

## Vibrational and rotational analysis of diatomic molecules : an alternative approach

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**Abstract** : A diatomic molecule within the framework of Born-Oppenheimer approximation is a two body problem just like hydrogen atom, and may be treated on similar basis by assuming a suitable form of central potential

In spite of difficulties associated with determining accurate inter-atomic potential, a simple potential expressed as power series of  $1/r$  reproduce energy levels and dissociation constants with a reasonable accuracy. The new equation of energy is consistent with isotopic shift and may be expressed in conventional form for low vibrational and rotational levels. The vibrational and rotational constants originate from a single formula, and are therefore, related to each other.

**Keywords** : Vibrational-rotational analysis, diatomic molecules, calculation method.

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### 1. Introduction

It has become an established convention in molecular spectroscopy to consider the vibration and rotation of a diatomic molecule as two independent modes. The classical frequency of vibration also does not have any correlation with that of the rotational motion, and vibrational and rotational constants of a diatomic molecule are therefore, independent of each other.

In the conventional method, the interatomic potential is expanded in terms of displacement from the equilibrium inter-atomic position. The expansion brings about drastic changes in anharmonic oscillator and a non-rigid rotator irrespective of the original form of the interatomic potential. The vibrational and rotational wave functions are decoupled except for minor perturbation of one by the other.

Though, different forms of the molecular potential have been suggested by a number of investigators, all of them are confined to the conventional picture of diatomic molecules [1–6]. The methods for constructing experimental potential curve from vibrational and rotational levels of a diatomic molecule are also based upon such convention [7–10].

However, the vibrational and rotational motions of a diatomic molecule are closely linked with each other and may be considered as manifestation of a complex motion of constituent atoms about the centre of mass.

Within the framework of Born-Oppenheimer approximation however, a diatomic molecule is a two-body problem just like hydrogen atom. As such, it may be treated on similar basis without expressing the motion in terms of vibration and rotation. The wave functions and energy levels would be different for each diatomic molecule depending upon the nature of the interatomic potential, and we expect a better understanding of the system.

Unfortunately, the interatomic potential is not known *a priori*. It is expected to be very complicated even in the case of simple molecules. From general consideration, it is understood that the potential is electromagnetic in nature and tends monotonously to zero as  $r$  tends to infinity and tends to large values as  $r$  equals zero. Therefore, we suggest a tentative potential for a diatomic molecule as,

$$V(r) = a/r + b/r^2 + c/r^3 + d/r^4 + \dots \quad (1)$$

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The following discussion should be considered tentative due to the arbitrary nature of eq. (1). Besides, the Schrodinger equation does not have the exact solution, and one has to use perturbation technique to determine the contribution of last two terms in the potential. In spite of such limitations, the energy equation is consistent with the requirement of isotopic shift, and can be expressed in conventional form of vibrational and rotational energy levels. Vibrational and rotational constants originate from the same equation, and are therefore related to each other. A number of such relations have been derived.

## 2. Calculations

### (i) Wave equation :

The potential of a diatomic molecule does not contain any angular term, and therefore, angular part of the wave function is given by spherical harmonics. The radial component of wave function for a diatomic molecule with a central potential eq. (1) will be

$$(1/\rho^2) d/d\rho(\rho^2 dR/d\rho) + [\lambda/\rho - 1/4 - l^*(l^* + 1)/\rho^2] R = 0, \quad (2)$$

where  $\rho = \alpha r$ , is a dimensionless variable,

$$\lambda = 2a\mu/\hbar^2\alpha,$$

$$l^*(l^* + 1) = l(l+1) + 2\mu b/\hbar^2.$$

$2\mu|E|/\alpha^2\hbar^2 = 1/4$  (since  $E < 0$  for bound states, we have  $E = -|E|$ ), and  $\mu$  is the reduced mass of the molecule. We have assumed that the terms  $c/r^3$  and  $d/r^4$ ... are small and may be treated as perturbation. Eq. (2) can be referred as unperturbed Schrodinger equation and thus has an exact solution. The solution is hydrogenic in nature with effective atomic number  $z = a/e^2$  and effective angular momentum  $l^*$ . Solution of (2) may be put as

$$R(\rho) = F(\rho)e^{-\rho/2}, \quad (3)$$

$$\text{where } F(\rho) = \sum_{m=0}^{\infty} C_m \rho^{m+l^*}$$

and the recursion relation is

$$C_{m+1} = \frac{(l+m+1-\lambda) C_m}{(m+1)(2l^*+m+2)}, \quad (4)$$

$$|E| = \frac{\mu a^4}{2\hbar^2 \lambda^2}, \quad (5)$$

where  $(l^* + m + 1) = \lambda$ .

As the series breaks off after finite number of terms (let  $\rho^m = \rho^n$ ), we have after replacing  $m$  by  $n'$  and  $\lambda$  by  $n$ ,

$$E_n = -|E_n| \cdot \frac{1}{2\hbar^2 n^2}, \quad (6)$$

where  $n = (n' + l^* + 1)$  is a positive integer and may be termed as total quantum number.

Using perturbation method [11], the first order corrected energy level takes the final form.

$$E = \frac{B}{(n'+l^*+1)^2} + \frac{B}{(n'+l^*+1)^3} + \frac{B}{(n'+l^*+1)^4} \quad (7)$$

Here  $A, B, C, \dots$ , are functions of  $a, b, c, \dots$ . While deriving eq. (7), we have considered  $l^*$  partly as a constant term. The eq. (7) may be expressed in power series of  $(n' + 1/2)$  and  $l(l+1)$ ;  $n'$  and  $l$  may be renamed as vibrational and rotational quantum number respectively. If the vibrational and rotational quantum numbers are small, only a few terms of the expansion will be sufficient for reasonable accuracy. On the other hand for higher vibrational and rotational levels, it will be advisable to use eq. (7) in its original forms.

The term  $2\mu b/\hbar$  is quite large even for light molecules, of the order of 346991.14 for  $N_2$  in the ground state ( $X^1\Sigma_g^+$ ) and therefore  $l^*$  changes slowly with  $l$ , generating closely packed energy levels. The energy levels are arranged as (1s, 2p, 3d, 4f,.....), (2s, 3p, 4d, 5f,.....), (3s, 4p, 5d,.....). Levels within a bracket are closely related to each other generating closely packed rotation energy levels and each bracketed set of levels is separated from that of the other bracketed set like vibrational levels in the conventional sense of speaking.

The conventional picture of diatomic molecules is quite parametric, and the energy of vibration tends to  $(-)$  or  $(+)$  infinite values as vibration quantum number is increased. For example, the vibrational levels of nitrogen molecule in the ground state ( $X^1\Sigma_g^+$ ) are given by the equation :

$$G(\text{cm}^{-1}) = 2358.027(n+1/2) - 14.1351(n+1/2)^2 - 0.01751(n+1/2)^3 + 0.0001144(n+1/2)^4. \quad (8)$$

Eq. (8) is quartic in vibration quantum number, and in general, there will be four vibrational quantum numbers for a given energy level. For instance, vibrational levels for  $n = 11$  (at 25223.31  $\text{cm}^{-1}$ ), for  $n = 155$  (at 25932.75  $\text{cm}^{-1}$ ), and for  $n = 343$  (at 25160.17  $\text{cm}^{-1}$ ) are close to each other. Out of these, levels  $n = 155$  and  $n = 343$  are treated as unphysical, even though these levels are allowed by equation. By convention,  $\Delta G = 0$  decides the upper limit of the vibrational quantum number. Eq. (8) therefore, does not carry full meaning of a mathematical equation. Moreover, equation gives 20 percent higher dissociation energy. No doubt, the error can be minimized by introducing large number of terms in equation of energy in rather empirical manner. As a matter of fact, as we approach the dissociation limit of diatomic molecule, we have to add more terms in the eq. (8) for correct description of vibrational levels.

We have similar problems with rotational energy levels expressed as power series of  $l(l+1)$ . As the rotational

quantum number is increased, one has to add extra terms in the energy expression. Besides, rotational and vibrational constants vary with energy levels. They are not constants in the real sense. It may be pointed out that the dissociation energy of a diatomic molecule as anharmonic oscillator may be accounted for by eq. (8) if a large number of parameters are included. In comparison, only a few constants of eq. (7) are expected to reproduce energy and dissociation levels of the diatomic molecule with better accuracy.

For low vibrational and rotational quantum numbers, we can expand eq. (8) in power series of  $(n' + 1/2)$  and  $l(l + 1)$  to obtain the following molecular constants in the conventional sense.

$$\begin{aligned}
 E_e &= \frac{A}{(x+0.5)^2} + \frac{B}{(x+0.5)^3} + \frac{C}{(x+0.5)^4} + \dots \\
 Ch\omega_e &= -\frac{2A}{(x+0.5)^3} - \frac{3B}{(x+0.5)^4} - \frac{4C}{(x+0.5)^5} + \dots \\
 Ch\omega_e x_e &= \frac{3A}{(x+0.5)^4} + \frac{6B}{(x+0.5)^5} + \frac{10C}{(x+0.5)^6} + \dots \\
 Ch\omega_e y_e &= -\frac{4A}{(x+0.5)^5} - \frac{10B}{(x+0.5)^6} - \frac{20C}{(x+0.5)^7} + \dots \\
 Ch\omega_e Z_e &= -\frac{5A}{(x+0.5)^6} + \frac{15B}{(x+0.5)^7} + \frac{35C}{(x+0.5)^8} + \dots \\
 ChB_e &= \frac{A}{x^4} - \frac{3B}{2x^5} - \frac{2C}{x^6} + \dots \\
 ChD_e &= \frac{3A}{4x^6} + \frac{3B}{2x^7} + \frac{5C}{2x^8} + \dots \\
 Ch\alpha_e &= \frac{3A}{x^5} + \frac{6B}{x^6} + \frac{10C}{x^7} + \dots \quad (9)
 \end{aligned}$$

where  $x^2 = 2\mu b/\hbar^2$ ,  $A = -\mu a^2/2\hbar^2$ ,

and  $E_e$  the electronic energy levels with  $n', l = 0$ . On retaining only the first term in the set of eqs. (9), we can write the following approximate relations :

$$\omega_e x_e \approx 3B_e \text{ and } \omega_e y_e \approx 4/3\alpha_e.$$

Table 1 gives the values of  $\omega_e x_e/B_e$  for light molecules. Average value of this ratio for molecules as shown in Table 1 is 3.1, with standard deviation 0.3. Even such a limited success is rather encouraging in view of the fact that only one term of eq. (9) has been used for such calculation and we have selected a simple potential for a diatomic molecule.

#### (ii) Isotopic shift :

We do not have experimental energy levels of a molecule in the form of eq. (7), hence it is impossible to verify the isotopic mass shift of energy levels directly. However, it can be shown that this equation is consistent with the requirement of isotopic shift, if we expand it in the conventional form of energy.

Table 1. Ratio of  $\omega_e x_e/B_e$  for some molecules, values are in  $\text{cm}^{-1}$ .

Molecules	Electronic states	$\omega_e x_e$	$B_e$	$\omega_e x_e/B_e$
$^1\text{H}_2$	$B' \ ^1\Sigma_u^+ (3p\sigma)$	83 406	26 705	3.1
	$K \ ^1\Sigma_g^+$	30	10.8	2.8
	$I^4 \ ^3\Pi_u$	106.0	36	2.9
	$O^+ \ ^3\Sigma_u^+$	91.0	35	2.6
$^2\text{H}_2$	$E \ ^1\Sigma_g^+ (2s\sigma)$	48 105	16 369	2.9
	$B' \ ^1\Sigma_u^+ (3p\sigma)$	45 679	13 605	3.3
	$I \ ^1\Pi_g (3d\pi)$	39 42	14 739	2.6
	$B'' \ ^1\Sigma_u^+ (4p\sigma)$	35 416	13 685	2.6
	$e \ ^3\Sigma_u^+ (3p\sigma)$	34.51	13.856	2.5
$^3\text{H}_2$	$E \ ^1\Sigma_g^+ (2s\sigma)$	30.52	10 9306	2.8
$^1\text{H}_2^+$	$B \ ^2\Sigma_g^+ (3d\sigma)$	5 247	1.530	3.4
	$C \ ^2\Pi_u (2p\pi)$	6 454	1.899	3.4
$^2\text{H}_2^+$	$B \ ^2\Sigma_g^+ (3d\sigma)$	2.62	0.766	3.4
	$C \ ^2\Pi_u (2p\pi)$	3.14	0.950	3.3
$^7\text{Li}_2$	$A \ ^1\Sigma_u^+$	1 582	0.4975	3.2
$^7\text{Li}^2\text{H}$	$X \ ^1\Sigma^+$	23 20	7.5131	3.1
$^7\text{LiH}$	$X \ ^1\Sigma^+$	12 935	4.2394	3.1
$^{23}\text{NO}$	$A \ ^1\Sigma_u^+$	0.3576	0.11078	3.2
$^9\text{Be}^1\text{H}$	$X \ ^2\Sigma^+$	36.31	10.3164	3.5
$^9\text{Be}^2\text{H}$	$X \ ^2\Sigma^+$	20.71	5.6872	3.6
$^9\text{Be}^2\text{H}^+$	$X \ ^1\Sigma^+$	21.9	5.955	3.7
$^{90}\text{K}_2$	$C \ ^1\Pi_u$	0.133	0.04404	3.2

The values of molecular constants derived from eq. (7), depends upon the reduced mass of the molecule in accordance with the requirement of isotopic shift. The following relations may be obtained easily if we retain only the first dominant term in eq. (9).

$$\begin{aligned}
 \omega_e &\propto 1/\sqrt{\mu}, \quad \omega_e x_e \propto 1/\mu, \quad \omega_e y_e \propto 1/\mu^{3/2}, \\
 \omega_e Z_e &\propto 1/\mu^2, \quad B_e \propto 1/\mu, \quad \alpha_e \propto 1/\mu^{3/2}. \quad (10)
 \end{aligned}$$

The electronic energy of a molecule also depends upon reduced mass as

$$E_e = -\frac{a^2}{4b} + \frac{a^2\hbar}{4\sqrt{2}b^{3/2}\sqrt{\mu}} \quad (11)$$

In eq. (11), higher terms have been neglected. The electronic energy therefore, depends slightly on the

reduced mass of a molecule. If we consider three isotopic molecules of reduced masses  $\mu_1$ ,  $\mu_2$  and  $\mu_3$  with energies  $E_1$ ,  $E_2$  and  $E_3$  respectively, eq. (11) leads to the following relation :

$$\frac{E_2 - E_1}{E_3 - E_1} = \frac{\sqrt{\mu_3}(\sqrt{\mu_2} - \sqrt{\mu_1})}{\sqrt{\mu_1}(\sqrt{\mu_3} - \sqrt{\mu_1})}. \quad (12)$$

Table 2 gives the values of  $(E_2 - E_1)/(E_3 - E_1)$  for three isotopic molecules of  $H_2$  in different electronic states [9].

**Table 2.** Electronic energy levels of isotopic molecules of hydrogen energy levels are in  $cm^{-1}$

Electronic states	$^1H_2(E_1)$	$^2H_2(E_2)$	$^3H_2(E_3)$	$(E_2 - E_1)/(E_3 - E_1)$
$B^1\Sigma_u^+(2p\sigma)$	91700.00	91697.2	91696.3	0.76
$C^1\Pi_u(2p\pi)$	100089.8	100097.2	100099.7	0.74
$E^1\Sigma_g^+(2s\sigma)$	100082.3	100128.1	100136.7	0.84
$F^1\Sigma_x^+(2p\sigma)$	100911.0	100931.2	100935.9	0.81
$a^3\Sigma_g^+(2s\sigma)$	95936.1	95958.0	95965.4	0.74
$e^3\Sigma_u^+(3p\sigma)$	107774.7	107774.0	107770.8	0.18
$d^3\Pi_u(3p\pi)$	112700.3	112729.8	112736.0	0.83
$f^3\Sigma_u^+(4p\sigma)$	116705.0	116640	116653	1.25
$k^3\Pi_u(4p\pi)$	118366.2	118396.7	118403.2	0.82
$n^3\Pi_u(5p\pi)$	120952.9	120976.9	120984	0.77

Reduced masses of  $^1H_2$ ,  $^2H_2$  and  $^3H_2$  are 0.50391261, 1.00705111 and 1.50802486 in A.U respectively.

The average value for all electronic states except for  $e^3\Sigma_u^+(3p\sigma)$  which is perturbed, is 0.8 against the theoretical value of 0.7. The new equation for energy is therefore, consistent with isotopic shift. It will be futile to expect very accurate results for such simple potential form, with only three terms. For such potential, there will be infinite number of vibrational energy levels and the graph of  $\Delta G$  vs. vibrational quantum number will approach zero asymptotically. In the majority of the diatomic molecules, only a few vibrational levels are determined experimentally and it is not possible to have any definite conclusion about variation of  $\Delta G$  for high vibrational levels, especially in the neighbourhood of dissociation limit. In ionic molecules,  $\Delta G$  definitely approaches zero asymptotically [12], but we do not have an extended graph of the other non-ionic molecules. Indeed, if we include higher terms in the expression of potential,  $\Delta G$  may be tailored to fit the experimental graph of any diatomic molecule. A number of other approximate relations for a diatomic molecule may also be derived from such equation.

### (iii) Isoelectronic molecules :

Several attempts have been made to understand the variation of molecular constants for similar molecules or same molecule in different electronic states, using a number of empirical rules [12]. One such rule is that  $r^2\omega_e$  should be constant for different electronic states of the same molecule [12]. The present picture of a diatomic molecule may help in framing approximate relations of molecular constants for similar molecules. Assuming that the potential energy for isoelectronic molecules or isotopic molecules are comparable, one can obtain a number of relations of molecular constant for isoelectronic molecules. According to the eq. (9), we have the following relation :

$$C\hbar Be. = a^2\hbar^2/8b^2.\mu,$$

$$\text{or } Be.\mu = a^2\hbar^2/8b^2.C. \quad (13)$$

Value of  $Be.\mu$  will be constant for isoelectronic molecules with same potential energy. Table 3 gives the value of  $Be.\mu$  for isoelectronic molecules  $N_2$  and  $Co$ , which is approximately constant in a given electronic state.

**Table 3.**  $Be.\mu$  for  $N_2$  and  $Co$  isoelectronic diatomic molecules.

Electronic states	$N_2$ $Be.\mu(cm^{-1} \times A.U.)$	$Co$ $Be.\mu(cm^{-1} \times A.U.)$
$X^1\Sigma_g^+$	13.9907	13.2413
$a^3\Sigma_u^+$	10.1844	9.2189
$b^3\Pi_g$	11.4647	11.5955
$A^1\Pi_g$	11.3208	11.0488
$W^1\Delta_u$	10.4883	8.6183
$E^3\Sigma_g^+$	13.4941	13.6164
$C^1\Sigma_u^+$	13.7314	13.4464
$O_3^1\Pi_u$	12.1400	13.5554

### (iv) Vibrational and rotational analysis :

We have fitted vibrational and rotational energy levels, eq. (7) to  $H_2^+$  and  $H_2$  molecules as for three states  $X^1\Sigma_g^+$ ,  $B^1\Sigma_u^+$  and  $C^1\Pi_u$ , and have been analysed according to our approach as below

$$H_2^+(X^2\Sigma_g^+) :$$

$$E(n', l') = -1.6951 R/d^2 + 4.1264 R/d^3 - 2.0854 R/d^4,$$

where  $d = (n'/31.1207 + l'/31.1207)$

and  $l'(l' + 1) = l(l + 1) + 1470.0218$ .

$$H_2(X^1\Sigma_g^+) :$$

$$E(n', l') = -3.0204 R/d^2 + 6.7899 R/d^3 - 3.2596 R/d^4,$$

where  $d = (n'/31.1207 + l'/31.1207)$   
 and  $l'(l' + 1) = l(l + 1) + 1222.7234$ .

$H_2(B^1\Sigma_u^+)$  :

$$E(n', l') = -0.2877 R/d^2 + 0.7265 R/d^3 - 4.6542 R/d^4,$$

where  $d = (n'/31.1207 + l'/31.1207)$   
 and  $l'(l' + 1) = l(l + 1) + 1175.4141$ .

$H_2(C^1\Pi_u)$  :

$$E(n', l') = -2.1374 R/d^2 + 5.0265 R/d^3 - 2.5461 R/d^4,$$

where  $d = (n'/31.1207 + l'/31.1207)$   
 and  $l'(l' + 1) = l(l + 1) + 1505.4396$ .

$R$  is the Rydberg constant. (14)

These equations have been fitted with 100% accuracy of the dissociation energy values.

### 3. Concluding remarks

The present discussion is based upon potential form expressed in inverse power series of  $r$  which is a simplifying assumption for the problem of a diatomic molecule. We expect that each molecule rather each electronic state of a molecule would have different potential form and as such, we may have a better scope for understanding molecular spectroscopy. With these limitations, we have interpreted the vibrational and rotational energy levels of some simple molecules  $H_2^+$  and  $H_2$ . They have been interpreted in accordance with the theory developed in the present discussion. Only one equation with

four constants represents both vibrational and rotational levels of these diatomic molecules with good accuracy. The equation also gives the dissociation energy with hundred percent accuracy. In these calculations, we have used only four terms in the expression for diatomic potential. In conventional picture, we require eight to ten parameters for accurate representation of vibrational and rotational levels of a diatomic molecule and even then, the error in dissociation energy is more than 20 percent. It can be concluded that with increasing number of terms and hence a more suitable potential form, the proposed method has a better scope of yielding improved and more accurate results for diatomic molecules.

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