

AN ESSENTIAL APPROACH TO THE ARCHITECTURE OF DIATOMIC MOLECULES

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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 B&O Approximation, together with the cast $E_{0e} m_{0e} R_0^2 \sim h^2$ (we established previously), written for the electronic description (with fixed nuclei). Our approach yields an *essential relationship* for T_0 , the *fundamental vibration period*, at the *total electronic energy* E_{0e} , i.e. $T_0 = [4\pi^2 / (\sqrt{n_1 n_2} h)] \sqrt{g M_0 m_e} R_0^2$, where M_0 is the *reduced mass of the nuclei*, m_e the *mass of the electron*, g a *dimensionless and relativistically invariant coefficient*; n_1 and n_2 , are basically the *principal quantum numbers* of electrons making up the bond(s) of the diatomic molecule in hand. The latter relationship *essentially* yields $T_0 \sim R_0^2$, for the *lowest vibrational periods* versus the square of the *internuclear distance* at different *electronic states of a given molecule*, which happens to be an *approximate relationship* known since 1925, but not disclosed so far. Further, for electronic states configured similarly, we determine $n_1 n_2$ to be R_0 / R_{00} , where R_0 is the *internuclear distance* at the given electronic state, and R_{00} the *internuclear distance* at the ground state. This allows us to draw a complete systematization of diatomic molecules, given that we expect g (appearing to be purely dependent on just the *electronic structure of the molecule*), to stay constant for *chemically alike molecules*, and we identify $n_1 n_2$ to be R_0 / R_{00} for diatomic molecules, whose bonds are electronically configured in the same way, R_{00} now being the *internuclear distance of the molecule* picked up as the *reference molecule* within the *chemical family* in consideration.

This work is issued from a totally different perspective than the one considered herein. We are not going to reinforce this substantial perspective through this article. Nevertheless we should state it briefly, since it allowed us, long ago to derive practically everything we present herein.^{1, 2, 3} 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” this displays, ought to be made in just a given manner.*

In effect a *natural entity*, has got an *internal dynamics*. Thus it works as a *clock*. This bears a *clock period* T_0 ; the mechanism in question involves a *given mass* M_0 , which we call the “*clock mass*”, and is 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. One can define several *clock masses*, for the same entity, regarding different *internal dynamics* this 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) x (the electron mass), or just the *electronic mass* m_e , were the coefficient of concern accounted for, in a different way. On the other hand, the *clock mass of the vibrational motion of a diatomic molecule* is $m_e \sqrt{M_0} / m_e$, where 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 in a *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 be already 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, 2, 3, 4} This was our *original idea*, which we will not stress any further, here.

In this article though, 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 and Oppenheimer (B&O) approximation*, and a *fundamental cast* we have derived previously, which we shall briefly sketch (Sections 1, 2 and 3). Then we will elaborate on the *quantum numbers* that come into play (Section 4). Our approach yields the disclosure of an empirical relationship established back in 1925 (Section 5). Thus we conclude with a novel systemtization of all diatomic molecules (Sections 6 and 7).

1. THE UMA CAST

For an atomistic or molecular wave-like object existing in nature, we have shown elsewhere the following theorem, first, on the basis of the Schrödinger Equation, as complex as this may be, then on the basis of the Dirac Equation, whichever may be appropriate, in relation to the object in hand.⁴

Theorem 1: In a “*real wave-like 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’s motion of the object is increased as much, *and* 2) the *size* R_{0k} of the object in which the given clock’s motion takes place, contracts as much; in *mathematical words* this is

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

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

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

The occurrence stated by Eq.(1) further yields an *invariance*, interestingly strapped to the square of the Planck Constant, h^2 .

This is the content of our Theorem 2, restated right here.

Theorem 2: The quantities, $E_{0k} M_{0k} R_{0k}^2$ ($k=1, \dots, K$) (*associated with the k^{th} internal motion of the wave-like object in hand*), are invariant in regards to a “mass change”, and are all strapped to h^2 .

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

$$E_{0(\text{GrandTotal})} = E_{01} + E_{012} + \dots + E_{0k} + \dots ,$$

$$E_{0k} \sim \frac{h^2}{M_{0k} R_{0k}^2}, k = 1, \dots, K. \quad (2)$$

We call this occurrence, the UMA (Universal Matter Architecture) Cast.

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

Soon we shall figure out that the *proportionality constant* embodied by Eq.(2), besides a usual *geometry factor* and *quantum numbers*, fortunately, is made of a “*transferable constant*”; indeed this *constant* seems to depend mainly on 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 *electronically* configured similarly.
- ii) *Furthermore*, it stays still *fairly* the same, regarding the ground electronic states of molecules belonging to a given chemical family (*thus all bearing similar electronic configurations*).

2. THE B&O 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 B&O approximation, is reduced into the separate descriptions of the “*nuclear*” and “*electronic*” motions. We thus come to solve separately the two following Schrödinger Equations, written with the usual notation⁵:

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

$$\left(-\frac{\hbar^2}{8\pi^2 m_e} \sum_i \nabla_{e_i}^2 \Psi_e + \sum_{i,i'} \frac{e^2}{r_{ii'}} + \frac{Z_A Z_B e^2}{r_{AB}} - \sum_i \frac{Z_A e^2}{r_{Ai}} - \sum_i \frac{Z_B e^2}{r_{Bi}} \right) \Psi_e = E_e \Psi_e \quad (4)$$

Here “A” and “B” designate the nuclei, and “e” designates the electrons. We have then the following familiar notation.

m_A	: mass of A	r_{Ai}	: i^{th} electron's distance to A
m_B	: mass of B	r_{Bi}	: i^{th} electron's distance to B
Z_A	: atomic number of A	$r_{ii'}$: distance between the i^{th} and the i'^{th} electron
Z_B	: atomic number of B	r_{AB}	: distance in between the nuclei
m_e	: electron's mass	$\Psi_{A,B,e}$: eigenfunction associated with the molecule
e	: electron's charge	$E_{A,B,e}$: eigenvalue associated with the molecule

Eq.(3) describes the nuclei vibrational motion, about the internuclear distance r_{AB} to be input to this equation (*for a given electronic state of the molecule*), whereas Eq.(4) describes the electronic motion around the two “fixed” nuclei. Thus, *as usual*, one solves Eq.(4), for a given electronic state, in order to determine how the *eigenvalue* E_e varies with respect to r_{AB} , and find the internuclear distance r_{AB} , which makes minimum E_e , more precisely $E_e(r_{AB})$; we call r_{ABmin} and E_{emin} , respectively, the *internuclear distance* and the *eigenvalue* in question (*for the given electronic state*); this is then r_{ABmin} as r_{AB} , to be input to Eq.(3). Normally E_{emin} is negative; yet below, by E_{emin} we shall mean $|E_{emin}|$.

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

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

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

$E_{A,B}$ becomes,

$$E_{A,B} = \frac{j(j+1)\hbar^2}{8\pi^2 I_{AB}} + \left(v + \frac{1}{2} \right) \hbar \varpi_{A,B}, \quad j = 0, 1, \dots; \quad v = 0, 1, \dots; \quad (6)$$

I_{AB} is the “*moment of inertia*” of the nuclei:

$$I_{AB} = M_{AB} r_{AB}^2, \quad (7)$$

where M_{AB} is the nuclei reduced mass.

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

$$T_{A,B} = 2 \pi \sqrt{\frac{M_{AB}}{k_0}} . \quad (8)$$

Thus, along this definition, $E_{A,B}$ [as expressed by Eq.(6), above], is the solution of Eq.(3), for the nuclear motion of the molecule.

3. THE “VIBRATION PERIOD”, VERSUS THE “DIATOMIC MOLECULE CLOCK MASS” AND THE “INTERNUCLEAR DISTANCE”

The B&O 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 different masses taking part in the internal motion of the molecule, and the “*internuclear distance*” coming into play.

Thus, Eq.(2), i.e. $E_{ok} M_{ok} R_{ok}^2 \sim h^2$, must hold on the basis of Eq.(4); this equation indeed embodies a potential energy term *strictly* made of *Coulombian potential energies*. The eigenvalue E_e [more precisely $E_e(r_{AB})$], assumes the value E_{emin} when r_{AB} takes the value of r_{ABmin} . Furthermore, the *only mass* that comes into play in Eq.(4), is the *electron mass*, m_e ; in other terms the “*clock mass*” in question to be associated with the electronic motion of the molecule (*with fixed nuclei*), is made of only electron masses coming into play, and obviously all bearing the mass m_e .

Thence

$$E_{emin} m_e r_{ABmin}^2 g_{IN} \sim h^2 \quad [\text{Eq.(2), written based on Eq.(4)}] , \quad (9)$$

where we inserted the *proportionality constant* g_{IN} of the invariance in question (cf. Theorem 2); the setting of of this relationship as an *equality*, now only requires a *geometry factor* and appropriate *quantum numbers*, as elaborated below.

The validity of Eq.(9) is checked elsewhere.⁶ Nevertheless the check of our end results derived via Eq.(9), should already constitute a “*proof*” of it.

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

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

It is true that this relationship does not display characteristics such as “*anharmonicity*” and “*dissociation*”; but 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 the *ground vibrational level* of it.

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

$$r_{AB} = p r_{ABmin} \text{ [value which makes } E_e(r_{AB}), \text{ vanish] ;} \quad (11)$$

p is an unknown parameter at this stage, though it appears to be *roughly* 2.

Eqs.(10) and (11), provides us with the possibility of expressing E_{emin} , as

$$E_{emin} = \frac{1}{2} k_0 (p - 1)^2 r_{ABmin}^2 . \quad (12)$$

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

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

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

Below for simplicity, we call $T_{A,B}$, T_0 ; $\varpi_{A,B}$, ϖ_0 ; M_{AB} , M_0 , and r_{AB} , r_0 .

The quantity

$$M_0 = \sqrt{M_0 m_e} = m_e \sqrt{\frac{M_0}{m_e}} \quad (14)$$

(*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* in Eq.(13) shall embody a *geometry factor*, and as discussed below, *quantum numbers*. A *geometry factor* of 2π originates from the use of Eq.(9) [where h^2 may be read as $h^2/4\pi^2$, and accordingly, 2π is left after the square rooting, on the way to Eq.(13)]; an other 2π factor originates from the use of Eq.(8); thus altogether, a *geometry factor* of $4\pi^2$ should multiply Eq.(13).

Recall that because of quantum defects, n_1 and n_2 are not *integer numbers*.

The *quantum numbers* to be introduced in Eq.(13) appear to be more peculiar, and we *elaborated* on it, as *summarized* below. Nonetheless, one can sense that $[h^2]$ in Eq.(9), should be in fact read as usual, as $[n^2 h^2]$, more precisely as $[n_1 n_2 h^2]$, n_1 and n_2 being *principal quantum numbers* of electrons making up the bond(s) of the diatomic molecule in hand³ (*we shall soon work them out*).

Eq.(13), thus becomes

$$T_0 = \frac{4\pi^2}{h\sqrt{n_1 n_2}} \sqrt{g M_0 m_e} r_0^2, \quad (15)$$

where g replaces $g_{IN} g_k$.

Note here that, the quantum numbers n_1 and n_2 are not necessarily associated with *excited states of a given ground state*. As it will become clear soon, we also propose to associate them, with respectively, the *ground states of members of a given chemical family*, in reference to a given member of this family, more precisely the one possessing the lowest vibrational period.

Eq.(15), though g is not known beforehand, is somewhat *rigorous*. In other terms, despite the B&O approximation we adopted, also the approximate Morse potential we introduced at the level of Eq.(10), the use of g (*to be determined*), ultimately insures the equality of Eq.(15).

It is apparent that, g is necessarily related to the *electronic structure* of the molecule's 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 it can be checked that, the *inverse* of it is nearly proportional to the *dissociation energy of the molecule*.

Our approach allows us to draw a whole *new systematization of diatomic molecules*, and more, such as and the elucidation of an *empirical relationship* known since long ago, as well as *H₂ irregular spectroscopic data*.^{7,8}

The introduction of the product of *quantum numbers*, $n_1 n_2$ requires a *demonstration*, and that is what we undertake briefly right below, primarily on the basis of the *H₂ molecule spectroscopic data*. Yet Eq.(15) is worth to be analyzed, even before the elaboration of quantum numbers. Indeed already 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 Figures 1 - 7.

4. ELABORATION ON THE QUANTUM NUMBERS

The presence of quantum numbers in Eq.(15), is right away induced by the *identification* of the RHS of Eq.(2) as h^2 . This equation is further transformed into Eq.(9), written for the mere *electronic description* of the molecule [cf. Eq.(4)].

The *excited electronic eigenstates* of the molecule should anyway involve quantum numbers.* The simplicity of Eq.(2) or Eq.(9), *clearly leaves no other room to quantum numbers that shall come into play in these equations*, other than that, *right next to h^2* .

* Any excited eigenstate shall obviously involve quantum numbers. But here, we are particularly interested in *electronic excited eigenstates*.

Thus a composite quantum number \mathcal{N} (i.e. *the product of the two principal quantum numbers to be associated with the bond electrons, in the case of a diatomic molecule*), should come to multiply h^2 , in Eq.(2) or Eq.(9), regarding an *excited eigenstate*, in just the same way the *square of an integer quantum number* related to an excited state of the *simplest* wave-like objects (*for example, the hydrogen atom*), comes in a similar relationship, to multiply to h^2 .

This *piece of information* makes that, were \mathcal{N} somehow known, one can introduce it *right next* to h^2 , into the *framework* of the *ground level wave-like description* (i.e. *the Hamiltonian*) of the entity in hand, and consequently determine the *eigenvalue*, and the *characteristic length* induced by the *resulting formulation*.

Though here, there is a *peculiarity*.

Eq.(9), in the simplest case of the hydrogen atom, shall (*with the usual notation*) be written as

$$8\pi^2 E_n g_{\text{IN}} m_e \mathcal{R}_n^2 = n^2 h^2 ; \quad (9) \text{ (rewritten)}$$

(*for the hydrogen atom, g_{IN} is unity*)

here E_n is the *total energy* of the n^{th} electronic state, \mathcal{R}_n is the corresponding *characteristic size*, and n the *principal quantum number*; g_{IN} is a *coefficient* related to the *electronic configuration* we visualized (*next to the geometry factor*), at the level of Eq.(9).

In the case of the hydrogen atom, g_{IN} is *unity*, regardless n . Thus, in this case i) g_{IN} is *unity*, at the ground state, *but also* ii) g_{IN} remains the *same* at all electronic levels.

Neither property holds for systems of *higher complexities*, though as we show, an equation similar to Eq.(9) can well be written for any diatomic molecule, or further any wave-like entity.

Since g_{IN} [of Eq.(9)], more generally g [of Eq.(15)] appears to be *purely* related to the *electronic structure* of the entity in hand, we expect them to remain the *same*, for *alike electronic configurations*. This occurrence holds within the frame of *alike* electronic states of a given molecule, as well as within the frame of *alike* ground states of molecules belonging to a given chemical family.

However, as one jumps from the ground state of a complex system, such as that of a diatomic molecule, to an excited state of this entity, it is not obvious that the electronic configuration shall stay the same; in fact, generally it will not. Take for instance the *hydrogen molecule*. Its excited electronic states a priori, will not bear the *same electronic configuration* as that of the ground state, unless the two electrons are excited in a *complete symmetry*. Even then, the *shielding effects* may not be the same.

This is the peculiarity we wanted to clarify.

Thus, as the molecule jumps from its ground state to an excited state, in general, it is not only that, h^2 is multiplied within the framework of the wave-like description, by the appropriate quantum number; but we should *further* represent the *change* that takes place in the *electronic structure*. That can be taken care of, by a *corresponding change* in the coefficient g_{IN} of Eq.(9).

In fact, altering just h^2 , and altering both h^2 and g_{IN} , so that h^2 / g_{IN} is changed by the same amount, within the frame of Eq.(9), are *mathematically equivalent operations*, yet as discussed, *physically* they appear to be quite different.

Thereby we can conceive an *excited electronic state* as achieved in two steps: 1) Switching the ground state electronic configuration into the new configuration by just changing g_{IN} . 2) Jumping from this configuration to the new quantum state.

For electronic states configured like the ground state, we will have to achieve only the second step.

This yields the content of our Theorem 3.

Theorem 3: Were the atomic or molecular wave-like object in hand, at a given electronic state, characterized by the *composite quantum number* \mathcal{N} , then the *eigenvalue* and *characteristic length* associated with this state, becomes the output of the formulation one obtains by multiplying h^2 with \mathcal{N} , in the *framework of the ground state description*, provided that the two states are configured similarly.

So the introduction of appropriate quantum numbers in Eq.(9), next to h^2 (*within the framework of the wave-like description*), in order to take care of the *excited electronic eigenstates* of the molecule as complex as this may be, appears to be as *standard* as this is, for the simplest atomic object, *provided that the two states are configured similarly*.

We can predict the solution of the *new set up*, through Theorem 1. It can be obtained based on a *reformulation* of this theorem. Thus we establish our Theorem 4 regarding an excited electronic level of the wave-like object in hand.

Theorem 4: In a “*real wave-like ground description*” if, in the aim of expressing an excited eigenstate, h^2 is multiplied by the *composite quantum number* \mathcal{N} (*the inverse of the eigenvalue related to this eigenstate, were the ground state energy normalized to unity*), then *concurrently*, a) the magnitude of the *total ground energy* E_0 associated with the given wave-like object, is decreased as much, to become E , the *new eigenvalue*, and b) the corresponding *ground state size* \mathbf{R}_0 stretches as much, to become \mathbf{R} , the *new size*, provided that the two states are configured similarly; in *mathematical words* this is

$$[h^2 \rightarrow \mathcal{N} h^2] \Rightarrow \{[E_0 \rightarrow E = \frac{E_0}{\mathcal{N}}], [\mathbf{R}_0 \rightarrow \mathbf{R} = \mathcal{N} \mathbf{R}_0]\}. \quad (16)$$

Note that Theorem 6 holds for any excited eigenstate (*rotational, vibrational, electronic, or else*).

This theorem, for *excited states* of the molecule, *configured like the ground state*, yields at once

$$\mathcal{N} = \frac{\mathbf{R}}{\mathbf{R}_0} \quad (17)$$

(*composite quantum number of the excited eigenstates, were this configured like the ground state*).

This interestingly holds no matter how complex the molecule may be.

Accordingly we establish our next theorem.

Theorem 5: The *composite quantum number* to be associated with an excited eigenstate, is the mere ratio of the *size the object displays at this excited state*, to the *size the object displays at the ground state*, provided that the two states are configured similarly.

Theorem 5 can be checked for the electronic states of hydrogen atom. It is surprising that it holds for any object and for any excited eigenstate the object may involve.

What if the *electronic structure* of the excited state is not the same as that of the ground state?

The answer is fortunately not complicated. Since the coefficient g_{IN} in Eq.(9) comes to multiply the *mass of the electron*, which happens to be the *only mass* taking place in the description of the electronic motion of the diatomic molecule, *any change* in g_{IN} , evidently can be represented by a *corresponding hypothetical change in the mass of the electron*.

If further, we are *concomitantly* to consider a *quantum number* \mathcal{N} to be associated with the excited eigenstate in question (*i.e. configured in a different way than the ground state*), then based on Eq.(9), this state can well be described by merely altering h^2/m_e in the framework of the ground state of the molecule by $\mathcal{N}(g_{\text{IN}})_{\text{initial}} / (g_{\text{IN}})_{\text{final}}$, where the subscripts “initial” and “final” refer respectively to the *ground state* and the *excited electronic state* in consideration.

The ultimate output, can be right away established via Theorems 1 and 2.

Theorem 6: The *ratio* of the *size* a diatomic molecule displays at an *excited state*, to the *size it displays at the ground state*, is equal to $\mathcal{N}(g_{\text{IN}})_{\text{initial}} / (g_{\text{IN}})_{\text{final}}$, i.e. the *composite quantum number* to be associated with the excited state, *times a coefficient*, the *inverse of which* quantifies how much the overall *ground state electronic configuration* is altered.

In what follows we shall solely focus on excited electronic eigenstates [since we visualize Eq.(15), for just the lowest vibrational state of an electronic eigenstate].

Note that the usage of Eq.(17) along Eq.(15), requires that the coefficient g is not altered as the molecule passes from its ground level to the given excited electronic state, so that we can plot T , the *largest vibrational period* at the given *excited electronic state*, versus $N^{-1/2}R^2$, where R is the size of concern, at this eigenstate.

5. THE DISCLOSURE OF THE AGED EMPIRICAL RELATIONSHIP $\omega r^2 = \text{Constant}$, AND THE COMPLETE SET OF H_2 ELECTRONIC VIBRATIONAL DATA

Recall that the following *approximate empirical relationship*, evoking very much Eq.(15), had been established for a given diatomic molecule, back in 1925, yet not unveiled so far:^{9, 10, 11, 12, 13}

$$\omega r^2 \approx \text{Empirical Constant} ; \quad (18)$$

*(approximate relationship written in 1925
for the electronic states of a given molecule)*

here, ω is the *lowest vibration frequency*, i.e. the inverse of the *largest vibrational period* T , related to a given *electronic state of the molecule*, and r the corresponding *internuclear distance*.

The “*Empirical Constant*” is then to be determined separately, for each diatomic molecule.

Eq.(18) bears the same cast as that of Eq.(15) (*as far as the dependency of the vibrational period on the internuclear distance is concerned*); yet it does not include the *quantum numbers*.

Eq.(15), together with Theorem 5, alternatively suggests that we should look at the relationship

$$T = \frac{4\pi^2}{h \sqrt{\frac{r}{r_0}}} \sqrt{gM_0 m_e} r^2 = \frac{4\pi^2}{h} \sqrt{gM_0 r_0 m_e} r^{3/2} , \quad (19)$$

*(relationship written for the largest vibrational period
of excited electronic states of a given molecule)*

where r_0 is the *internuclear distance* at the *very ground state*, as usual.

r/r_0 taking place in the above relationship, following Theorem 5, is just the *composite quantum number* to be associated with the electronic state taken in consideration.

Eq.(19) makes that based on any molecule, regarding the *electronic states bearing similar configurations*, for which g , the *bond looseness factor*, remains about the same, T^2 versus r^3 should display a *straight line*.

The *approximate empirical constant* of Eq.(18), can now be evaluated from Eq.(19), as

$$\text{Empirical Constant} = \frac{\sqrt{\mathcal{N}h}}{4\pi^2 \sqrt{gM_0 m_e}} ; \quad (20)$$

recall that \mathcal{N} is the *composite quantum number*, i.e. r/r_0 (staying indeed roughly the same, were r is not far from r_0), making up that the “*constant*” is question is indeed only *approximately*, a constant, supposing anyway that the electronic states in question, are configured similarly, so that g stays practically constant, throughout.

This entirely discloses the mechanism behind the *approximate empirical relationship* [Eq.(20)], established back in 1925.

Thus, Eq.(20) makes that, it is not *really* the quantity ωr^2 which is a *constant* for electronic states of a given molecule, configured similarly, but based on Eq.(19), *more likely* it is the quantity

$$\text{Constant} = \omega r^{3/2} . \quad (21)$$

(written by the author, for similar electronic states of a given molecule)

This *new constant* then is

$$\text{Constant} = \frac{h}{4\pi^2 \sqrt{gM_0 m_e r_0}} ; \quad (22)$$

(written by the author for similar electronic states of a given molecule)

recall that r_0 dominates the *internuclear distance, at the ground state*.

As an example, T^2 versus r^3 for H_2 molecule, is sketched in Figure 8. Thus some 23 states out of 29, for which data is available, are neatly aligned. Herein, we included H_2^+ , which too seems to display the same g as that of H_2 ground state; we find $g \approx 0.8$. The remaining 6 electronic excited states of H_2 seem to be configured *differently*. We call these “*ambiguous states*” (the previous 23, being seemingly all configured approximately like the molecule’s ground state).

The study of the electronic vibrational data of H₂ molecule is undertaken elsewhere.⁸

To analyze the remaining 6 data (out of 29), we note, out of Eq.(15) that, switching *the nuclei reduced mass M₀ of alkali molecules or alkali hydrides into that of the hydrogen molecule*, should virtually transpose the *corresponding vibrational period*, into the *vibrational period of H₂ electronic state of of the same electronic character*; recall that switching the *nuclei mass* does not practically affect the *electronic structure* of the molecule, and accordingly we should expect that, *amongst H₂ electronic states there are states, configured like the ground electronic states of alkali molecules and alkali hydrides*.

Therefore we anticipate that the *6 ambiguous electronic states* of H₂ should be configured just like the respective *ground electronic states of alkali molecules and alkali hydrides*, and vice versa.

6. SYSTEMATIZATION OF GROUND STATES OF ALL DIATOMIC MOLECULES

Our approach makes that we can visualize Eq.(19) not only regarding the *electronic states of a given molecule*, but also regarding the *ground states of molecules belonging to a given chemical family*, thus exhibiting *similar electronic configurations*, with virtually the same *g*.

Let us elaborate on this a little.

Above we have rigorously proven that Eq.(15) holds for any diatomic molecule, i.e.

$$T_0 = \frac{4\pi^2}{h\sqrt{n_1 n_2}} \sqrt{g M_0 m_e r_0^2}, \quad (15) \text{ (rewritten)}$$

$n_1 n_2$ being quantum numbers induced by the Planck Constant [cf. Eq.(9)(rewritten)].

Within the frames of Theorems 4 and 5, regarding the electronic states of a given molecule, we have established that $n_1 n_2$ turns out to be the ratio of the internuclear distance of the molecule at the given excited state, to the internuclear distance of the molecule at the ground state, provided that these states are configured alike.

We have further demonstrated that already the cast $T_0 \sim \sqrt{M_0} r^2$ holds fairly well regarding diatomic molecules belonging to a given chemical family, thus being configured similarly, so that *g* stays virtually the same, throughout each one of the Figures 1-7.

Further straightening up of these curves, requires to specify $n_1 n_2$.

At this stage consider Figure 8, where we analyzed H_2 spectroscopic data, and found out that the *ambiguous states* are configured like *alkali hydrides*, and Li_2 .

This suggests that, *quantum mechanically* we can well describe, say the ground state of Li_2 , on the basis of an *equivalent* H_2 excited state.

Therefore the corresponding quantum numbers $n_1 n_2$, we propose to associate with Li_2 ground state, in comparison with the H_2 ground state, following Eq.(17) and Theorem 5, becomes the mere ratio of the internuclear distance of Li_2 at its ground state, to the internuclear distance of H_2 at its ground state, given that the H_2 and Li_2 bonds, are configured similarly.

Hence, we rewrite Eq.(19) (*not for the excited levels of a given molecule*), but for the *ground states of molecules* belonging to a given chemical family, and accordingly being configured alike:

$$T_{0i} = \frac{4\pi^2}{h \sqrt{\frac{r_{0i}}{r_{00}}}} \sqrt{g M_{0i} r_{0i}^2} = \frac{4\pi^2}{h} \sqrt{g M_{0i} r_{00} r_{0i}^{3/2}} ; \quad (23)$$

(written by the author for the ground vibrational period of molecules belonging to a given chemical family)

here T_{0i} is the *ground state largest vibrational period* of the i th member of the chemical family in consideration; M_{0i} is the reduced mass and; r_{0i} is the ground state internuclear distance of this member; r_{00} is *the internuclear distance of the ground state of the family's member*, chosen as the *reference molecule*; more precisely we pick up as the member bearing the lowest vibrational period.

Therefore T_{0i}^2 versus $M_{0i} r_{0i}^3$ for *chemically alike molecules*, should display a *linear behavior*, the slope of which shall furnish g , to be associated with the chemical family in consideration.

Thus we can now write an equation similar to Eq.(21), in regards to the ground states of molecules belonging to a given chemical family:

$$\text{Constant} = \frac{\omega_{0i} M_{0i} r_{0i}^2}{\sqrt{n_1 n_2}} = \omega_{0i} M_{0i} r_{00} r_{0i}^{3/2} , \quad (24)$$

(written by the author, for the ground states of chemically alike molecules)

where ω_{0i} is the inverse of the ground state *vibrational period* of the molecule of concern.

The *constant* in question shall be expressed as

$$\text{Constant} = \frac{h}{4\pi^2 \sqrt{gm_e}} . \quad (25)$$

Although r_{00} is a constant within a given chemical family, we still included it, in the RHS of Eq.(24), to define our constant to be the same for all chemical families, if g remained the same, thus as suggested by the RHS of Eq.(25).

In Figures 9-15, based on experimental data,^{13, 14, 15} we present T_{0i} versus $\sqrt{M_{0i}r_{0i}^3}$, for *seven chemical families*, for which the coefficient g , stays indeed neatly constant. The constancy of $\omega_{0i}M_{0i}r_{0i}^{3/2}$ in harmony with Eqs.(24) and (25), is *quantitatively* demonstrated, in (*the fifth column of*) Tables 1-7.

g 's are calculated from Eq.(25) for different chemical families, and are presented in Table 8. Note that g 's vary between 0.79 and 0.01.

Note that following Eqs. (24) and (25), the *value of constancy* of $\omega_{0i}M_{0i}r_{0i}^{3/2}$ depends, both on g and r_{00} (*the reference internuclear distance of the family of concern*), which makes that the "*constants*" calculated in (*the fifth columns of*) Tables 1-7, differ.

Note further that, the *standart deviation* on the constants in question, is roughly *ten percent*. There seems to be *two reasons* for this. The *first one* is that chemically alike molecules, on the contrary to our assumption, are not exactly configured similarly, which may make that g is not a constant throughout. The *second one* is that our supposition that the RHS Eq.(17), can be used to replace the the *composite quantum number* n_1n_2 in Eq.(15), even for chemically alike molecules (*where we choose the molecule with the lowest vibrational period, as the reference molecule*), may not be rigorous. Along this line it seems interesting to recall that, when we use the *principal quantum numbers associated with the bond electrons, straight*, to compose n_1n_2 , instead of using Eq.(17), we come out with the *constancy* of $\omega_{0i}M_{0i}r_{0i}^2 / \sqrt{n_1n_2}$, not any worse than that of $\omega_{0i}M_{0i}r_{0i}^{3/2}$ [cf. Eq.(24)].^{7,8}

Since g happens to be roughly, *inversely proportional to the dissociation energy of the molecule*, as one can observe from Table 1, it indeed decreases as the bond becomes stronger. Thus, the smaller g is, the higher is the number of the covalent bonds, making the overall bond of the diatomic molecule, or the higher is the number of free electrons an atom possesses, the looser will be the bond it will make with, say, an halogen, thus the higher will g be, etc.¹⁶

Table 1 Checking the Validity of Eq.(23), for Alkali Molecules

Molecules	M_0 (amu)	T_0 (cm ⁻¹) $\times 10^3$ c)	r_0 (Å)	$\frac{T_0}{\sqrt{M_0} r_0^{3/2}}$	Relative Error as Referred to the Average
H ₂	0,50	0,24	0,74	0,53	0,52
Li ₂	3,50	2,89	2,67	0,35	0,01
LiNa	5,33	3,89	2,90	0,34	0,03
Na ₂	11,50	6,34	3,08	0,35	0,01
NaK	14,48	8,06	3,50	0,32	0,08
K ₂	9,49	10,80	3,92	0,45	0,29
KRb	26,83	13,2	4,07	0,31	0,11
Rb ₂	42,47	17,3	4,21	0,31	0,12
RbCs	52,04	20	4,42	0,30	0,15
Cs ₂	66,47	23,8	4,64	0,29	0,17
Average				0,36	0,15

Table 2 Checking the Validity of Eq.(23), for O₂ - like Molecules

Molecules	M_0 (amu)	T_0 (cm ⁻¹) $\times 10^3$ c)	r_0 (Å)	$\frac{T_0}{\sqrt{M_0} r_0^{3/2}}$	RelativeError as Referred to the Average
O ₂	8,00	0,64	1,21	0,17	0,21
S ₂	15,99	1,39	1,89	0,13	0,07
Se ₂	39,97	2,56	2,16	0,13	0,07
Te ₂	63,82	4,00	2,59	0,12	0,14
SO	10,67	0,90	1,49	0,15	0,07
Average				0,14	0,11

Table 3 Checking the Validity of Eq.(23), for N₂ - like Molecules

Molecules	M ₀ (amu)	T ₀ (cm ⁻¹ x10 ³ c)	r ₀ (Å)	$\frac{T_0}{\sqrt{M_0 r_0^{3/2}}}$	RelativeError as Referred to the Average
N ₂	7,00	0,43	1,09	0,14	0,06
P ₂	15,49	1,29	1,89	0,12	0,06
PN	9,65	0,76	1,49	0,13	0,00
Average				0,13	0,04

Table 4 Checking the Validity of Eq.(23), for Halogens

Molecules	M ₀ (amu)	T ₀ (cm ⁻¹ x10 ⁴ c)	r ₀ (Å)	$\frac{T_0}{\sqrt{M_0 r_0^{3/2}}}$	RelativeError as Referred to the Average
F ₂	11,21	9,50	1,44	1,64	0,06
Cl ₂	17,96	17,49	1,99	1,47	0,15
Br ₂	31,15	39,96	2,28	2,08	0,19
I ₂	46,87	63,47	2,67	2,13	0,22
BrF	15,04	15,35	1,76	1,69	0,02
ClF	12,93	12,31	1,63	1,64	0,05
ICl	26,23	27,42	2,32	1,51	0,13
Average				1,74	0,12

Table 5 Checking the Validity of Eq.(23), for CsBr - like Molecules

Molecules	M_0 (amu)	$T_0(\text{cm}^{-1})$ $\times 10^4 \text{c}$	r_0 (Å)	$\frac{T_0}{\sqrt{M_0} r_0^{3/2}}$	RelativeError as Referred to the Average
CsBr	52,63	49,92	3,14	1,24	0,51
CsI	71,63	64,94	3,41	1,22	0,49
NaCl	26,46	13,95	2,51	0,68	0,17
NaBr	31,98	17,86	2,64	0,74	0,09
NaI	35,15	19,45	2,90	0,66	0,19
KF	25,64	12,78	2,55	0,62	0,24
KCl	35,95	18,59	2,79	0,67	0,19
KBr	43,55	26,26	2,94	0,79	0,03
KI	47,48	29,89	3,23	0,75	0,08
RbCl	39,53	25,07	2,89	0,81	0,01
Average				0,82	0,20

Table 6 Checking the Validity of Eq.(23), for BF - like Molecules

Molecules	M_0 (amu)	$T_0(\text{cm}^{-1})$ $\times 10^4 \text{c}$	r_0 (Å)	$\frac{T_0}{\sqrt{M_0} r_0^{3/2}}$	RelativeError as Referred to the Average
BF	7,26	6,72	1,26	1,76	0,26
BCl	12,06	8,38	1,72	1,07	0,24
BBr	14,77	9,66	1,88	0,98	0,31
AlCl	20,95	15,24	2,13	1,071	0,24
AlBr	26,64	20,11	2,29	1,12	0,20
InCl	31,71	26,82	2,31	1,36	0,03
InI	56,72	60,32	2,86	1,66	0,18
TlCl	35,09	29,87	2,55	1,24	0,12
TlBr	52,27	57,98	2,68	1,83	0,30
TlI	66,67	78,31	2,87	1,97	0,40
Average				1,41	0,23

Table 7 Checking the Validity of Eq.(23), for CO - like Molecules

Molecules	M_0 (amu)	T_0 (cm^{-1} $\times 10^4 \text{c}$)	r_0 (\AA)	$\frac{T_0}{\sqrt{M_0} r_0^{3/2}}$	RelativeError as Referred to the Average
CO	4,67	6,86	1,13	2,64	0,47
CS	7,86	8,73	1,53	1,65	0,09
SiO	8,13	10,18	1,51	1,92	0,07
SiS	13,43	14,93	1,93	1,52	0,16
GeO	10,23	13,15	1,65	1,94	0,08
SnO	12,27	14,09	1,84	1,61	0,10
SnS	20,62	25,25	2,06	1,88	0,04
PbO	14,00	14,85	1,92	1,49	0,17
PbS	23,49	27,72	2,39	1,55	0,14
Average				1,80	0,15

**Table 8 Bond Looseness Factors of the Chemically Alike
Diatomic Molecules**

Chemical Family	Bond Looseness Factor (g)
$\text{H}_2, \text{Li}_2, \text{Na}_2, \text{K}_2$	0.79
$\text{O}_2, \text{S}_2, \text{Se}_2, \text{Te}_2, \text{OS}$	0.05
$\text{N}_2, \text{P}_2, \text{PN}$	0.04
$\text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{BrF}, \text{ClF}, \text{ICl}$	0.04
$\text{CsF}, \text{CsBr}, \text{CsI}, \text{NaCl}, \text{NaBr}, \text{NaI},$ $\text{KF}, \text{KCl}, \text{KBr}, \text{KI}, \text{RbCl}$	0.01
$\text{BF}, \text{BCl}, \text{BBr}, \text{AlCl}, \text{AlBr}, \text{InCl},$ $\text{NBr}, \text{InI}, \text{TlCl}, \text{TlBr}, \text{TlI}$	0.05
$\text{CO}, \text{CS}, \text{SiO}, \text{SiS}, \text{GeO}, \text{SnO}, \text{SnS},$ PbO, PbS	0.13

7. CONCLUSION

It is interesting to note that Eq.(19) frames the force constant k of the molecule at the excited state of concern, as

$$k = \frac{fe^2}{r^3} , \quad (26)$$

along

$$fe^2 = \frac{h^2}{4\pi^2 r g_{IN} m_e} ; \quad (27)$$

here, e is the electron charge, and f is a dimensionless constant.

Eq.(26) dimension-wise, is somewhat obvious, if one proposes to relate the force constant to the internuclear distance. This correlation was in effect proposed sometime ago, by Bratoz et al., for alkali hydrides,^{17,18} for which f is reported to be 2. Our estimation, based on the data¹² is, on the average, 2.6.

f was subsequently obtained by Salem and Ohwada^{19,20} which then, based on *empirical presumptions*, chiefly for molecules containing alkali atoms, leads to

$$f = \frac{1}{2} (N_i + 1)(N_j + 1) , \quad (28)$$

where N_i and N_j , are the respective number of electrons residing outside of the complete shells of the atoms making up the diatomic molecule.

Note thence that, under this form f , thus g , indeed stay constant, just the way we had originally conjectured.

Eq.(26) yields 8 for alkali halides, whereas based on the data, and on the average, we come out with 11.1.

Recall nonetheless that in order to obtain our results, we followed a totally different path, than that induced by Eq.(26). Moreover we arrived at our result, primarily regarding the *electronic states of a given molecule*. The literature we reviewed does not coop at all with such an aspect.

Note further that recent trials, on the “*problem of transferable spectroscopic constants*”, despite satisfactory results they may furnish, are far from displaying how the *fundamental quantities of mass, space and time (i.e. clock mass, clock size and period of time of the clock motion)*, are structured in interrelation with each other, in the architecture of molecules,²¹ in fact just the way Eq.(19) reveals.

ACKNOWLEDGEMENT

The author would like extend his profound gratitude to Professor V. Rozanov. He would like to further thank to Drs. N. Vezirođlu, O. Sinanođlu, E. Hasanov, C. Marchal, Ő. Koçak, for very many hours of discussions, which helped a lot to improve the work presented herein.

The author would further like to thank to Dear Research Asistant Fatih Özaydın, who has kindly helped the typing of the manuscript and drawn the figures.

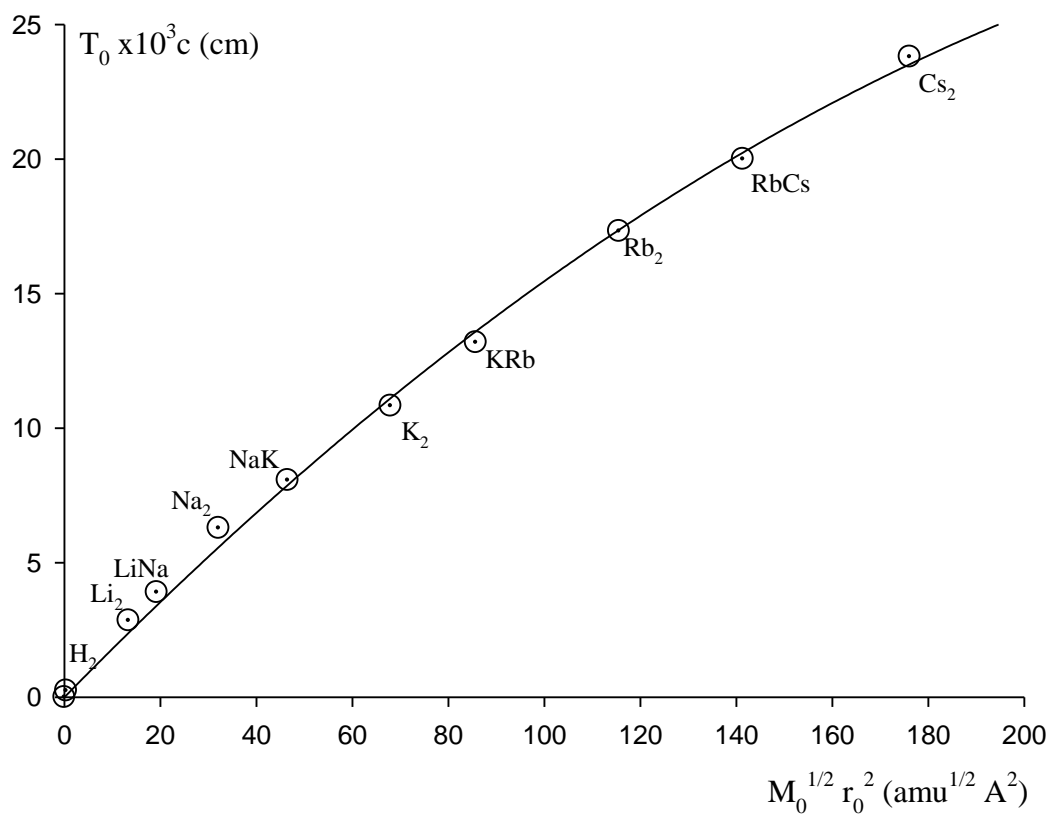


Figure 1 Period of alkali molecules versus $M_0^{1/2} r_0^2$

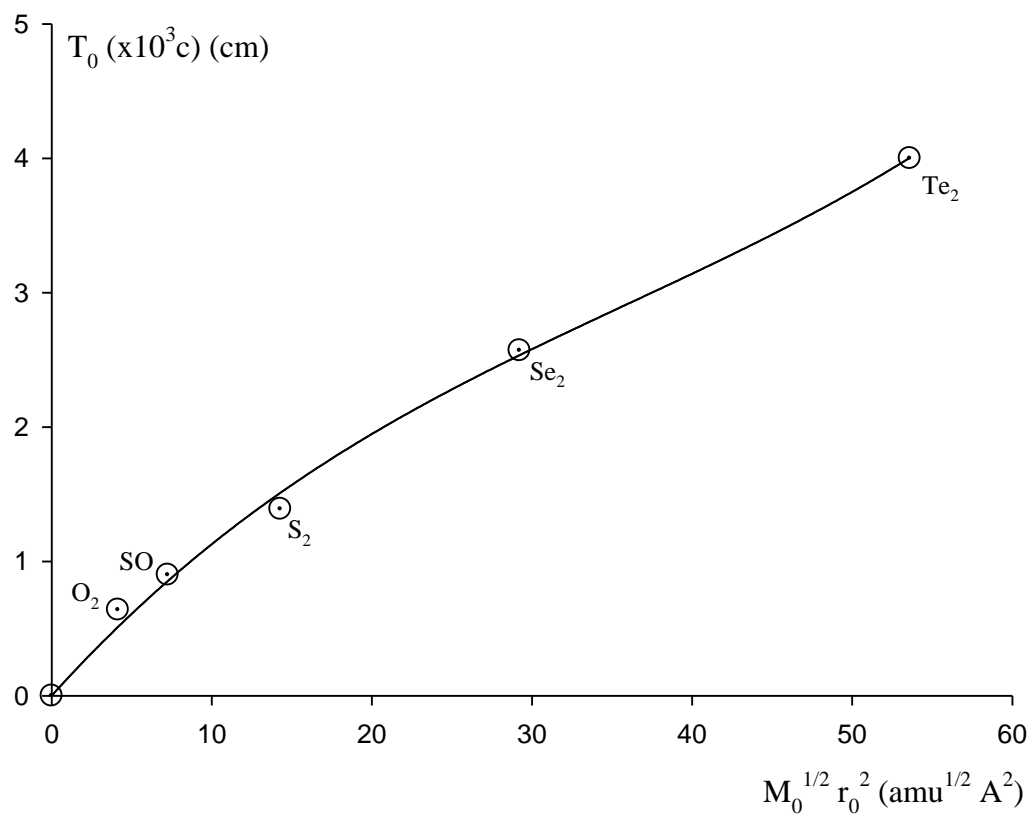


Figure 2 Period of (O₂, S₂, Se₂, Te₂) versus $M_0^{1/2} r_0^2$

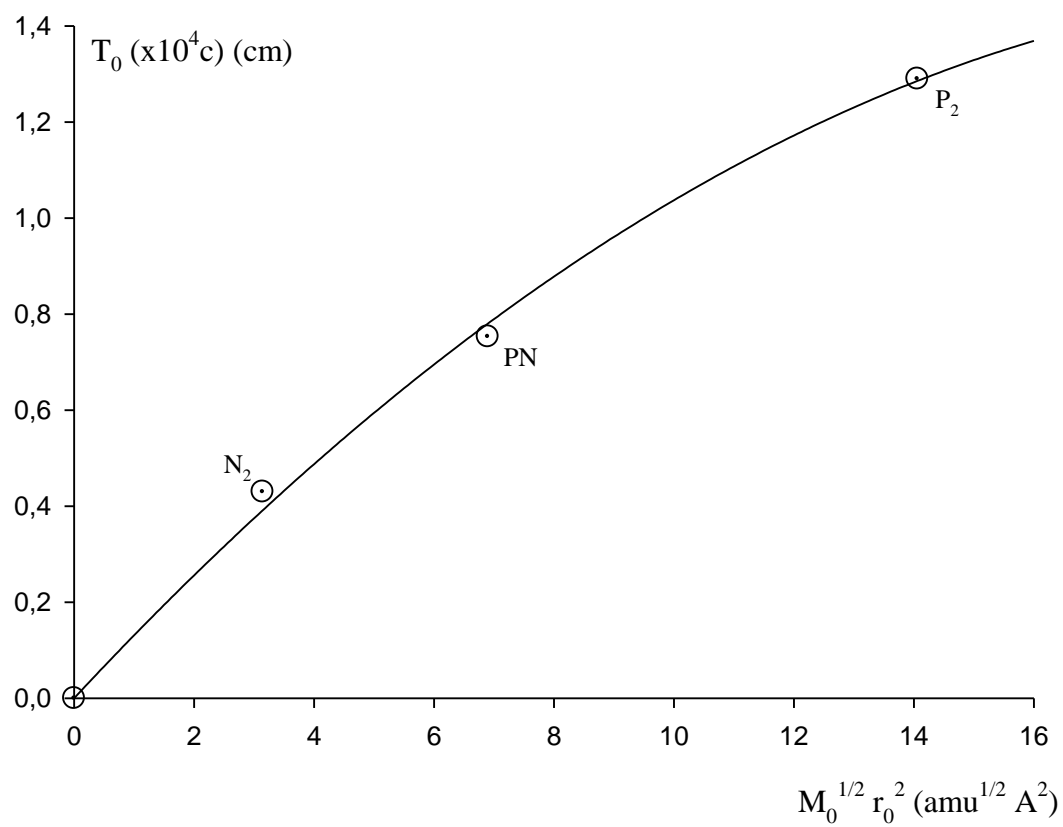


Figure 3 Period of (N₂, PN, P₂) versus $M_0^{1/2} r_0^2$

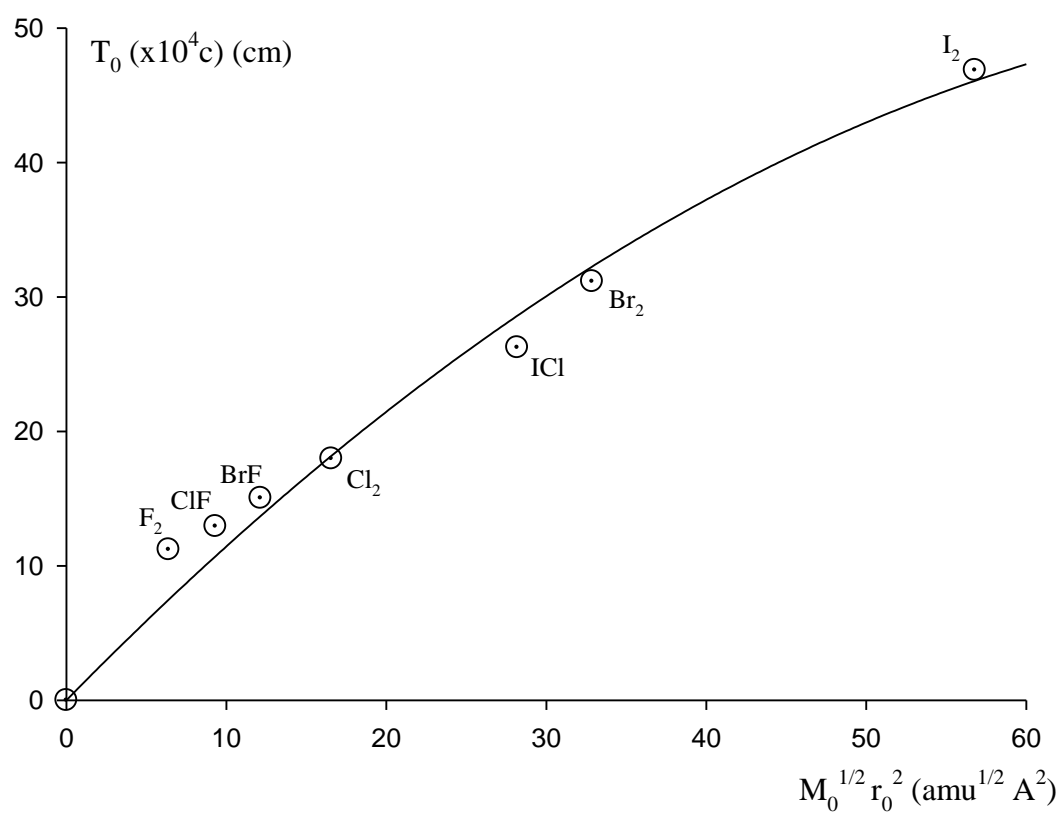


Figure 4 Period of diatomic molecules, made of combinations of halogen atoms, versus $M_0^{1/2} r_0^2$

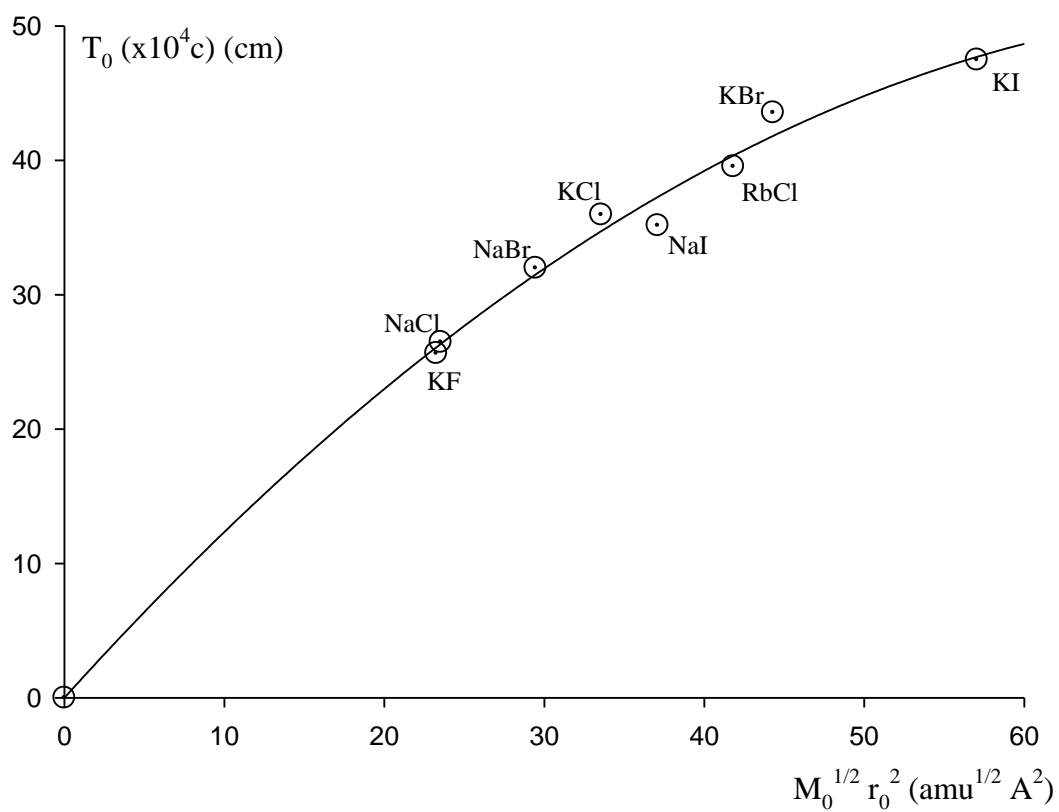


Figure 5 Period of different alkali-halogen molecules versus $M_0^{1/2} r_0^2$

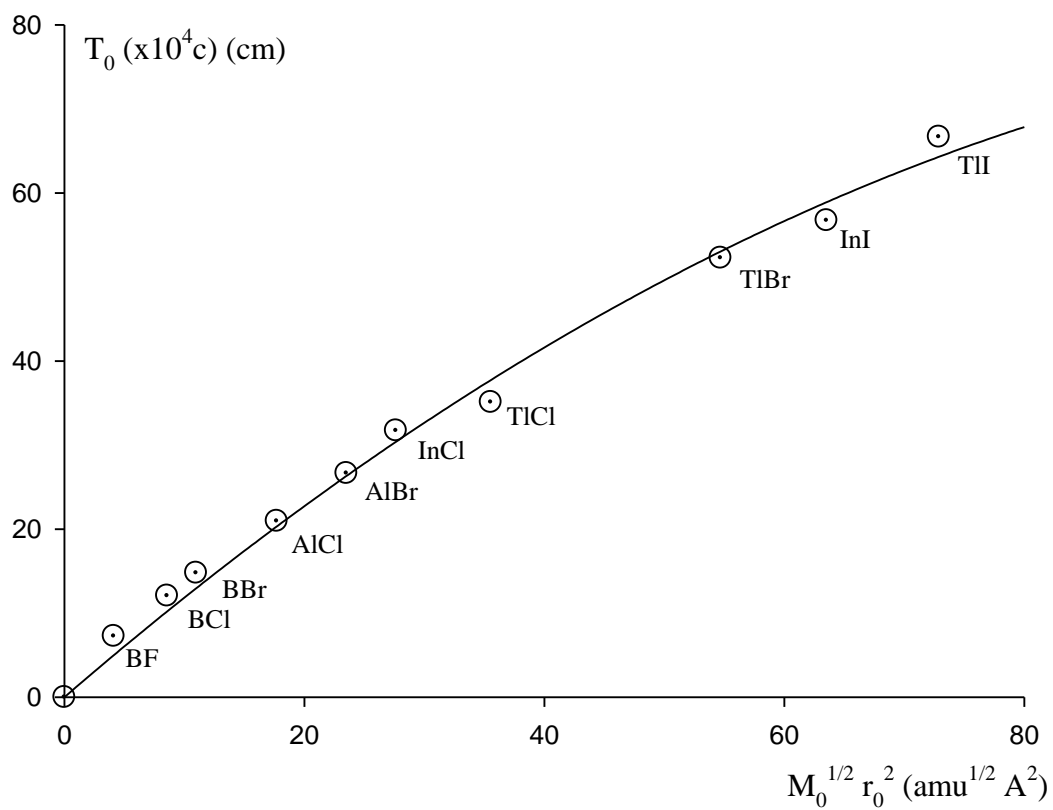


Figure 6 Period of diatomic molecules, made of atoms belonging to respectively the 3th and 7th columns of the periodic table, versus $M_0^{1/2} r_0^2$

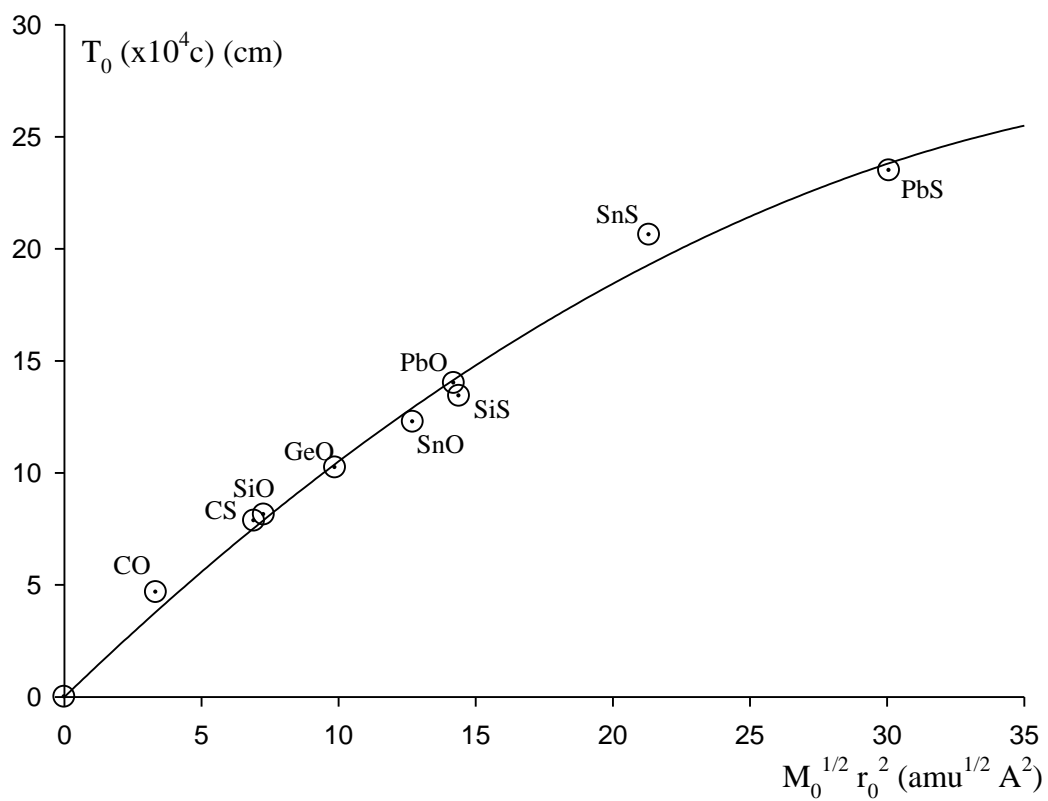


Figure 7 Period of diatomic molecules, made of atoms belonging to respectively the 4th and 6th columns of the periodic table, versus $M_0^{1/2} r_0^2$

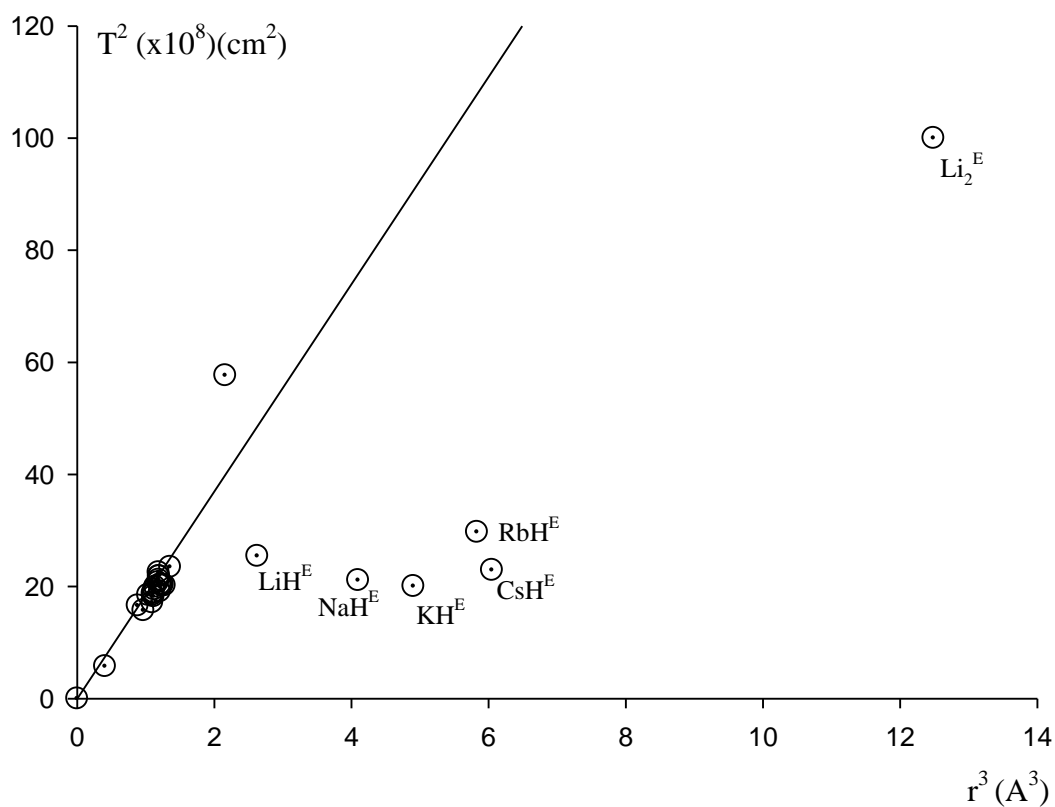


Figure 8 T^2 versus r^3 for different electronic states of H_2
 (The states corresponding to data *off the straight line*
 and denominated by the superscript "E" have been
 identified to be configured, as indicated, like the
 ground states of respectively, *alkali hydrides* and Li_2 .)

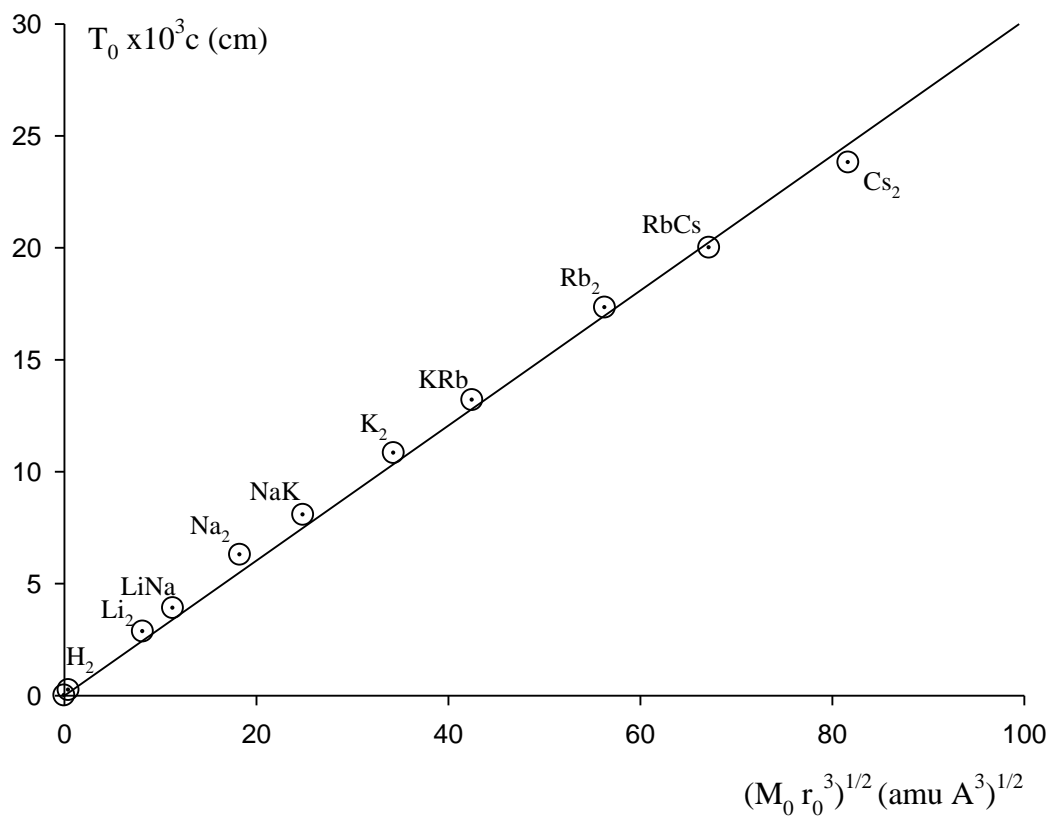


Figure 9 Period of alkali molecules versus $(M_0 r_0^3)^{1/2}$

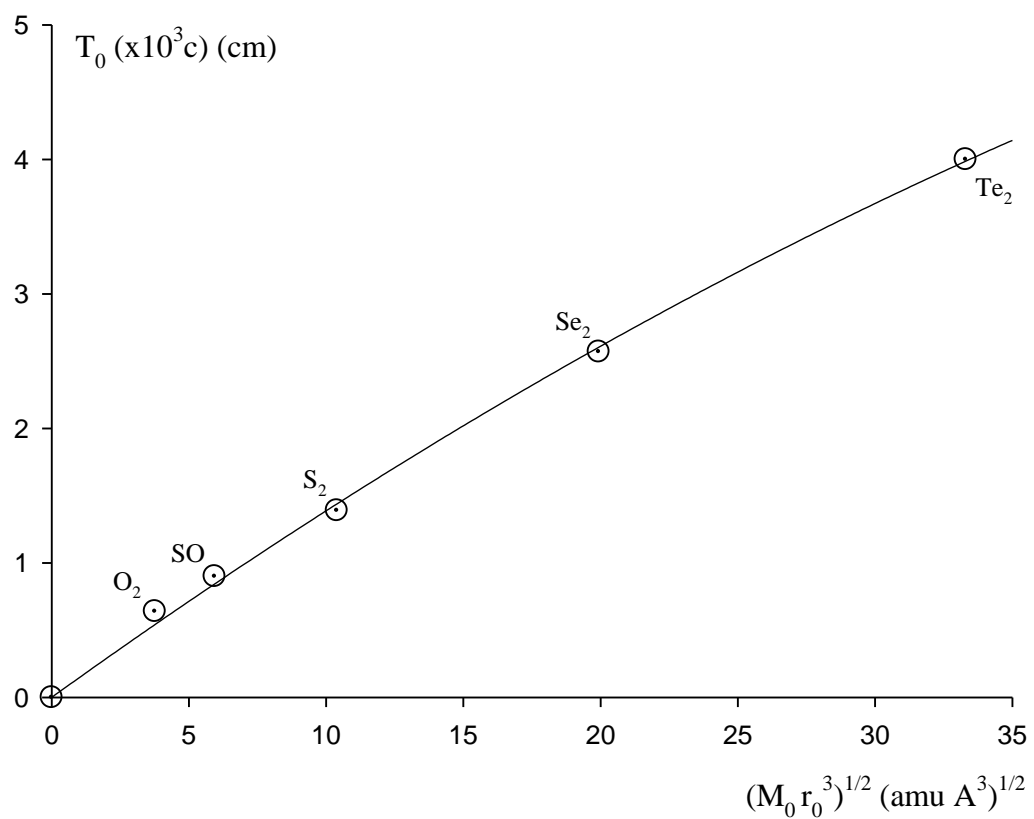


Figure 10 Period of (O_2 , S_2 , Se_2 , Te_2) versus $(M_0 r_0^3)^{1/2}$

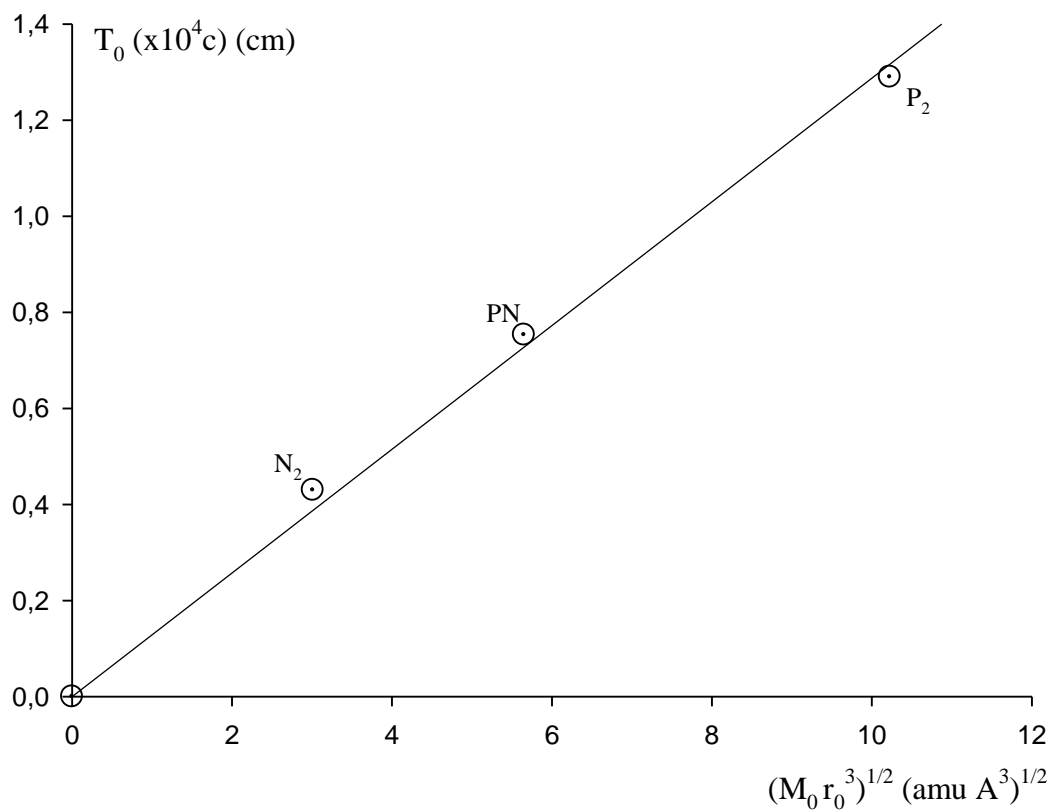


Figure 11 Period of (N_2 , PN , P_2) versus $(M_0 r_0^3)^{1/2}$

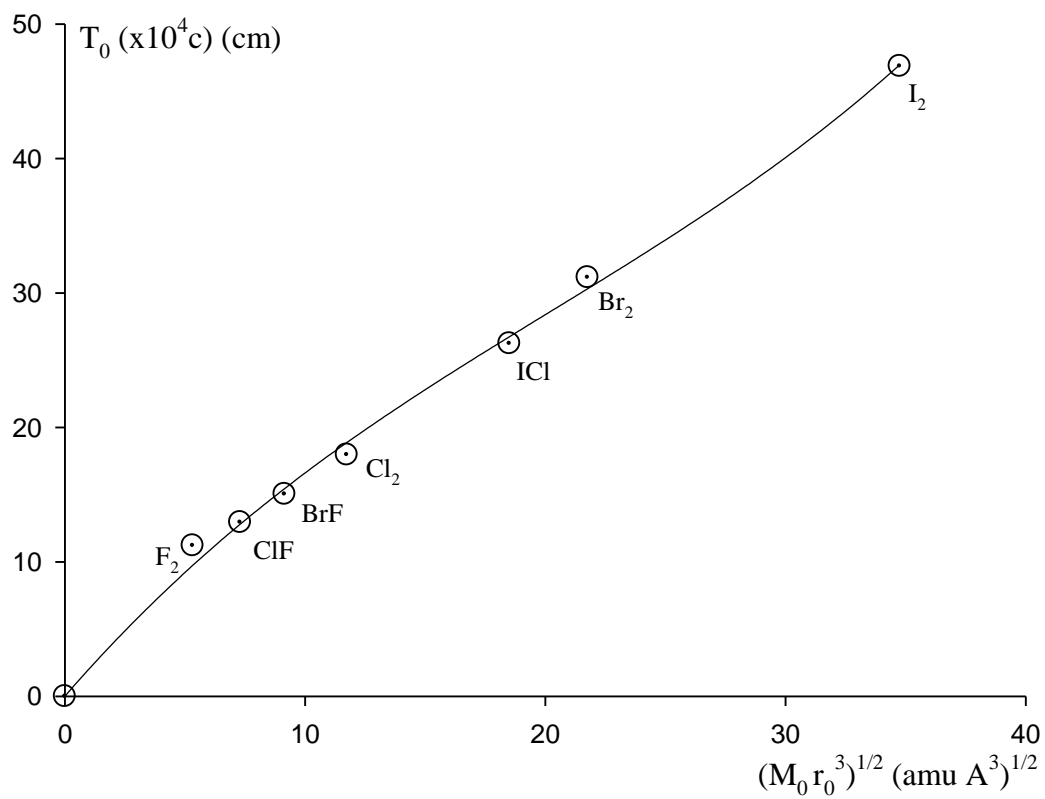


Figure 12 Period of diatomic molecules, made of combinations of halogen atoms, versus $(M_0 r_0^3)^{1/2}$

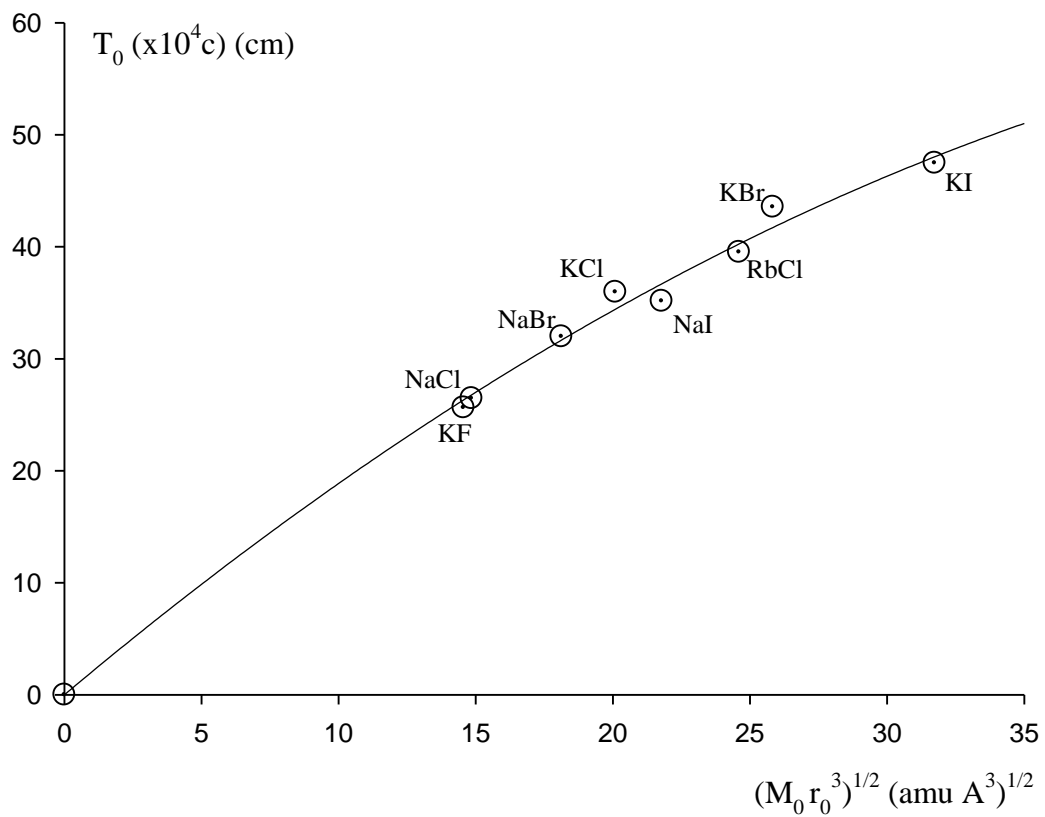


Figure 13 Period of different alkali-halogen molecules versus $(M_0 r_0^3)^{1/2}$

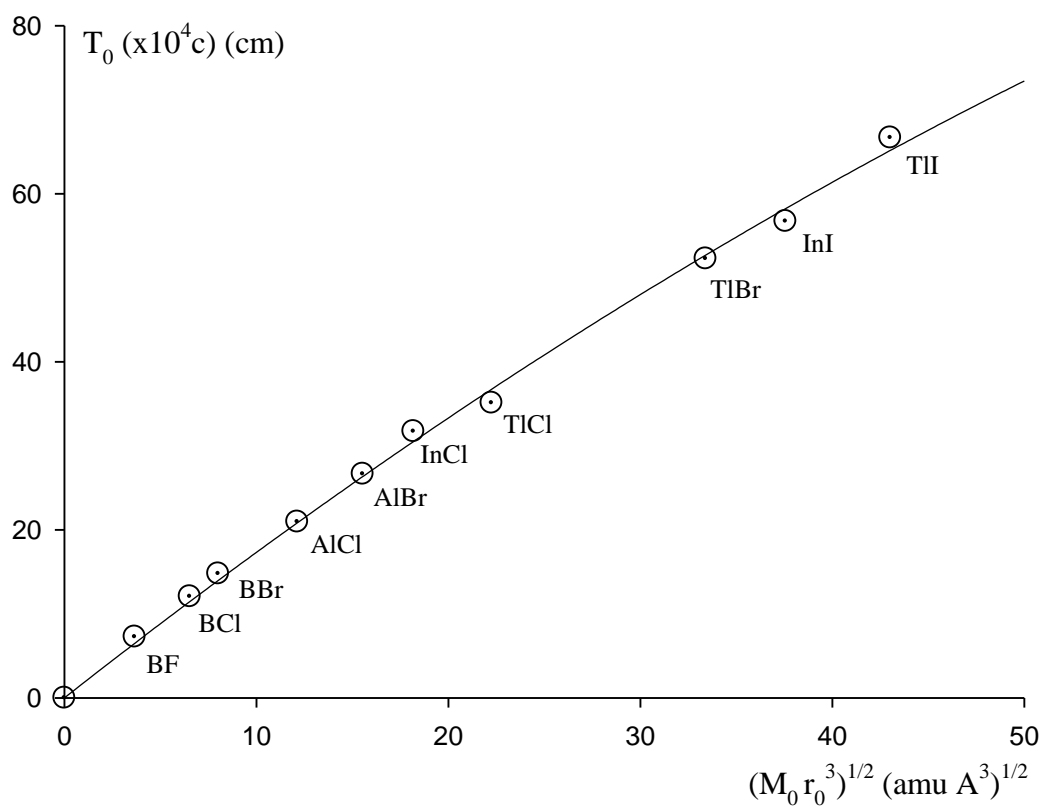


Figure 14 Period of diatomic molecules, made of atoms belonging to respectively the 3th and 7th columns of the periodic table, versus $(M_0 r_0^3)^{1/2}$

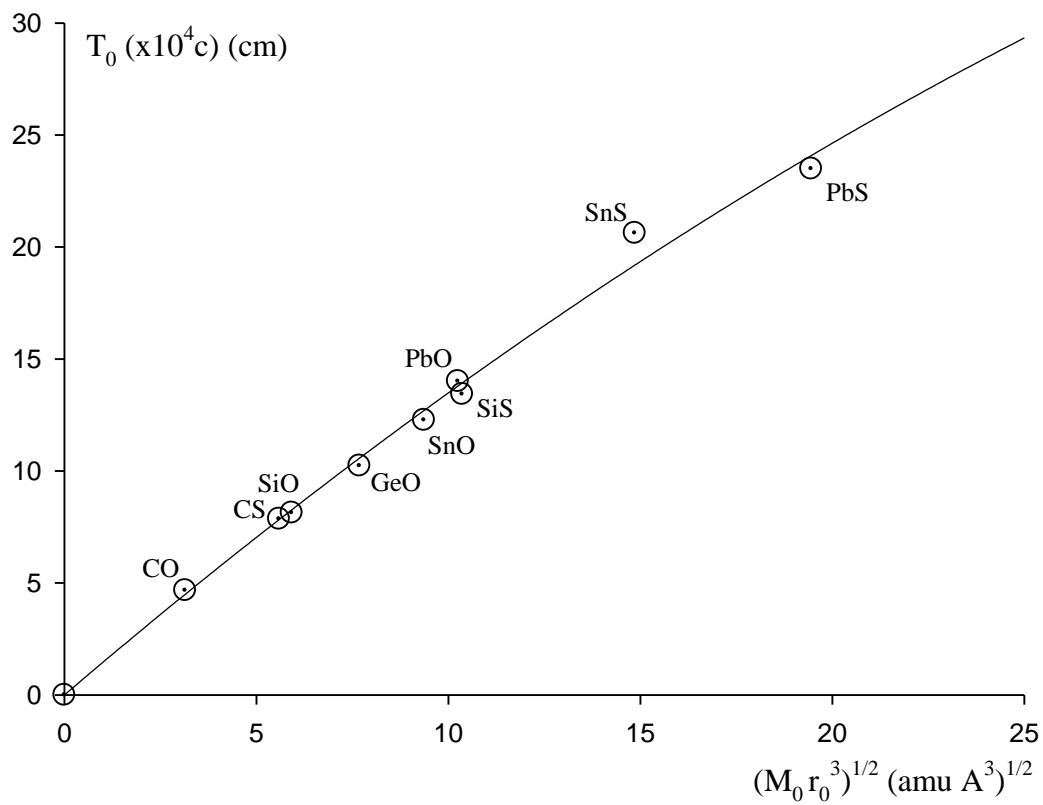


Figure 15 Period of diatomic molecules, made of atoms belonging to respectively the 4th and 6th columns of the periodic table, versus $(M_0 r_0^3)^{1/2}$

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Keywords: systematic diatomic molecules, quantum numbers of diatomic molecules

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