UNIFIED APPROACH TO VIBRATIONS AND ROTATIONS
OF MOLECULES AND MACROMOLECULES

Maria A. Krupina[1] and Alexander I. Melker[1]*

[1]Department of Experimental Physics

[2]Department of Physics of Strength and Plasticity of Materials

St. Petersburg State Polytechnic University, Polytekhnicheskaya 29

195251, St. Petersburg, Russia

* E-mail: newton@imop.spbstu.ru

Abstract. In this contribution we have briefly analyzed the approach lying at the basis of semi-empirical calculation of the potential barrier for molecule internal rotations. In opposite to it, we have suggested the way how to find this barrier on purely theoretical grounds. For this purpose, we have used the bond-charge model with clamped charges, and in this contribution restricted ourselves by the simplest case of such molecules as ethane. It was found that this approach leads to theoretical results which are in a good agreement with experimental data. It means that the electronic theory of molecule vibrations developed earlier has a large degree of generality and can be used to study not only vibrations but also rotations of molecules and macromolecules on the basis of one and the same approach, excluding a lot of empirical parameters which are often do not clarify a subject but immerse it into darkness.

1. Introduction

The problem of internal rotation is very important for predicting and understanding the structure of polymers. However up to now there are no reliable rigorous approach for the calculation of the internal rotation potentials not only for chain macromolecules but even for simple molecules, e.g. such as ethane, $CH_3 - CH_3$. The analysis of different approaches to this problem was given many years ago by Flory [1] and Wunderlich [2]. The main conclusion was as follows: "In spite of a principal possibility for the quantum mechanics calculation of a rotation potential, such calculations are very complex and connected with approximations which depend on a calculation scheme chosen. For this reason, for polymers the more convenient and precise is a semi-empirical approach". From those times nothing has changed significantly [3]. However any semi-empirical approach, although very promising and useful at the first stage of investigation, leads at the final stage to a typical situation when the number of input parameters becomes to prevail over the number of predicted values [4, 5]. The most perfectly frank example is the so-called inverse spectral problem, i.e. the determination of potential energy characteristics of a molecule on the basis of a known geometric structure and vibration frequencies. Nevertheless the situation seems not so gloomy after the appearance of the electron theory of molecule vibrations [6]. The theory incorporates two main ideas:

- Geometry of a forming molecule is dictated by the repulsion of valence electron pairs,
- Valence electron pairs can be considered as point charges which behavior is described by classical equations of motion.

The charges are called bond-charges and can be treated in two approximations: clamped charges and oscillating charges. The developed theory allowed to improve the prediction of vibration frequencies of triatomic molecules, and, what is more, to define the bond charges of shared and unshared electron pairs. The number of atoms which form organic molecules is not large. The number of bonds is larger, but also is limited, so it is possible to define the bond charges for all the bonds, and using the values obtained to calculate not only the elastic constants of valence angles, as it was done in [6], but the potentials of internal rotation. It should be emphasized that both types of values can be found on the basis of one and the same set of input parameters, namely, vibration frequencies of molecules.

In this contribution we give at first a sketch of existing empirical approaches for polymers and biopolymers. Then we consider taking as an example one of the simplest molecule, ethane, how to calculate potentials of internal rotation. After that we compare calculated results with experimental data. In conclusion we discuss possibilities which the bond-charge theory opens not only for theoretical investigation but also for computer simulation by molecular dynamics method.

2. Internal rotation and conformations of molecules

Semi-empirical approach. Consider the internal rotation in the simplest form using an ethane molecule, $CH_3 - CH_3$. This molecule is a typical one, with the help of which the internal rotation is illustrated in literature (Fig. 1). In this molecule the internal rotation of one methyl group CH_3 with respect the other takes place around the $C - C$ bond. One can imagine two specific positions of both groups. The first position (Fig. 1b) is called a *cis*-conformation. It corresponds to a maximum of energy and is unstable. The second position (Fig. 1c) is called *trans*-conformation which refers to energy minimum and therefore more stable. Since the group CH_3 has C_{3v} symmetry, the internal rotation potential is usually approximated by the empirical expression

$$U = \frac{U_0}{2}(1 - \cos 3\varphi).$$

Here φ is the rotation angle counting from a *trans*-conformation and U_0 is the potential barrier.

One can see that ethane has three indistinguishable conformers with an identical minimal energy at the rotation angles 0, 120 and 240 grades. The transfer to more complex molecules, increases the number of conformations [2], e.g. for butane $CH_3 - CH_2 - CH_2 - CH_3$ up to 27. To take into consideration the ability of possible conformations, one is compelled to introduce additional terms into the potential energy of internal rotation, as a rule, on empirical grounds relying on one's intuition.
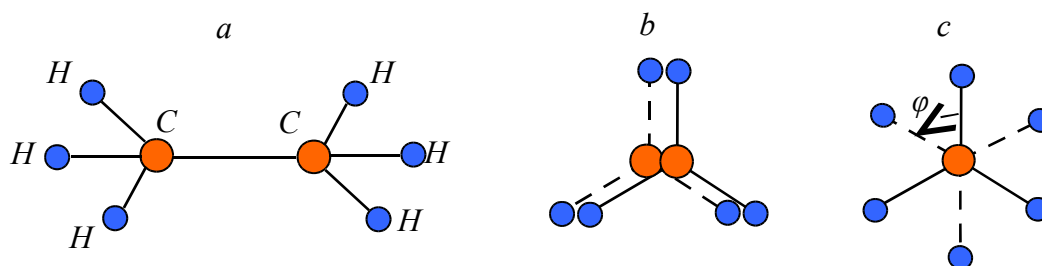

Fig. 1. Model of a ethane molecule (a) and its cis (b) and trans (c) conformations.

The similar situation exists in polymers [7]; the typical conformations for polyethylene are shown in Fig. 2. As a result, the potential energy of macromolecules has more a complicated form (Fig. 3) in comparison with simple molecules. This leads to new problems; one of them, how to describe interactions between atoms that are separated by three covalent bond in a molecule [8]. The situation becomes all the more complex when one studies biopolymers. Here in addition to the rotation about single bonds, it is necessary to take into consideration a rotational energy barrier for double bonds. Some ways of simulating this barrier, rather artificial but at the same time very unusual, are considered in [3].
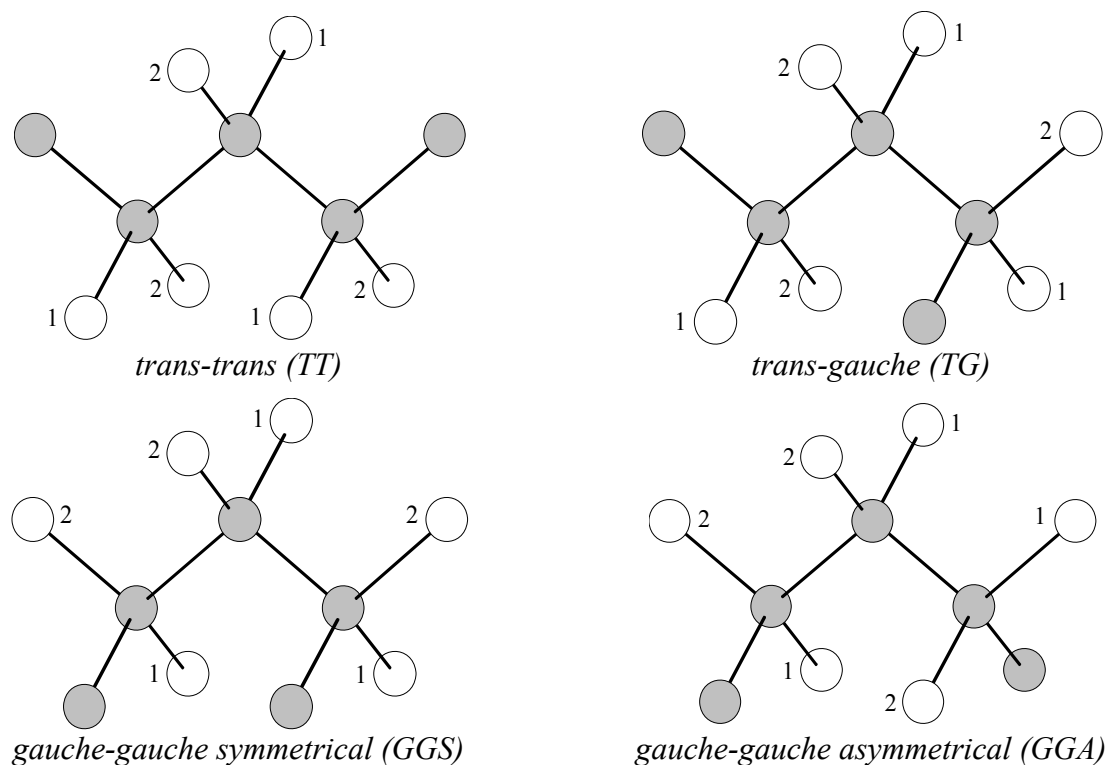

trans-trans (TT)   *trans-gauche (TG)*

gauche-gauche symmetrical (GGS)   *gauche-gauche asymmetrical (GGA)*

Fig. 1. Possible positions of carbon (gray) and hydrogen (white) atoms
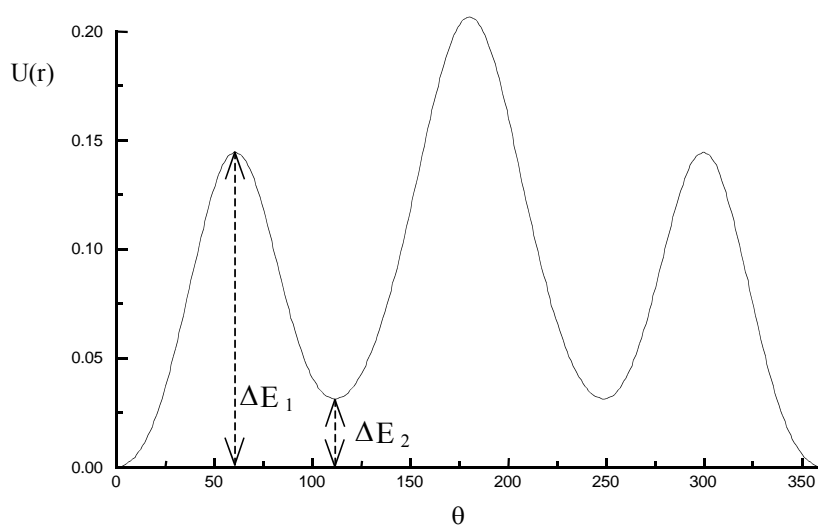for some typical conformations [7].

Fig. 3. Potential energy of internal rotation about a single bond for polyethylene in eV [8].

Bond-charge model. The approximations discussed seem reasonable; however the problem is how to find the potential barrier on purely theoretical grounds. For this purpose, we will use the bond-charge model [6] with clamped charges. We restrict ourselves to the simplest case of such molecules as ethane (Fig. 4).
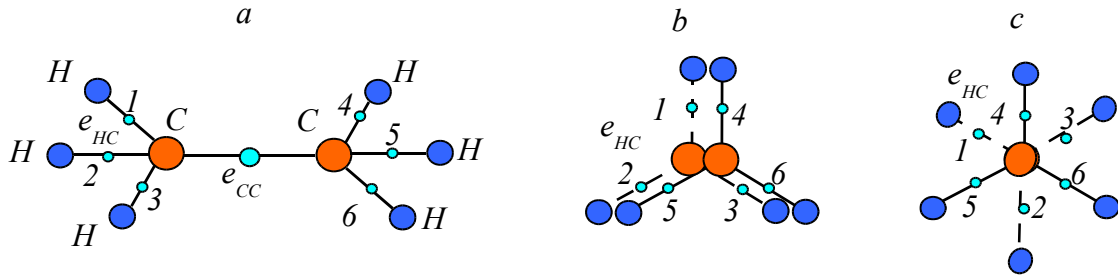

Fig. 4. Ethane molecule with covalent-bond charges added (a)
and its cis (b) and trans (c) conformations.

The geometric parameters of ethane are as follows [9]:

r (C–C)=1.543 Å, r (C–H)=1.102 Å, angle CCH=109°37', angle HCH= 109°19'.

Let us denote the bond charges of one methyl group CH_3 by numbers *1, 2, 3* and the corresponding bond charges of the second group by numbers *4, 5, 6*. The potential energy which defines the internal rotation of such molecule has the form

$$U = e_c^2 \left(\frac{1}{r_{14}} + \frac{1}{r_{15}} + \frac{1}{r_{16}} + \frac{1}{r_{24}} + \frac{1}{r_{25}} + \frac{1}{r_{26}} + \frac{1}{r_{34}} + \frac{1}{r_{35}} + \frac{1}{r_{36}} \right),$$

where $e_c \equiv e_{HC}$. Here we do not take into consideration the interactions between the bond charges e_{HC} and e_{CC}, and between e_{HC} of one and the same group, bearing in mind that the distances *r(C-H)* are not changing during the internal rotation.

Consider at first the cis-conformation. From the group theoretical standpoint, the cis-conformation belongs to the symmetry group D_{3h} which describes the symmetry of a regular triangle prism [10]. The group has, among other elements, one axis of the third order going through the prism axis C_3 and three 'vertical' planes of reflection σ_v going through this main axis. The symmetry allows decrease the number of necessary calculations. In our case for the cis-conformation we have

$$r_{14} = r_{25} = r_{36}, \qquad r_{15} = r_{16} = r_{24} = r_{26} = r_{34} = r_{35},$$

so

$$U_{cis} = 3 e_c^2 \left(\frac{1}{r_{14}} + \frac{2}{r_{15}} \right).$$

Denote the angle between the direction *C–1–H* and the plane containing bond charges *2, 3, 5, 6* by *β*. This angle can be found with the help of angles *CCH* and *HCH* characterizing the structure of an ethane molecule. Other characteristic features of the molecule we designate so that *r(C–C)=a, r(C–H)=a₁*. From Fig. 4b it follows that

$$r_{14}^C = a + a_1 \cos \beta,$$

the bond charges being at the centers of the bonds. The distance *4–5* is equal to

$$r_{45} = a_1 \sin \beta \sin(\pi / 3),$$

and therefore

$$r_{15}^C = \sqrt{(a + a_1 \, cos \, \beta \,)^2 + \tfrac{3}{4} a_1^2 \, cos^2 \, \beta} \; ,$$

Now consider the trans-conformation. It belongs to the symmetry group D_{3d}. The group describes the symmetry of a solid composed of two regular triangle prisms having a common base which are turned through the angle $\pi/3$ with respect to each other [10]. However, there is no special sense to go to other detail because we have all the necessary data from the previous consideration. In the trans-conformation,

$$r_{14} = r_{15} = r_{25} = r_{26} = r_{34} = r_{36} \, , \; r_{16} = r_{24} = r_{35}$$

so

$$U_{trans} = 3 \, e_c^2 \left(\frac{2}{r_{14}} + \frac{1}{r_{16}} \right).$$

However, now the distance r_{14} has changed (Fig. 4c). It is equal to

$$r_{14}^T = \sqrt{(a + a_1 \, cos \, \beta \,)^2 + \tfrac{1}{2} a_1^2 \, cos^2 \, \beta} \; .$$

Besides, from this figure it follows that

$$r_{16}^T = \sqrt{a^2 + a_1^2 + 2 \, a \, a_1 \, cos \, \beta + \tfrac{1}{2} a_1^2 \, cos^2 \, \beta} \; .$$

Therefore the potential barrier equals

$$U_0 = U_{cis} - U_{trans} = 3 \, e_c^2 \left(\frac{1}{r_{14}^C} + \frac{2}{r_{15}^C} - \frac{2}{r_{14}^T} - \frac{1}{r_{16}^T} \right).$$

Taking into consideration the geometric parameters of ethane, this expression can be approximated as

$$U_0 \cong \frac{3 \, e_c^2}{r_{14}^C} \; .$$

According to [6] the elasticity constant for deformation vibrations has the sense of the second derivative of the potential energy for repulsion of covalent-bond charges and is equal to

$$k_\theta = \frac{e_c^2}{a^3} \, ,$$

where a is the bond length. Therefore $e_c = \sqrt{k_\theta a^3}$. For *H-C* bond [6] $e_c = 0.077 \, e$, where e is the electron charge. From this it follows that in our case $U_0 \cong 0.13 \; eV$. This value practically coincides with the experimental data for ethane and polyethylene [1, 2, and 8].

3. Conclusion

We have briefly analyzed the approach lying at the basis of semi-empirical calculation of the potential barrier for molecule internal rotations. In opposite to it, we have suggested the way how to find this barrier on purely theoretical grounds. For this purpose, we have used the bond-charge model [6] with clamped charges, and in this contribution restricted ourselves by the simplest case of such molecules as ethane. It was found that this approach leads to theoretical results which are in a good agreement with experimental data. It means that the electronic theory of molecule vibrations developed earlier [6] has a large degree of generality and can be used to study not only vibrations but also rotations on the basis of one and the same approach, excluding a lot of empirical parameters which are often do not clarify a subject but immerse it into darkness.

It should be emphasized that when the bond-charged model is used in molecular dynamics simulation, there is no artificial separation of motion into different parts [11]. Here electronic and atomic (ionic) types of motion are well correlated and the potential barrier is generated automatically.

References

[1] Paul J. Flory, *Statistical Mechanics of Chain Molecules*, Interscience Publishers, New York-London- Sydney-Toronto, 1969.

[2] Bernhard Wunderlich, *Macromolecular Physics, Volume1, Crystal Structure, Morphology, Defects,* Academic Press, New York and London, 1973.

[3] Z.M. Frenkel and A.I. Melker // *Proceedings of SPIE* **5127** (2003) 63.

[4] A.I. Melker // Reviews on Advanced Materials Science **20** (2009) 1.

[5] A.I. Melker and M.A. Vorobyeva // Reviews on Advanced Materials Science **20** (2009) 14.

[6] A.I. Melker and M.A. Vorobyeva // *Proceedings of SPIE* **6253** (2006) 625305.

[7] A.I. Melker and D.V. Soloviev // *Proceedings of SPIE* **3687** (1999) 132.

[8] D.V. Soloviev and A.I. Melker // *Modelling Simul. Mater. Sci. Eng.* **6** (1998) 361.

[9] L.M. Sverdlov, M.A. Kovner, E.P. Krainov, *Vibration Spectra of Polyatomic Molecules* (in Russian), Nauka, Moscow, 1970.

[10] G.Ya. Lubarskii, *Groups Theory and its Application in Physics* (in Russian), Fizmatgiz, Moscow, 1958.

[11] A.I. Melker // *Proceedings of SPIE* **6597** (2007) 659701.