
MOLECULAR SPECTROSCOPY

*Dedicated to the Memory of Professor Nikolay G. Basov**

An Essential Approach to the Architecture of Diatomic Molecules: 1. Basic Theory¹

T. Yarman

Işik University, Maslak, Istanbul, Turkey

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Abstract—We consider the quantum-mechanical description of a diatomic molecule of electronic mass m_{0e} , internuclear distance R_0 , and total electronic energy E_{0e} . We apply to it the Born–Oppenheimer approximation, together with the relation $E_{0e}m_{0e}R_0^2 \sim h^2$ (which we established previously), written for the electronic description (with fixed nuclei). Our approach yields an essential relationship for T_0 , the classical vibration period, at the total electronic energy E_{0e} ; i.e., $T_0 = [4\pi^2/(\sqrt{n_1 n_2} h)] \sqrt{g \mathcal{M}_0 m_e R_0^2}$. Here, \mathcal{M}_0 is the reduced mass of the nuclei; m_e is the mass of the electron; g is a dimensionless and relativistically invariant coefficient, roughly around unity (this quantity is associated with the particular electronic structure under consideration; thus, it remains practically the same for bonds bearing similar electronic configurations); and n_1 and n_2 are the principal quantum numbers of electrons making up the bond(s) of the diatomic molecule in hand; because of quantum defects, they are not integer numbers. The above relationship holds generally, although the quantum numbers n_1 and n_2 need to be refined. This task is undertaken in our next article, yielding a whole new systematization regarding all diatomic molecules. © 2004 MAIK “Nauka/Interperiodica”.

This work is put forth from a totally different perspective than the one considered herein. We are not going to reinforce this substantial perspective through this paper. Nevertheless, we should state it briefly since it allowed us long ago to derive practically everything that we present herein [1–4].

Thus, it was the author’s original idea that, in order to insure the validity of the theory of relativity, in any entity existing in nature, the architecture of the internal dynamics it displays ought to be constructed in a certain manner.

In effect, any natural entity has an internal dynamics; it works as a clock bearing a clock period T_0 . The dynamics in question involves a given mass M_0 , which we call the “clock mass,” installed in a space of size R_0 . The clock mass, as we shall see, is not a trivial quantity; nonetheless, it is not the total mass of the entity in hand.

It is usually a complex mass that carries the oscillation motion of the internal dynamics under consideration.

One can define several clock masses for the same entity with regard to the different internal dynamics it displays. The clock mass of the electronic motion of a diatomic molecule, for instance, is the electronic mass m_{0e} , which can be expressed as (a coefficient) \times (the electron mass), or merely the electronic mass m_e , where the coefficient of concern is accounted for in a different way. On the other hand, the clock mass of the vibrational motion of a diatomic molecule is $m_e \sqrt{\mathcal{M}_0/m_e}$, where \mathcal{M}_0 is the reduced mass of the molecule.

Now, the Lorentz transformations on T_0 , M_0 , and R_0 were the object brought into uniform translational motion or, similarly, the transformations that these quantities would undergo were the object embedded in a gravitational field impose that there ought to already be an intrinsic relationship between T_0 , M_0 , and R_0 ,

which turns out to be $T_0 \sim M_0 R_0^2$ [1–4]. This was our original idea, which we will not stress any further here.

However, to mark this idea, in this paper, we would like to keep the subscript “0” pinned to the symbols representing the mentioned basic quantities defined at rest (versus the corresponding Lorentz-transformed quantities).

* The author had the pleasure of meeting Professor N.G. Basov, together with Professor V. Rozanov, at the meeting “Forum on an Acceptable Nuclear Energy Future of the World,” held in 1977 in Miami; he was further honored by Professor Basov’s invitation to the XII European Conference on Laser Interaction with Matter, held in 1978 in Moscow. The author continues to enjoy the privilege of pursuing collaboration with colleagues of the Lebedev Physical Institute.

¹ This article was submitted by the author in English.

In this paper, we will present a derivation of the relationship we conjectured between T_0 , M_0 , and R_0 , chiefly for diatomic molecules, through the Born–Oppenheimer approximation, and a fundamental relation we derived previously, which we shall briefly sketch. We will elaborate on quantum numbers that come into play in Part 2 of this work; our approach yields an empirical relationship established back in 1925. We will conclude with a novel systematization of all diatomic molecules.

We are embarrassed to be unable to furnish basic references other than our work; however, we found nothing similar to what we present herein.

THE UNIVERSAL MATTER ARCHITECTURE RELATION

For an atomistic or molecular wavelike object existing in nature, we have shown elsewhere the following assertion, first, on the basis of the Schrödinger equation, as complex as this may be, and then on the basis of the Dirac equation (whichever may be appropriate in relation to the object in hand) [4].

Assertion 1. In a real wavelike description composed of I electrons and J nuclei, if the (same) electron masses m_{i0} , $i = 1, \dots, I$, and in general different nuclei masses m_{j0} , $j = 1, \dots, J$, involved by the object are overall multiplied by the arbitrary number γ , then, concurrently, (1) the total energy E_{0k} associated with the given clock motion of the object is increased as much and (2) the size R_{0k} of the object in which the given clock motion takes place contracts as much; in mathematical words, this is

$$\begin{aligned} & \{[(m_{i0}, i = 1, \dots, I) \rightarrow (\gamma m_{i0}, i = 1, \dots, I)], \\ & [(m_{j0}, j = 1, \dots, J) \rightarrow (\gamma m_{j0}, j = 1, \dots, J)]\} \quad (1) \\ & \Rightarrow \{[E_{0k} \rightarrow \gamma E_{0k}], [R_{0k} \rightarrow R_{0k}/\gamma]\}. \end{aligned}$$

By “real,” we mean not “artificially gedanken”; for atomistic and molecular wavelike objects, “real object” means an object embodying a potential energy made of just Coulomb potentials.

If the object is an atom, then R_{0k} is its radius; if the object is a diatomic molecule, then R_{0k} is the internuclear distance, etc.

As we will see, the operation consisting of multiplying the masses of concern by an arbitrary number γ , within the framework of the above assertion, can be in fact not as arbitrary as one may think it is at first glance. Indeed, γ can well point to the mass change when the object is brought into uniform translational motion or planted in a gravitational field or in any field with which the object in hand can interact.

Anyhow, the occurrence stated by Eq. (1) yields an invariance, interestingly, linked with the square of Planck’s constant, h^2 .

This is the content of our Assertion 2, restated below.

Assertion 2. The quantities $E_{0k}M_{0k}R_{0k}^2$ ($k = 1, \dots, K$) (associated with the k th internal motion of the wavelike object in hand) are invariant in regard to a mass change and are all linked with h^2 .

Thus, the grand total energy $E_{0(\text{GrandTotal})}$ becomes

$$\begin{aligned} E_{0(\text{GrandTotal})} &= E_{01} + E_{02} + \dots + E_{0k} + \dots, \\ E_{0k} &\sim \frac{h^2}{M_{0k}R_{0k}^2}, \quad k = 1, \dots, K. \end{aligned} \quad (2)$$

We call this occurrence the universal matter architecture (UMA) relation.

Note that, primarily, what we do here is not a dimensional analysis. Anyhow, the occurrence we disclose would not work (i.e., $E_{0k}M_{0k}R_{0k}^2$, for the given clock motion, would not be invariant in regard to a mass change) if the wavelike object in hand were not “real,” though of course there would still be no problem dimensionwise.

Soon we shall determine that the proportionality constant embodied by Eq. (2), in addition to a usual geometry factor and quantum numbers, fortunately, is made of a “transferable constant”; indeed, this constant seems to depend on just the electronic configuration of the molecule. Therefore,

(i) it remains the same regarding the electronic states of a given molecule, provided that these states are similarly configured electronically;

(ii) furthermore, it stays the same regarding the ground electronic states of molecules belonging to a given chemical family, bearing similar electronic configurations.

Below, we provide a direct derivation of Eq. (2), mainly for the electronic motion of a diatomic molecule, based on the Schrödinger description of it.

THE BORN–OPPENHEIMER APPROXIMATION

The quantum-mechanical description of a diatomic molecule can be achieved via the usual Schrödinger equation, involving the two nuclei and the surrounding electrons. This equation, through the Born–Oppenheimer approximation, is reduced to the separate descriptions of the nuclear and electronic motions. We thus

come to solve separately the two following Schrödinger equations, written with the usual notation [5]:

$$\left[-\frac{\hbar^2}{8\pi^2} \left(\frac{1}{m_A} \nabla_A^2 + \frac{1}{m_B} \nabla_B^2 \right) + \frac{1}{2} k_0 (r_{AB} - r)^2 \right] \Psi_{A,B} \quad (3)$$

$$= E_{A,B} \Psi_{A,B},$$

$$\left(-\frac{\hbar^2}{8\pi^2 m_e} \sum_i \nabla_{ei}^2 + \sum_{i,i'} \frac{e^2}{r_{ii'}} + \frac{Z_A Z_B e^2}{r_{AB}} \right. \quad (4)$$

$$\left. - \sum_i \frac{Z_A e^2}{r_{Ai}} - \sum_i \frac{Z_B e^2}{r_{Bi}} \right) \Psi_e = E_e \Psi_e.$$

Here, A and B designate the nuclei and e designates the electrons. We have then the following familiar notation: m_A , the mass of A ; m_B , the mass of B ; Z_A , the atomic number of A ; Z_B , the atomic number of B ; m_e , the electron mass; e , the electron charge; r_{Ai} , the distance of the i th electron to A ; r_{Bi} , the distance of the i th electron to B ; $r_{ii'}$, the distance between the i th and the i' th electrons; r_{AB} , the distance between the nuclei; $\Psi_{A,B,e}$, the eigenfunction associated with the molecule; and $E_{A,B,e}$, the eigenvalue associated with the molecule.

Equation (3) describes the vibrational motion of the nuclei about the internuclear distance r_{AB} to be input into this equation (for a given electronic state of the molecule), whereas Eq. (4) describes the electronic motion around the two fixed nuclei. $E_{A,B}$ is the eigenvalue of the system vibrating around r_{AB} , which may rotate as well; E_e is the electronic eigenvalue, which is in fact the electronic energy of the system whose nuclei are at a fixed distance r_{AB} from each other. Thus, as usual, one solves Eq. (4), for a given electronic state, in order to determine how the electronic energy E_e varies with respect to r_{AB} and to find the internuclear distance r_{AB} that minimizes the eigenvalue E_e ; we call $r_{AB\min}$ and $E_{e\min}$, respectively, the internuclear distance and the eigenvalue in question (for the given electronic state); this is then $r_{AB\min}$ as r_{AB} , to be input into Eq. (3). Normally, $E_{e\min}$ is negative; however, below, by $E_{e\min}$ we shall mean $|E_{e\min}|$.

The constant k_0 to be input into Eq. (3) is given by

$$k_0 = \left. \frac{\partial^2 E_e(r_{AB})}{\partial r_{AB}^2} \right|_{r_{AB} = r_{AB\min}} \quad (5)$$

(to be determined, for the electronic state of concern, from Eq. (4)). Knowing k_0 and r_{AB} related to the given electronic state of the diatomic molecule in hand, one can subsequently construct Eq. (3) and solve it as usual for the vibrational and also rotational eigenvalues $E_{A,B}$

associated with the electronic state of the molecule of concern.

$E_{A,B}$ as usual becomes [6]

$$E_{A,B} = \frac{j(j+1)\hbar^2}{8\pi^2 I_{AB}} + \left(v + \frac{1}{2} \right) \hbar \omega_{A,B}, \quad (6)$$

$$j = 0, 1, \dots; \quad v = 0, 1, \dots,$$

I_{AB} is the moment of inertia of the nuclei:

$$I_{AB} = \mathcal{M}_{AB} r_{AB}^2, \quad (7)$$

where \mathcal{M}_{AB} is the nuclei reduced mass.

$\omega_{A,B}$ is the classical vibrational frequency of the molecule, the inverse of which, $T_{A,B}$, is the classical vibrational period of the molecule,

$$T_{A,B} = 2\pi \sqrt{\frac{\mathcal{M}_{AB}}{k_0}} \quad (8)$$

(the classical vibrational period for the given electronic state written on the basis of Eq. (3), where k_0 was determined on the basis of Eq. (4)). Thus, by this definition, $E_{A,B}$ (as expressed by Eq. (6) above) is the solution of Eq. (3) for the nuclear motion of the molecule.

THE VIBRATION PERIOD VERSUS THE DIATOMIC MOLECULE CLOCK MASS AND THE INTERNUCLEAR DISTANCE

The Born–Oppenheimer approach, together with the UMA cast, stated above, i.e., Eq. (2), allows us to draw an elegant relationship for the vibrational motion of a diatomic molecule in terms of the different masses taking part in the internal motion of the molecule and with the internuclear distance coming into play.

Thus, Eq. (2), i.e., $E_{0k} M_{0k} R_{0k}^2 \sim \hbar^2$, must hold on the basis of Eq. (4); this equation indeed embodies a potential energy term made strictly of Coulomb potential energies. Furthermore, the only mass that comes into play in Eq. (4) is the electron mass, m_e ; in other words, the clock mass in question, to be associated with the electronic motion of the molecule (with fixed nuclei), is made up of only the electron masses coming into play, obviously all bearing the same mass m_e .

The eigenvalue E_e of Eq. (4) (more precisely, $E_e(r_{AB})$) assumes the value $E_{e\min}$ when r_{AB} takes the value of $r_{AB\min}$. These quantities will then come to replace E_{0k} and R_{0k} , respectively, in Eq. (2). Thence, regarding the electronic motion, Eq. (2) will be written as

$$E_{e\min} m_e r_{AB\min}^2 \sim \hbar^2 \quad (9a)$$

(Eq. (2) written within the framework of Eq. (4)). The proportionality constant in question is made up of (i) a geometry factor; (ii) appropriate quantum numbers to be associated with \hbar^2 ; and, finally, (iii) a dimensionless and relativistically invariant quantity that will insure the equality. We will call this quantity g_{IN} , thus associating it with the invariance (energy)(mass)(size)², underlined by Assertion 2.

The quantity g_{IN} is a characteristic of the electronic structure; we provide a quantum-mechanical definition of it in the Appendix. At this step, we rewrite Eq. (9a) as

$$E_{e\min} m_e r_{AB\min}^2 g_{IN} \sim \hbar^2 \quad (9b)$$

(Eq. (2) further elaborated). Equation (9b) is (together with the quantum numbers that will come into play) checked elsewhere [7, 8]. Nevertheless, the check of our end results derived via Eq. (8) should constitute a proof of its validity.

$E_e(r_{AB})$ can be as usual expressed fairly well in terms of the force constant k_0 , defined by Eq. (5), as

$$E_e(r_{AB}) = E_{e\min} + \frac{1}{2} k_0 (r_{AB} - r_{AB\min})^2. \quad (10)$$

It is true that this relationship does not display characteristics such as anharmonicity and dissociation; however, throughout this work, we are going to deal only with the ground vibrational level of the states of concern. Thus, even when we deal with an excited electronic state, Eq. (10) turns out to be quite valid for its ground vibrational level.

$E_e(r_{AB})$ vanishes at the abscissa r_{AB} , which we can define with respect to $r_{AB\min}$; i.e.,

$$r_{AB} = p r_{AB\min} \quad (11)$$

(the value that makes (value which makes $E_e(r_{AB})$ vanish); p is an unknown parameter at this stage, though it appears to be roughly 2. Equations (10) and (11) provide us with the possibility of expressing $E_{e\min}$ as

$$E_{e\min} = \frac{1}{2} k_0 (p-1)^2 r_{AB\min}^2. \quad (12)$$

We plug the right-hand side of this equation into Eq. (9b); next, we use Eq. (8) to eliminate the force constant k_0 ; thus, we arrive at a simple expression for $T_{A,B}$; i.e.,

$$T_{A,B} \sim \frac{1}{\hbar} \sqrt{g_{IN} g_k \mathcal{M}_{AB} m_e r_{AB}^2}, \quad (13)$$

where g_k replaces $(p-1)^2/2$.

Below, for simplicity, we call $T_{A,B}$, T_0 ; $\omega_{A,B}$, ω_0 ; M_{AB} , M_0 ; and r_{AB} , r_0 .

The quantity

$$M_0 = \sqrt{\mathcal{M}_0 m_e} = m_e \sqrt{\mathcal{M}_0 / m_e} \quad (14)$$

(the vibrational clock mass) formulated on the basis of the electron mass, has the dimension of a mass. We call it the ‘‘vibrational clock mass’’ (to be associated with the vibrational motion of the diatomic molecule in hand).

The proportionality constant formulated by Eq. (13) shall then embody a geometry factor and quantum numbers. A geometry factor of 2π originates from the use of Eq. (9) (where \hbar^2 may be read as $\hbar^2/4\pi^2$ and, accordingly, 2π is left after the square rooting on the way to Eq. (13)); another 2π factor originates from the use of Eq. (8); thus, altogether, a geometry factor of $4\pi^2$ should multiply Eq. (13) (cf. Eqs. (A.3) and (A.4) of the Appendix).

The quantum numbers to be introduced in Eq. (13) appear to be more peculiar, and we will elaborate on this problem in Part 2. Nonetheless, one can sense that [\hbar^2] in Eq. (9) should be in fact read as usual, as [$n^2 \hbar^2$], more precisely as [$n_1 n_2 \hbar^2$], n_1 and n_2 being the principal quantum numbers of electrons making up the bond(s) of the diatomic molecule in hand [3]. Recall that, because of quantum defects, n_1 and n_2 are not integer numbers. Equation (13) thus becomes

$$T_0 = \frac{4\pi^2}{\hbar \sqrt{n_1 n_2}} \sqrt{g \mathcal{M}_0 m_e r_0^2} \quad (15a)$$

(the classical excited vibrational period of the molecule versus the internuclear distance, n_1 and n_2 being the principal quantum numbers of the electrons making up the excited bond), where now g , an overall, dimensionless, and relativistically invariant quantity, replaces

² Note that, via the Bohr atom model, one can write

$$T_0 = 2\pi \sqrt{m_e / (e^2 / r_0^3)}, \quad (i)$$

for the hydrogen atom, the simplest wavelike entity; here, e is the electron charge and r_0 is the Bohr radius. Equation (i) compared with Eq. (8) yields e^2 / r_0^3 for the force constant k_0 . This, when plugged into Eq. (12), leads to $|E_e| = (1/2)(p-1)^2 e^2 / a_0$ for the magnitude of the electronic energy E_e of the hydrogen atom, a_0 being the Bohr atom radius; thus, to develop a sense of the coefficient $(p-1)^2$ of Eq. (12), we can conclude that it should be set to unity for the case of the hydrogen atom, given that $|E_e|$ for this case can be expressed as $(1/2)e^2 / a_0$; therefore, for the case of the hydrogen atom, g_k becomes 1/2. At the same time, since p is related to the electronic structure of the molecule, it is clear that g_k , just like g_{IN} , depends only on this structure. Note that g_k is anyway close to unity.

$g_{IN}g_k$; a quantum-mechanical definition of g is provided in the Appendix. Note here that the quantum numbers n_1 and n_2 are normally associated with the bond electrons of a given diatomic molecule in an excited electronic state. However, one can as well conjecture them to be associated with the bond electrons of the ground state of any diatomic molecule belonging to a given chemical family, in reference to the ground state of a diatomic molecule still belonging to this family but bearing, say, the lowest classical vibrational period, since g , depending only on the electronic configuration, will stay nearly constant throughout; we elaborate on this interesting idea in Part 2.

Thus, we rewrite Eq. (15a), yet now regarding not the electronic states of a diatomic molecule but instead the ground states of members of a given chemical family:

$$T_{0G} = \frac{4\pi^2}{h\sqrt{n_1 n_2}} \sqrt{g M_0 m_e} r_{0G}^2 \quad (15b)$$

(the classical ground vibrational period of the molecule T_{0G} versus its ground internuclear distance r_{0G} , n_1 and n_2 being the principal quantum numbers of the electrons making up the bond of the molecule at the ground level).

Recall that we kept the subscript “0” pinned to the symbols representing the basic quantities coming into play in Eq. (15a) to stress the fact that we define them in the resting framework (versus the corresponding Lorentz-transformed quantities); in Part 2, to simplify the notation, we will drop this subscript.

Equation (15a) or (15b), though g is not known beforehand, turns out to be somewhat rigorous. In other words, despite the Born–Oppenheimer approximation we adopted, as well as the approximate Morse potential we introduced at the level of Eq. (10), the use of g (to

be determined) ultimately insures the equality of these equations. It becomes apparent that g is necessarily related to the electronic structure of the molecular bond; thus, for alike bonds, in a given chemical family, we come to expect g to be virtually the same; we call g the “molecular bond looseness factor,” for, as we will elaborate in the Appendix, its inverse somewhat characterizes the strength of the bond of concern. Numerical values that g assumes for different molecules will be provided in Part 2.

CONCLUSIONS

The quantum numbers n_1 and n_2 that we introduced in Eqs. (15a) and (15b) should now be determined, and that is what we will undertake in Part 2, primarily on the basis of spectroscopic data for the H_2 molecule. The elucidation of an empirical relationship known since long ago, as well as of irregular H_2 spectroscopic data [9, 10], will then be achieved. Our findings will allow us to draw up a whole new systematization of diatomic molecules.

Following the idea we proposed on the extension of Eq. (15a), it is now worth analyzing the subsequent Eq. (15b) regarding all diatomic molecules, without even taking into account the quantum numbers. Indeed, the plots of T_0 versus $\sqrt{M_0} r_0^2$ for members of a given chemical family exhibit nicely increasing, almost faultless, smooth curves; we present eight examples in Figs. 1–7. It should be stressed that our approach discloses a simple architecture of diatomic molecules, which is otherwise concealed behind a much too cumbersome quantum-mechanical description. This architecture, telling how the vibrational period of time, size, and mass are determined, is Lorentz-invariant and can be considered as the mechanism of the behavior of the

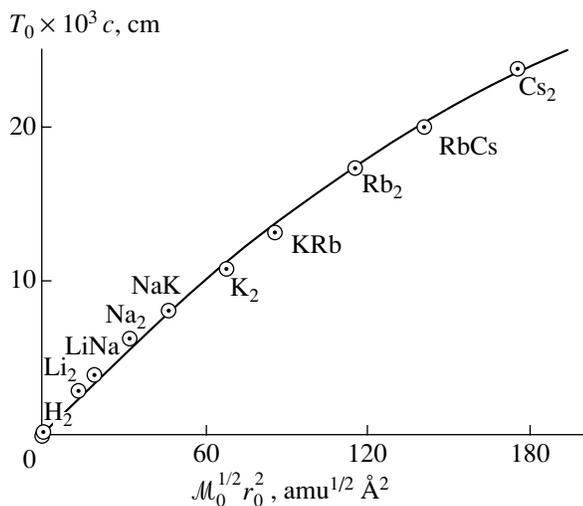


Fig. 1. Period of alkali molecules versus $M_0^{1/2} r_0^2$ (c is the speed of light).

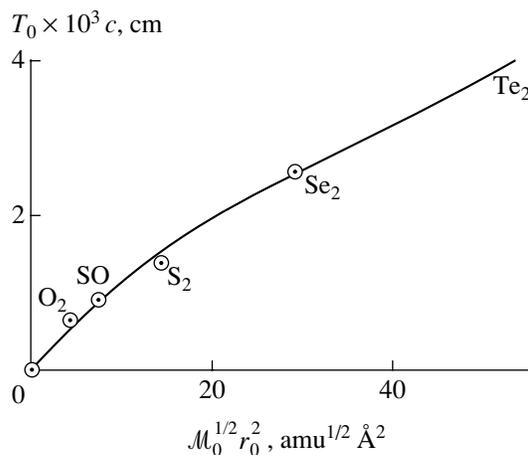


Fig. 2. Period of (O_2 , S_2 , Se_2 , Te_2) versus $M_0^{1/2} r_0^2$.

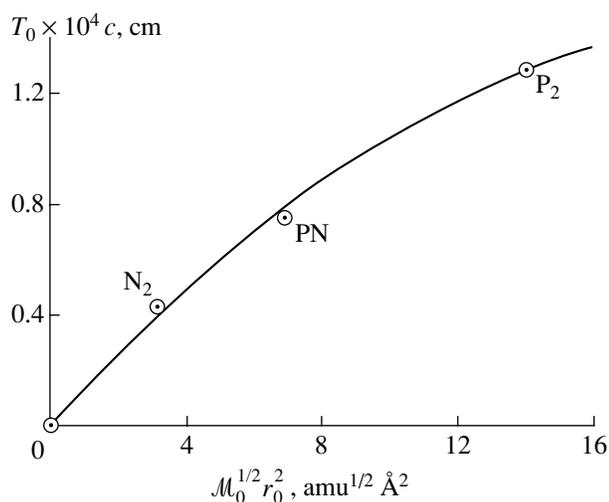


Fig. 3. Period of (N_2 , PN , P_2) versus $M_0^{1/2} r_0^2$.

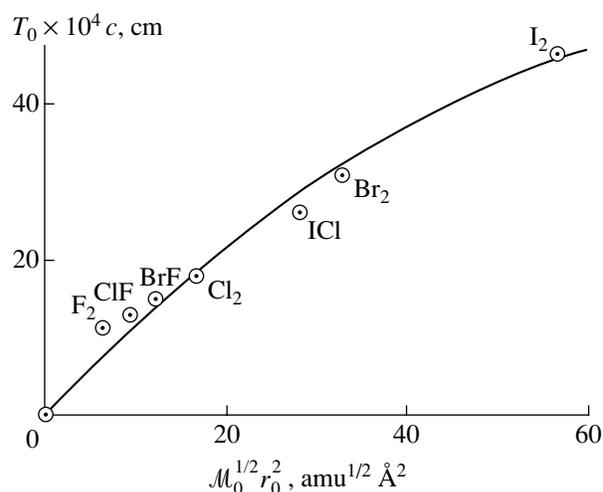


Fig. 4. Period of diatomic molecules made of combinations of halogen atoms versus $M_0^{1/2} r_0^2$.

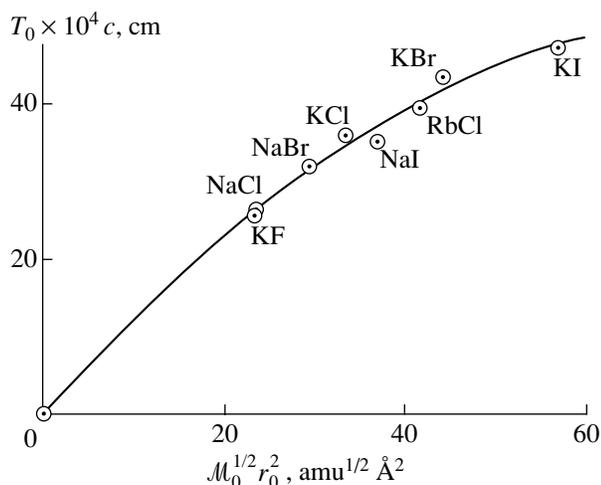


Fig. 5. Period of different alkali-halogen molecules versus $M_0^{1/2} r_0^2$.

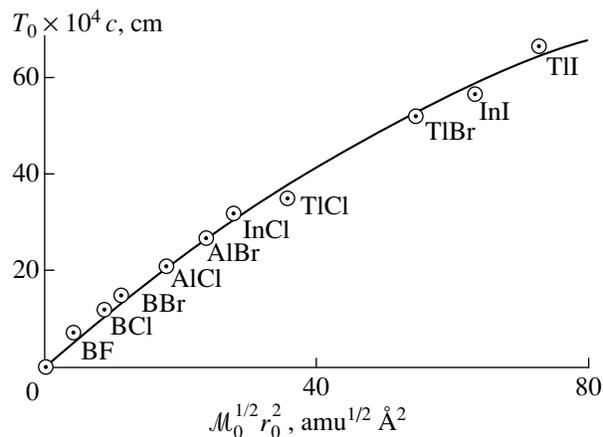


Fig. 6. Period of diatomic molecules made of atoms belonging to, respectively, the third and seventh columns of the periodic table versus $M_0^{1/2} r_0^2$.

quantities in question in interrelation with each other when the molecule is brought into uniform translational motion or transplanted into a gravitational field or, in fact, any field with which it can interact [11, 12]. This is the essence of our approach, and it will be further clarified in Part 2.

APPENDIX

Direct Derivation of the Relationship $E_e m_e r_{AB} \sim h^2$

Via the usual weighting and integration of Eq. (4) over the appropriate space domain, as well as the virial theorem [13, 14]

$$2 \int_{\text{space}} \psi_e E_e \psi_e dV = \int_{\text{space}} \psi_e U_0 \psi_e dV, \quad (\text{A.1})$$

where U_0 is the potential energy of concern, one can write

$$E_e = \frac{h^2}{8\pi^2} \int_{\text{space}} \psi_e \left(\frac{1}{m_e} \sum_i \nabla_{ei}^2 \right) \psi_e dV; \quad (\text{A.2})$$

this yields

$$8\pi^2 E_e m_e \frac{1}{\int_{\text{space}} \psi_e \left(\sum_i \nabla_{ei}^2 \right) \psi_e dV} = h^2 \quad (\text{A.3})$$

(the electronic motion equation integrated over the space).

One can check that, for the simplest real wavelike entity, i.e., the hydrogen atom, the integral quantity $\int_{\text{space}} \psi_e \nabla^2 \psi_e dV$ turns out to be equal to $-n^2/a_0^2$, where a_0 is the Bohr orbit radius and n is the principal quantum number associated with ψ_e . The quantity $\int_{\text{space}} \psi_e \nabla^2 \psi_e dV$ can further be evaluated within the framework of an even simpler case, i.e., the particle moving in just one dimension, in an infinitely high potential well; the result is $-n^2\pi^2/a_0^2$, where now a_0 is used to denominate the width of the well.

For other simple cases, such as the rotational motion of a diatomic molecule, the integral quantity in question turns out to be equal to $-N/a_0^2$, where a_0 is the space size in which the dynamics under consideration takes place and N (equal to $J(J+1)$ for the rotational motion of a diatomic molecule) is the composite quantum number coming into play.

On the basis of these findings, we can define the dimensionless, positive quantity g_{IN} in regard to the vibrational motion of a diatomic molecule as

$$g_{IN} = \frac{-n_1 n_2}{r_{AB\min}^2 \int_{\text{space}} \psi_e(r_0) \left(\sum_i \nabla_{ei}^2 \right) \psi_e(r_0) dV} \quad (\text{A.4})$$

(the quantum-mechanical definition of g_{IN}) in order to be able to express briefly the integral quantity $\int_{\text{space}} \psi_e \left(\sum_i \nabla_{ei}^2 \right) \psi_e dV$ in terms of the average internuclear distance $r_{AB\min}$; n_1 and n_2 are the bond electron principle quantum numbers. It is clear that g_{IN} depends only on the electronic structure. Following our approach, we further expect that g_{IN} is not far from unity.

At the same time, note that one can write

$$\int_{\text{space}} \psi_e \nabla_{ei}^2 \psi_e dV = \int_{\text{space}} (\nabla_{ei} \psi_e)^2 dV \quad (\text{A.5})$$

(written for the i th electron).

Thus, in principle, the more severe the gradient $\nabla_{ei} \psi_e$ based on Eq. (A.4), the smaller the coefficient g_{IN} will be. For the bond electrons, the gradient $\nabla_{ei} \psi_e$ is, roughly speaking, zero in between of the nuclei. However, for a given internuclear distance, the stronger the bond, the sharper the gradient along paths leading away from both nuclei will be. Thence, we expect g_{IN} to decrease as the bond gets tighter.

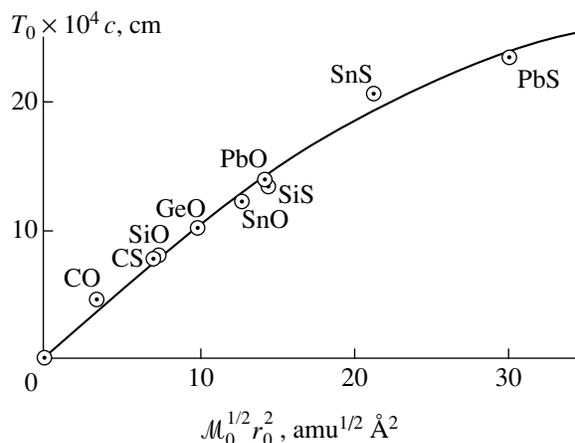


Fig. 7. Period of diatomic molecules made of atoms belonging to, respectively, the fourth and sixth columns of the periodic table versus $M_0^{1/2} r_0^2$.

It is further of interest to note that, if one defines an unusual de Broglie relationship for the diatomic molecule under consideration, though in the following familiar form

$$2\pi r_{AB\min} = \frac{h}{\sqrt{g_{IN} m_e} v_0} \quad (\text{A.6})$$

(a generalized de Broglie relationship proposed by the author for a diatomic molecule), v_0 being an average velocity to be associated with the electronic motion, then one can, via the use of the virial theorem (cf. Eq. (A.1)), derive in a straightforward way Eq. (A.3), in which the fraction embodying the integral term shall be replaced by its homologue defined by Eq. (A.4), i.e., by $g_{IN} r_{AB\min}$.

Equation (A.4) provides us with the possibility of establishing a quantum-mechanical definition of g of Eqs. (15),

$$g = g_{IN} g_k = \frac{-n_1 n_2}{r_{AB\min}^2 \int_{\text{space}} \psi_e(r_0) \left(\sum_i \nabla_i^2 \right) \psi_e(r_0) dV} \frac{(p-1)^2}{2} \quad (\text{A.7})$$

(a quantum-mechanical definition of g figuring in Eqs. (15)). Here, p is defined by Eq. (11); i.e., $r_{AB} = p r_{AB\min}$ (the internuclear distance that makes $E_e(r_{AB})$ vanish); with the thus-defined p , g_k is therefore a quantity associated with just the electronic structure; then g , just like g_{IN} , merely depends on the electronic structure of the molecule in hand, which leads us to expect g to indeed stay practically constant for chemically alike molecules.

At the same time, one can guess that the greater p , the smaller the dissociation energy will be and, thus, the looser the bond under consideration. Therefore, g_k behaves just like g_{IN} in regard to the bond strength. We conclude that the smaller g , the tighter the bond will be.

REFERENCES

1. T. Yarman and F. A. Yarman, DOGA—Turkish J. Phys. Sci. and Techn. Research Council of Turkey (Supplement) **16**, 596 (1992).
2. T. Yarman, DOGA—Turkish J. Phys. Sci. and Techn. Research Council of Turkey **16**, 552 (1992).
3. T. Yarman, *Chimica Acta Turcica* **26** (3), 87 (1999).
4. T. Yarman, *Chimica Acta Turcica* **27**, 1 (1999).
5. M. Born and J. R. Oppenheimer, *Ann. Physik* **84**, 457 (1927).
6. J. C. Davis, Jr., *Advanced Physical Chemistry* (The Ronald Press Company, 1965).
7. T. Yarman, F. Yarman, and F. Özeydin, *DAMOP 2003 Meeting, APS, May 20–24, 2003, Boulder, Colorado, USA*.
8. T. Yarman, F. Yarman, and F. Özeydin, *DAMOP 2003 Meeting, APS, May 20–24, 2003, Boulder, Colorado, USA*.
9. T. Yarman, *DAMOP 2001 Meeting, APS, May 16–19, 2001, London, Ontario, Canada*.
10. T. Yarman, *6th Europ. Conference on Atomic and Molecular Physics, ECAMP VII, 2–6 April, 2001, Berlin*.
11. T. Yarman, *DAMOP 2001 Meeting, APS, May 16–19, 2001, London, Ontario, Canada*.
12. T. Yarman, *Les Annales de la Fondation Louis de Broglie (Paris)* **29** (3), 459 (2004).
13. J. C. Slater, *J. Chem. Phys.* **1**, 687 (1933).
14. M. Born, W. Heisenberg, and P. Jordan, *Z. Physik* **35**, 557 (1925).