

ON THE INTERACTION OF MOLECULE VIBRATIONS

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Abstract. In this contribution we have analyzed main ideas and principles lying at the basis of mechanical models of molecule vibrations. We considered advantages and drawbacks of well-known models, such as the central force model, the valence force model and Urey-Bradley's model based on purely mechanical and volitional suggestions. A sketch of a newly developed electronic theory of molecule vibrations is also given. It is shown that the electronic theory clarifies the physical sense of vague parameters used in mechanical models and allows exclude excess ones. Besides of excluding excess parameters, the electronic theory of molecule vibrations has shown that valence vibrations are not independent and connected with deformation vibrations through electronic degrees of freedom. For example, in triatomic molecules *ABA*, the interaction of valence and deformation vibrations through electronic degrees of freedom leads to changing of elastic constants and frequencies. As a consequence, the rigidity of elastic constant k_s for symmetric longitudinal vibrations, and hence the corresponding frequency ω_s respectively, is increased whereas those, k_a and ω_a , for asymmetric ones are decreased in the following manner $k_s = k + 2k_\theta$, $k_a = k - 2k_\theta$, $\omega_a / \omega_s = \sqrt{1 + 2M_A / M_B} / \sqrt{1 + 4k_\theta / k}$. Here k and k_θ is a usual force constant of valence and deformation vibrations, respectively, and k_θ can be expressed in terms of effective electron charges of covalent bonds. As a result, calculated frequencies coincide practically with experimental data.

1. INTRODUCTION

The theory of molecule vibrations is of the utmost significance for many branches of physics [1,2]. In the framework of the existing theory, the problem of frequencies and form of vibrations was solving until recently on the basis of purely mechanical approach [1-4]. The approach is as follows. A geometric structure of a molecule is defined by positions of atoms incorporated into the molecule. The atoms are connected by springs with different elastic constants. On the basis of this approach the analytical solutions were obtained for triatomic molecules [4] and for some types of tetra-atomic ones [5,6]. In doing so the elastic constants are taken as input parameters and their physical nature remains beyond the scope of any mechanical theory. But what is worse, the mechanical approach

does not take into account an electronic structure of atoms excluding thus electronic degrees of freedom. The latter play the role of kinematic bonds which put restriction on the velocities of atoms. As a result, the so-called normal (independent) vibrations are in reality are connected through electronic kinematic bonds [7]. For this reason, the calculated frequencies of molecule vibrations on the basis of purely mechanical approach are far distant from those observed experimentally [7].

In principle, one can compose the quantum mechanical equations for vibrations of molecules [1], but now there is no one who is able to solve them analytically for polyatomic molecules. We do not consider here numerous commercial programs based on numerical methods of solution because we share the opinion by Hamming [8] that the pur-

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pose of calculations is an understanding of the question but not numbers. 'A person must know how the calculations are going on. If one does not understand how it is done, one sees only bare numbers, but their genuine significance is hidden in calculations'.

In this contribution we debate at first the basis on which different mechanical approaches are based, namely, the central force model, the valence force model and Urey-Bradley's model. Then we compare them with the recently developed bond-charge theory which takes into account electronic kinematic bonds [7].

2. ANHARMONIC VIBRATIONS

The theory of small vibrations is based on expanding of kinetic and potential energy in a Taylor series in powers of velocities and coordinates conserving the terms of the second order. In this case the equations of motion are linear, so one says about *linear (harmonic) vibrations*. In generalized coordinates the kinetic energy is a quadratic function of velocities, but can also depend on coordinates:

$$E_{kin} = \frac{1}{2} \sum_{i,j} a_{ij}(q) \dot{q}_i \dot{q}_j,$$

where q is a generalized coordinate. For small deviations from an equilibrium position

$$a_{ij}(q) = a_{ij}(q_0) + \left(\frac{\partial a_{ij}}{\partial q} \right)_0 q.$$

Here $a_{ij}(q_0) = m_{ij} = m_j$ are the masses of particles, if q is the Cartesian coordinate x .

Expand the kinetic energy in a power series in the velocities conserving the terms of the third order is

$$E_{kin} = \frac{1}{2} \sum_{i,j} m_{ij} \dot{x}_i \dot{x}_j + \frac{1}{2} \sum_{i,j,k} n_{ijk} \dot{x}_i \dot{x}_j x_k.$$

Here n_{ijk} are new constant coefficients. We see that the kinetic energy contains now new terms which are the products of velocities and coordinates. Expand then the potential energy

$$U = U_0 + \sum_i \left(\frac{\partial U}{\partial q_i} \right)_0 q_i + \frac{1}{2!} \sum_{i,j} \left(\frac{\partial^2 U}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{3!} \sum_{i,j,k} \left(\frac{\partial^3 U}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k.$$

Putting $U_0 = 0$ and taking into account the equilibrium condition $(\partial U / \partial q_i)_0 = 0$, we obtain in the Cartesian coordinates

$$U = \frac{1}{2} \sum_{i,j} k_{ij} x_i x_j + \frac{1}{3} \sum_{i,j,k} l_{ijk} x_i x_j x_k.$$

Here $k_{ij} = (\partial^2 U / \partial q_i \partial q_j)_0$ are elastic constants (they also are named elastic moduli or force constants) with $k_{ij} = k_{ji}$. Besides, the formula has the new constants l_{ijk} which are the elastic constants of the next order.

Transfer it to the normal coordinates. By virtue of the linearity of transformation, Lagrange function takes the form

$$L = E_{kin} - U = \frac{1}{2} \sum_i (\dot{Q}_i^2 - \omega_i^2 Q_i^2) + \frac{1}{2} \sum_{i,j,k} v_{ijk} \dot{Q}_i \dot{Q}_j Q_k - \frac{1}{3} \sum_{i,j,k} \lambda_{ijk} Q_i Q_j Q_k,$$

where v_{ijk} , λ_{ijk} are constants. Write down the Lagrange equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{Q}_i} - \frac{\partial L}{\partial Q_i} = 0,$$

which define the motion of the system

$$\ddot{Q}_i + \omega_i^2 Q_i + \frac{1}{2} \sum_{i,j} v_{ijk} (\ddot{Q}_j Q_k + \dot{Q}_j \dot{Q}_k) + \frac{1}{3} \sum_{j,k} \lambda_{ijk} Q_j Q_k = 0.$$

Rewrite them in the form

$$\ddot{Q}_i + \omega_i^2 Q_i = f_i(Q, \dot{Q}, \ddot{Q}),$$

where f_i are the second order homogeneous functions of the coordinates Q and their time derivatives.

Let us solve the equations by successive approximations method. As a first approximation, assuming that $f_i = 0$, we find that the solutions are the ordinary harmonic vibrations

$$Q_i^{(1)} = a_i \cos(\omega_i t + \alpha_i).$$

Putting the solutions into the initial equations, we obtain linear inhomogeneous differential equations to find the solutions of the second approximation

$$\ddot{Q}_i^{(2)} + \omega_i^2 Q_i^{(2)} = f_i(Q^{(1)}, \dot{Q}^{(1)}, \ddot{Q}^{(1)}).$$

The right part of this equation contains the terms of the type

$$Q_i^{(1)} Q_j^{(1)} = a_i a_j \cos(\omega_i t + \alpha_i) \cos(\omega_j t + \alpha_j).$$

By virtue of the trigonometric formula

$$\cos \alpha \cos \beta = \frac{1}{2} [\cos(\alpha - \beta) + \cos(\alpha + \beta)],$$

the terms can be transformed into the terms which correspond to the vibrations with the frequencies equal to the sums and differences of eigen frequencies of the system. In this case, the solution takes the form of just the same periodic functions. Therefore, in the second approximation, in addition to the normal vibrations with the frequencies ω_p , one obtains vibrations with the frequencies $\omega_i \pm \omega_j$. They are called combination frequencies. Among them there are double frequencies $2\omega_i$ and the zero frequency corresponding to a constant displacement. The higher approximations show that, in addition to the appearance of new combination frequencies, the eigen frequencies of normal vibrations also change a little [1,4].

3. SEMIEMPIRICAL POTENTIAL FUNCTIONS

For practical calculations in spectroscopy the interaction of vibrations is described with the help of models in which the potential energy of a molecule is constructed on the basis of volition decisions. Usually, as a starting point, one takes harmonic approximation where the potential energy as a function of generalized coordinates has the form

$$U = \frac{1}{2} \sum_{i,j} k_{ij} q_i q_j.$$

Here q_i are small changes of parameters characterizing an equilibrium configuration of a molecule. As would be expected, the question arises how to choose an optimal system of coordinates and how to transform the equations of motion to the form which contains such coordinates. For maximum visualization, one introduces such coordinates which are connected with the structure of a molecule. They are: equilibrium values of interatomic bond lengths, valence angles, distances and angles between atomic groups. The changes of these parameters are taken as *vibration coordinates* which play the role of generalized coordinates.

Then, in the framework of classical mechanics, one studies small vibrations, i.e. movements connected only with small variation of a molecule configuration.

The first historically and one of the simplest approaches is the *model of central forces*. Here one supposes that the forces holding atoms in equilibrium positions depend only on the distance between the atoms and act along the straight line connecting atom pairs. In doing so, the role of vibration coordinates is given to the changes of distances both between covalently bound atoms and between uncoupled. For example, the potential energy of a triatomic linear symmetric molecule *ABA* has the form

$$U_{\text{central}} = \frac{1}{2} k (q_{AB}^2 + q_{BA}^2) + \frac{1}{2} k_{AA} q_{AA}^2 + h_{12} q_{AB} q_{BA} + h_{13} q_{AA} (q_{AB} + q_{BA}).$$

Here k is the elastic constant of the covalent bond *AB*, k_{AA} is the elastic constant characterizing interaction of the extreme atoms *A*, h_{12} is the elastic constant of interaction of the covalent bonds *AB* and *BA*, h_{13} is the elastic constant of interaction of the covalent bond *AB* and the bond *AA*. Under the interaction of bonds, angles and other structure elements one understands the appearance of stress in one structure element as a result of deformation of another. Therefore the model contains four unknown elastic constants.

A triatomic linear asymmetric molecule *ABC* has more complex form of the potential energy

$$U_{\text{central}} = \frac{1}{2} (k_1 q_{AB}^2 + k_2 q_{BC}^2) + \frac{1}{2} k_{AC} q_{AC}^2 + h_{12} q_{AB} q_{BC} + h_{13} q_{AB} q_{AC} + h_{23} q_{BC} q_{AC}.$$

Here one has already six constants.

Similarly to the interaction matrix for particles, the elastic constants can be represented in the form of interaction tables between the vibration coordinates of molecules.

Interacting coordinates for ABA molecule	q_{AB}	q_{BA}	q_{AA}
q_{AB}	k	h_{12}	h_{13}
q_{BA}	h_{12}	k	h_{13}
q_{AA}	h_{13}	h_{13}	k_{AA}

Interacting coordinates for ABC molecule	q_{AB}	q_{BC}	q_{AC}
q_{AB}	k_1	h_{12}	h_{13}
q_{BC}	h_{12}	k_2	h_{23}
q_{AC}	h_{13}	h_{23}	k_{AC}

The central force model describes transverse (deformation) vibrations of linear molecules poorly so in spectroscopy one uses the *model of valence forces*. In this approach the role of generalized coordinates is given to the changes of covalent bonds, valence angles and the angles between atomic groups. The approach is nearer to the notion of quantum chemistry about interatomic forces in organic molecules with covalent bonds, and so such generalized coordinates are called natural vibration coordinates. (*E.B. Wilson, 1939-1941, M.A. Elyashevich, 1940*). In the model of valence forces the potential energy of a triatomic linear symmetric molecule *ABA* has the form

$$U_{valence} = \frac{1}{2}k(q_{AB}^2 + q_{BA}^2) + \frac{1}{2}k_{\theta}a^2(\Delta\theta)^2 + hq_{AB}q_{BA} + \alpha(a\Delta\theta)(q_{AB} + q_{BA}).$$

Here k is the elastic constant of the covalent bond *AB*, k_{θ} is the elastic constant of the valence angle, h is the elastic constant of interaction of the covalent bonds *AB* and *BA*, α is the elastic constant of interaction of the covalent bond and the valence angle, a is the equilibrium length of the covalent bond, $\Delta\theta$ is the change of the valence angle. Therefore in this model one has, as before, four unknown elastic constants. On transition to a triatomic linear asymmetric molecule *ABC* with the potential energy

$$U_{valence} = \frac{1}{2}(k_1q_{AB}^2 + k_2q_{BC}^2) + \frac{1}{2}k_{\theta}a^2(\Delta\theta)^2 + hq_{AB}q_{BC} + [\alpha_1(a_1\Delta\theta)q_{AB} + \alpha_2(a_2\Delta\theta)q_{BC}],$$

where $a_1 + a_2 = 2a$, the number of unknowns, as in the model of central forces, increases from four to six.

The interaction tables for vibration coordinates of molecules have the form

Interacting coordinates for ABA molecule	q_{AB}	q_{BA}	$\Delta\theta$
q_{AB}	k	h	α
q_{BA}	h	k	α
$\Delta\theta$	α	α	k_{θ}

Interacting coordinates for ABC molecule	q_{AB}	q_{BC}	$\Delta\theta$
q_{AB}	k_1	h	α_1
q_{BC}	h	k_2	α_2
$\Delta\theta$	α_1	α_2	k_{θ}

Both the model of central forces and the model of valence forces have the potential energy which contains not only coordinates squared but also the products of different coordinates, the potential energy of a *ABC* molecule having three diagonal and three off-diagonal terms. Clarify the physical sense of both type terms. For this purpose consider the forces acting in the molecules. The force changing the length of the bond *AB* is equal

$$f_{AB} = -\frac{\partial U}{\partial q_{AB}} = -k_1q_{AB} - hq_{BC} - \alpha_1(a_1\Delta\theta).$$

Here the first term is an ordinary elastic force depending on the value of a coordinate considered. The second and third terms give the elastic forces which change the given coordinate but depend on the change of the second bond *BC* and on the changing of the angle between the bonds. The force changing the length of the second bond *BC* is equal

$$f_{BC} = -\frac{\partial U}{\partial q_{BC}} = -k_2q_{BC} - hq_{AB} - \alpha_2(a_2\Delta\theta).$$

Compare two expressions. One can see that changing the length of the first bond as a result of changing the length of the second bond is defined by the same elastic constant, as in the case of changing the length of the second bond under the influence of changing the length of the first bond. Therefore, the elastic constant h defines the interaction of the bonds. Briefly one says about the 'interaction' of corresponding coordinates. Therefore, the diagonal elements of the matrix give the action of a coordinate on itself and the off-diagonal ones define the interaction of coordinates. If the off-diagonal elements are equal to zero, the forces considered could be reduced to the ordinary elastic forces which depend only on properties of a given bond or a given angle.

The force changing the angular coordinate,

$$f_{\Delta\theta} = -\frac{\partial U}{\partial(\Delta\theta)} = -k_{\theta}a^2(\Delta\theta) - [(\alpha_1a_1)q_{AB} + (\alpha_2a_2)q_{BC}],$$

is a generalized force; in this instance, it is the momentum of a force about the axis which is normal to the angle plane.

The distance between unbound atoms can be expressed in terms of the lengths of covalent bonds and the values of valence angles. This allows to correlate the force constants of both models, then to calculate the frequencies of molecule vibrations and to compare the results obtained with experimental data. Such correlation for the following molecules H_2O , H_2S , H_2Se , ClO_2 has shown that the model of valence forces surpasses the central force model in precision. However, the valence force model has also serious drawbacks.

- As the number of atoms in a molecule increases and the geometric and electronic structure of the molecule becomes more complex, the number of elastic constants, which are necessary for calculation, grows drastically. For instance, for the tetra-atomic linear symmetric molecule *ABBA* (e.g. acetylene $H-C\equiv C-H$) one needs five constants, for the tetra-atomic linear asymmetric molecule *ABBC* (e.g. chloroacetylene $H-C\equiv C-Cl$) the number of constants increases to eight, for ethane CH_3-CH_3 it is necessary to have ten constants, for ethylene $CH_2=CH_2$ fourteen. As a result, successive construction of the potential energy in accordance with chosen natural coordinates leads to so large number of different potentials that there is little point in the formulation of problem in itself.
- All the elements of the potential energy matrix are considered as independent, whereas it follows from experimental data that diagonal and off-diagonal elements are connected with each other. This connection cannot be obtained from the valence force model and one is compelled to take it into consideration empirically.
- If the physical sense of the elastic constants for deformation of covalent bonds and valence angles can be understood, i.e. these structure elements of a molecule can be considered as some basic bricks of a molecule, the physical sense of off-diagonal elements is unclear. In practice, the off-diagonal elements are introduced as some empirical parameters without thinking out their sense.

The inclusion of off-diagonal terms adds much complexity to the calculations of molecule vibrations. For this reason, a model was developed which is a combination of valence and central forces [2]. Here the potential energy contains only diagonal elements of the elastic constant matrix. Be-

sides, some linear terms describing central forces between unbound atoms are included into the potential energy. Such approach is known as Urey-Bradley's model (*H.C. Urey, C.A. Bradley, 1931*). In this model, the potential energy of a triatomic bent symmetric molecule *ABA* has the form

$$U_{UB} = \frac{1}{2}k(q_{AB}^2 + q_{BA}^2) + \kappa a(q_{AB} + q_{BA}) + \frac{1}{2}k_\theta a^2(\Delta\theta)^2 + \kappa_\theta a^2(\Delta\theta) + \frac{1}{2}k_{AA}q_{AA}^2 + \kappa_{AA}q_{AA}.$$

The distance between unbound atoms q_{AA} can be expressed through the length of covalent bond a and the value of valence angle α . Then one excludes this distance from the potential energy and assumes that $\kappa_{AA} = -0.1k_{AA}$ and that other elastic constants of the linear terms, κ , κ_θ , are equal to zero. As a consequence, only three elastic constants k , k_θ , k_{AA} remain in the potential energy

$$U_{UB} = \frac{1}{2}[k + g_1 k_{AA}](q_{AB}^2 + q_{BA}^2) + \frac{1}{2}[k_\theta + g_2 k_{AA}]a^2(\Delta\theta)^2 + g_3 k_{AA} q_{AB} q_{BA} + g_4 k_{AA} (a\Delta\theta)(q_{AB} + q_{BA}).$$

Here $g_i \equiv g_i(a, \alpha)$ are the trigonometric functions known from the expressions obtained when excluding q_{AA} . In comparison with the valence force model, Urey-Bradley's model leads to significant decreasing of the elastic constants, especially for complex molecules. Another advantage of Urey-Bradley's model is in transferability of the elastic constants. If they are found for some group of bonds and angles on the basis of the spectra for simple molecule, these constants can be used to calculate the frequencies of more complex molecules having the same groups of length and angles.

Compare the semi-empirical potential functions with the Lagrange function. One can see that the semi-empirical potential functions contain in an implicit form some terms of the Lagrange function. The choice of one or other type of these terms depends on the taste of an author. This leads to discussion about the correctness of choice. There is an opinion that this question can be solved on the basis of experiment, however, this is delusion; without theory the empirical way of cognition leads after all to a deadlock.

4. ELECTRONIC THEORY

In the theory of molecule vibrations one come up against two problems:

- Calculation of frequencies and types of vibrations on the basis of preset parameters of a molecule (so-called direct spectral problem);
- Determination of potential energy characteristics on the basis experimental data about frequencies and forms of vibrations (so-called inverse spectral problem).

Contrary to the first problem, the second problem has no unique solution in the frameworks of mechanical models. The reason is in the following. Consider, for example, a molecule of water H_2O . It has three eigen frequencies, but four elastic constants both in the central force model and as well in the valence bond model. It means that both models contain excess parameters. Suppose that the constant h , characterizing the interaction of covalent bonds, is equal to zero. Then we have that the number of constants coincides with the number of frequencies. However we can also suppose that $h \neq 0$, but the constant α , characterizing the interaction of covalent bond and valence angle is zero. It does not known beforehand which assumption is more reliable, and could be accepted any of them at all. In practice, both of them were used without any convincing proof.

Nevertheless the situation seems not so gloomy. Recently the electronic theory of molecule vibrations was developed [7] which overcomes this uncertainty. 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 effective charges which behavior is described by classical equations of motion.

The theory uses only two types of parameters (arguments): elastic constants of covalent bonds and their effective electron charges. All other parameters are functions which describe interaction of these arguments. For example, for linear molecules ABA and ABC the matrix elements are only such elastic constants which have clear physical sense, namely,

$$k_i = \frac{2\alpha_i^2 D_i}{a_i^2}, \quad k_\theta = \frac{e_{c1} e_{c2}}{a^3}.$$

where α_i , D_i are the parameters of Morse potential, (α is a constant, D is the dissociation energy of a covalent bond), a_i is the length of a covalent bond, e_{ci} is the effective electron bond charge, $a = (a_1 +$

$a_2)/2$. As a result, one have the following interaction matrices:

Interacting coordinates for ABC molecule	q_{AB}	q_{BA}	$\Delta\theta$
q_{AB}	k	k_θ	0
q_{BA}	k_θ	k	0
$\Delta\theta$	0	0	k_θ

Interacting coordinates for ABC molecule	q_{AB}	q_{BC}	$\Delta\theta$
q_{AB}	k_1	k_θ	0
q_{BC}	k_θ	k_2	0
$\Delta\theta$	0	0	k_θ

Compare these tables with the corresponding tables of the valence band model. We see:

- Off-diagonal elastic constant h , which describes vague, non-clarified interaction of covalent bonds has received clear physical sense. Now it is equal to k_θ so it is an excess parameter.
- Elastic constant α describing interaction of a covalent bond and a valence angle is also an excess parameter. Moreover, this constant has no physical sense at all because it incorporates not only the interaction of electron charges of different bonds but also the interaction of electron charge, belonging to one bond, with itself.

5. CONCLUSION

We have analyzed the main ideas and principles lying at the basis of mechanical models of molecule vibrations. We considered advantages and drawbacks of well known models, such as the central force model, the valence force model and Urey-Bradley's model based on purely mechanical and volitional suggestions. A sketch of a newly developed electronic theory of molecule vibrations is also given. It is shown that the electronic theory clarifies the physical sense of vague parameters used in mechanical models and allows exclude excess ones. Besides of excluding excess parameters the electronic theory of molecule vibrations has shown that normal valence vibrations are not independent and connected with deformation vibrations through electronic degrees of freedom. As a consequence, the rigidity of elastic constant k_s for symmetric longitudinal vibrations, and hence the corresponding frequency ω_s respectively, is increased whereas those, k_a and ω_a , for asymmetric ones are decreased in the following manner [7]

$$k_s = k + 2k_\theta, k_a = k - 2k_\theta,$$

$$\omega_a / \omega_s = \sqrt{1 + 2M_A / M_B} / \sqrt{1 + 4k_\theta / k}.$$

Here k and k_θ is a usual force constant of valence and deformation vibrations, respectively, and k_θ can be expressed in terms of effective electron charges of covalent bonds. As a result, calculated frequencies coincide practically with experimental data.

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