Na + H_2$$

Let us compare the acidity of methane, ethylene and acetylene [13]:

Methane, $\quad$ pKa = 40, $\quad$ Ka = 10^{-40}

Ethylene, $\quad$ pKa = 36.5, $\quad$ Ka = $10^{-36.5}$

Benzene, $\quad$ pKa = 37, $\quad$ Ka = 10^{-37}

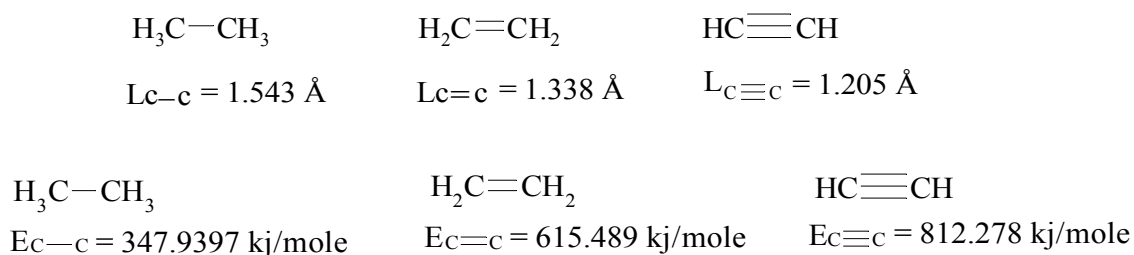Acetylene, $\quad$ pKa = 25, $\quad$ Ka = 10^{-25}

That is, the acidity of acetylene is 10^{15} times greater than the acidity of methane, and hence ethane. And the acidity of acetylene is $10^{11.5}$ times greater than that of ethylene. Recall that the multiplicity of C – H bonds in ethane, ethylene and acetylene, according to the classical approach, is equal to one. Agree that the real acidic properties of substances refute this approach.

Naturally, the rest of the molecule also affects the C–H bond. But, nevertheless, we must admit that, based on modern ideas about the multiplicity of bonds, we cannot correctly predict such a difference in acidity. We can explain this difference, but we cannot predict.

The problem is that even theoretically we cannot separate these connections, classify them, that they are different. If you try to calculate their multiplicity by different methods, then the numerical values will be within the error of the calculation method. These difficulties are the result of a misunderstanding of the

physical nature of the bond multiplicity. Therefore, we will try to understand what exactly is the physical essence of the chemical bond.

It can be shown that from a physical point of view, the multiplicity of a chemical bond is the density of the bond energy, more precisely, the linear density of the bond energy. To demonstrate, consider the chemical C–C bonds in ethane, ethylene, and acetylene. These bonds were not chosen randomly, they are the most studied, play an important role in organic chemistry, and, moreover, are non-polar. If we consider polar bonds (C - N, C - O, etc.), then the effects of polarization will introduce errors, and we will not be able to analyze the chemical bond "in its pure form". Let us consider the energies and lengths of these bonds [6].

$$H_3C-CH_3 \qquad H_2C=CH_2 \qquad HC\equiv CH$$
$$L_{C-C} = 1.543\ \text{Å} \qquad L_{C=C} = 1.338\ \text{Å} \qquad L_{C\equiv C} = 1.205\ \text{Å}$$

$$H_3C-CH_3 \qquad\qquad H_2C=CH_2 \qquad\qquad HC\equiv CH$$
$$E_{C-C} = 347.9397\ \text{kj/mole} \qquad E_{C=C} = 615.489\ \text{kj/mole} \qquad E_{C\equiv C} = 812.278\ \text{kj/mole}$$

To get the bond energy density (linear), we perform a simple operation - we divide the energy of a chemical bond by the length of a given chemical bond.

$$F = E / L$$

We get the following numerical values:

Ethane, $\qquad$ F(1) = 225.496 kJ/(mol*Å)

Ethylene, $\qquad$ F(2) = 460.007 kJ/(mol*Å)

Acetylene, $\qquad$ F(3) = 674.090 kJ/(mol*Å)

And now let's take F(1) as a unit of measurement, that is, we assume that F(1) = 1. Then we get the following values of the multiplicity C - C of the bond (f).

Ethane, $\qquad$ f(1) = 1

Ethylene, $\qquad$ f(2) = 2.040 ≈ 2

Acetylene, $\qquad$ f(3) = 2.989 ≈ 3

That is, we have obtained the usual for chemistry values of the multiplicity of C - C bonds in ethane, ethylene and acetylene (1, 2, 3). If in this way we calculate the multiplicity of the C - C bond in benzene, we get the value 1.695.

Benzene, $\quad$ C – C, $\quad$ E = 534.0723 kJ/mol, $\quad$ L = 1.397Å [7, p. 10]

Benzene, $\quad$ f = 1.695

Moreover, we can now determine the multiplicity of the previously considered C-H bonds. So, for C–H bonds, we have the following energy and length values [length - 6, p. 143; energy – 12]:

CH$_3$–CH$_2$−H,   Lc-н = 1.0914 Å,   Ec-н = 405.848 kJ/mol

H$_2$C=CH−H,   Lc-н = 1.085 Å,   Ec-н = 435.136 kJ/mol

HC≡C−H,   Lc-н = 1.059 Å,   Ec-н = 476.976 kJ/mol

Using the above method, we determine their multiplicity (we take the multiplicity of C − H bonds in ethane as a unit). Then we will get the following values.

Ethan,   C−H,   F = 371.860 kJ/(mol*Å),   f = 1

Ethylene,   C−H,   F = 401.047 kJ/(mol*Å),   f = 1.079

Acetylene,   C−H,   F = 450.402 kJ/(mol*Å),   f = 1.211

That is, the multiplicity of C - H bonds in ethane is 1, in ethylene - 1.079. And in acetylene, the multiplicity of the C − H bond is 1.211. Here we have obtained different multiplicity values for different bonds, and this is true, since the chemical properties of these bonds are different.

The described approach is convenient in that using the linear density of a chemical bond, one can compare various chemical bonds and easily calculate their real multiplicity, which correspond to the real properties of substances.

Let us calculate the C − H bond multiplicity for benzene (if for 1 we take the C − H bond multiplicity in ethane).

Benzene, C−H, Lc-н = 1.084 Å [6, p. 143],   Ec-н = 439.066 kJ/mol (calculated below by the equation)

Then F = 405.042 kJ/(mol*Å),

and the multiplicity of bond (C−H) will be equal to f = 1.089

Consequently, the multiplicity of the C - H bonds in benzene is somewhat greater than in ethylene (compare: 1.089 and 1.079), but significantly less than in acetylene (1.211), which is true and is confirmed by chemical properties: C - H bond of benzene does not react with metallic sodium, and for the C - H bond of acetylene, the reaction with sodium is a characteristic reaction.

Note that the linear density of a chemical bond has a physical interpretation; in fact, it is a force that holds the nuclei of atoms. Recall that energy divided by length equals force.

$$F = E / L$$

Thus, the multiplicity of a chemical bond can be considered as the force holding atoms together. In fact, this force can be seen as a specific analogue of Hooke's force:

$$F = - k * \Delta x$$

In a simplified form, a chemical bond can be viewed as a spring with a certain stiffness. The stiffness of the spring is the multiplicity of the chemical bond. The stronger the chemical bond, the greater the multiplicity of the bond, the more rigid our spring will be. This analogy is directly confirmed by the data of infrared spectroscopy - it is easy to distinguish bonds with different multiplicity (1, 2, 3) from the IR spectrum.

"...Perhaps surprisingly, molecular vibrations can be treated using Newtonian mechanics to calculate the correct vibration frequencies. The basic assumption is that each vibration can be treated as though it corresponds to a spring. In the harmonic approximation the spring obeys Hooke's law: the force required to extend the spring is proportional to the extension. The proportionality constant is known as a force constant, k...

In the harmonic approximation the potential energy of the molecule is a quadratic function of the normal coordinate. It follows that the force-constant is equal to the second derivative of the potential energy…

Solving the Schrödinger wave equation, the energy states for each normal coordinate are given by

$$E_n = h * (n + 1/2) * v = h * (n + 1/2) * 1/(2*\pi) * (k/m)^{0.5}$$

where n is a quantum number that can take values of 0, 1, 2... In molecular spectroscopy where several types of molecular energy are studied and several quantum numbers are used, this vibrational quantum number is often designated as v.

The difference in energy when n (or v) changes by 1 is therefore equal to h * v, the product of the Planck constant and the vibration frequency derived using classical mechanics. For a transition from level n to level n+1 due to absorption of a photon, the frequency of the photon is equal to the classical vibration frequency v (in the harmonic oscillator approximation)...
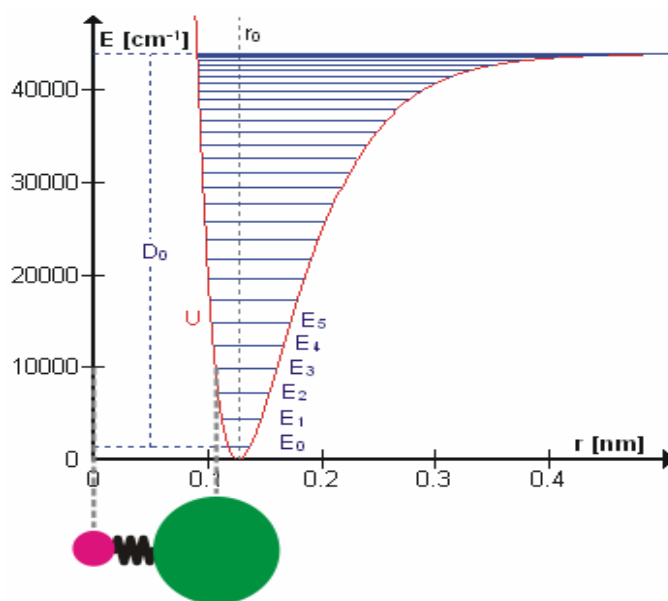

The HCl molecule as an anharmonic oscillator vibrating at energy level E3. D0 is dissociation energy here, r0 bond length, U potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve…" [14].

Using data on C-H bonds in ethane, ethylene and acetylene, one can obtain the dependence of energy on the chemical bond length $E = a + b/r + c/r^2$. For the C-H bond, we get the following equation:

$$E \, (C\text{-}H) = -112104.88181312 + \frac{239481.07645903}{L} - \frac{127352.04548799}{L^2}$$

If the bond lengths are taken in angstroms, then the bond energy is obtained in kJ/mol. The dependence E = f(L) for the C–H bond was calculated using the previously tested algorithm [7, p. 12-16].

For bond lengths, we use the data [6, p. 143]:

$CH_3CH_2{-}H$ $H_2C{=}CH{-}H$ $HC{\equiv}C{-}H$

$L_{C-H} = 1.0914$ Å $L_{C-H} = 1.085$ Å $L_{C-H} = 1.059$ Å
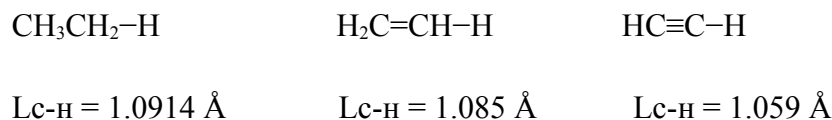
For the bond energies, we take the data (these are the dissociation energies of these bonds) [12]:

$CH_3CH_2{-}H$ $H_2C{=}CH{-}H$ $HC{\equiv}C{-}H$

$E_{C-H} = 405.848$ kJ/mol $E_{C-H} = 435.136$ kJ/mol $E_{C-H} = 476.976$ kJ/mol
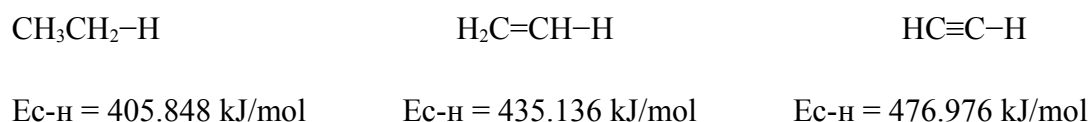
Table 1. Calculation of the coefficients for the dependence E = f(L) for the C−H bond.

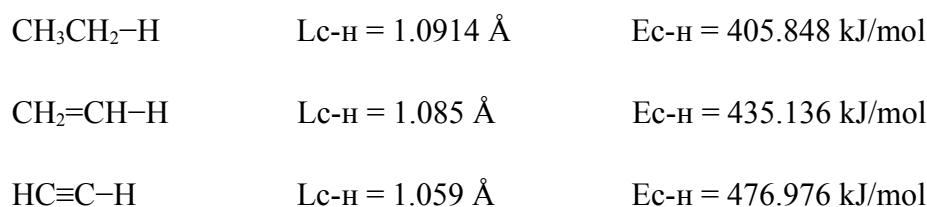|	$1/x$	$1/x^2$	$\dfrac{(y-y_1)}{(1/x-1/x_1)}$	$\dfrac{((1/x)(y-y_1))}{(1/x-1/x_1)}$	x (L, Å)	y (E, kJ/mol)
					1.0914	405.848
	0.92165899	0.84945529	5419.05338625	4994.51925000	1.0850	435.136
	0.94428706	0.89167806	2537.32148311	2395.95985185	1.0590	476.976
$\sum$	1.86594605	1.74113334	7956.37486936	7390.47910185	3.2354	1317.960

$1/x_1 = 0.91625435$ $x_1 = 1.0914$ $y_1 = 405.848$
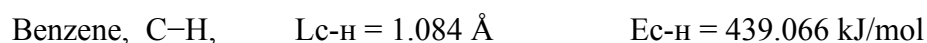
$\Sigma(1/x^2) = 2.58065538$ $\Sigma(1/x) = 2.78220040$

$c = -127352.04548799$ $b = 239481.07645903$ $a = -112104.88181312$

$$E\,(C\text{-}H) = -112104.88181312 + \frac{239481.07645903}{L} - \frac{127352.04548799}{L^2}$$

From the equation we obtain the following energy values:

$CH_3CH_2{-}H$ $L_{C-H} = 1.0914$ Å $E_{C-H} = 405.848$ kJ/mol

$CH_2{=}CH{-}H$ $L_{C-H} = 1.085$ Å $E_{C-H} = 435.136$ kJ/mol

$HC{\equiv}C{-}H$ $L_{C-H} = 1.059$ Å $E_{C-H} = 476.976$ kJ/mol

$L_{C-H} = 1.084$ Å is the length of the C–H bond in benzene [6, p. 143].

Benzene, C−H, $L_{C-H} = 1.084$ Å $E_{C-H} = 439.066$ kJ/mol

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