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Counting the number of vibrational states of a molecule to improve the Born-Oppenheimer estimate

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I derive an approximate estimate for the number N of states in a vibrational band of a diatomic molecule. The number N may be used to redefine and improve by a factor π a well-known estimate of Born and Oppenheimer [Ann. Phys. (Leipzig) **84**, 457 (1927)]. The formulas for N are compared to data for H_2 and a few other molecules.

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The spectra of diatomic molecules are well understood [1]. Modern computers calculate energy levels very precisely and for very many molecules. Approximate estimate thus seem old-fashioned and useless. Nevertheless in this paper I discuss a simple, approximate estimate for the typical number N of vibrational states in any diatomic molecule, and use this result to sharpen a well-known [2] formula due to Born and Oppenheimer [3]. The result is so simple and the derivation so trivial that they could have been found any time in the last 70 years, but apparently have not. Approximate formulas *are useful* in helping us understand more precise results, both from experiment and from computers.

I. INTRODUCTION

The spectrum of any diatomic molecule is distinct. For each allowed angular momentum, the energy levels occur in closely spaced bands, the vibrational states, which are (usually) well separated from the next band, the vibrational states of the next electronic state. The number of states in each band is finite; this is in contrast to atomic energy levels which are usually infinite in number at each allowed angular momentum.

This grouping into bands is a well-known and understood consequence of the disparity in mass between electrons (mass m) and nuclei (mass $M \gg m$). The motion of electrons is studied for a fixed nuclear configuration, and the resulting electronic energy, together with the Coulomb repulsion between nuclei, serves as potential energy $V(r)$ for the motion of the nuclei. This scheme was first described in quantum mechanics by Born and Oppenheimer [3] in a widely quoted article though it had been discussed earlier by Born and Heisenberg [3]. Many textbooks [2] discuss this approximation and quote [3] an estimate for the typical vibrational energy spacing ω_v of a molecule, relative to an electronic spacing ω_e, $\omega_v/\omega_e \approx \sqrt{m/M}$. I have not seen any (numerical) examples for this equation in textbooks. It is also not clear, since the number of states in the vibrational band is finite, whether the vibrational spacing is between the two bottom states in the well, or the two top energy states. In H_2 these two "frequencies" differ by a factor of 6.

I will discuss the number N of vibrational energy levels in a given electronic state of the molecule, and will show that for the ground state of typical stable molecules this is reasonably well approximated by the formulas

$$N=\frac{1}{\pi}\left[\frac{M}{m}\right]^{1/2}, \tag{1a}$$

$$N=\frac{1}{\pi}\left[\frac{2\mu}{m}\right]^{1/2}, \tag{1b}$$

where m is the electronic mass while μ is the reduced mass of two nuclei of mass M_1,M_2:

$$\mu=\frac{M_1M_2}{M_1+M_2}. \tag{2}$$

Formula (1a) is for a homonuclear molecular $M_1=M_2=M$ while formula (2) is for a heteronuclear molecule.

Equations (2) involve the *inverse* of the dimensionless parameter $\sqrt{m/M}$, with an extra factor of π, so they suggest that we try to reformulate the Born-Oppenheimer estimate.

Equation (1) is very accurate for the ground states of alkali-metal-atom molecules; the error is less than 5%. I quote a few examples below:

Molecule	Formula (1)	Experiment	Reference
Li_2	35.6	37	[18]
Na_2	64.8	66	[19]
Cs_2	155.9	156±1	[20]

I hope to discuss these and other examples elsewhere.

The average vibrational spacing $\langle \hbar\omega_v \rangle$ in a band may be defined by dividing the dissociation energy of a molecule (in the given electronic state) D_e by the number of spacings $(N-1)$:

$$\langle \hbar\omega_v \rangle \equiv \langle E_v - E_{v-1} \rangle = \frac{D_e}{N-1} \simeq \pi\left[\frac{m}{M}\right]^{1/2} D_e \tag{3}$$

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*On leave of absence from the Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1. Electronic address: PHYGKARL@VM.UOGUELPH.CA (where I assumed $N \gg 1$), and one can rewrite (3) in the form

$$\frac{\langle \hbar\omega_v \rangle}{D_e} \simeq \pi \left[\frac{m}{M} \right]^{1/2} . \tag{4}$$

In (3) and (4) I have only used Eq. (1a) appropriate to the homonuclear case. As already mentioned, in the early 1920s, Born, Heisenberg, and Oppenheimer [3] estimated ω_v/ω_e, where ω_e is an "electronic frequency" to be of order $\sqrt{m/M}$. Their estimate neglects anharmonicity in vibrations, so that all vibrational spacings in the band are identical. The estimate (4) based on defining an average vibrational spacing for the molecule is more precise, and provides an improvement by a factor of π. The dissociation energy D_e is, as is well known, of the same order of magnitude as an electronic spacing.

II. DERIVATION OF EQS. (1)

The number of bound states N for the vibrational motion of two nuclei, of masses M_1, M_2, due to a potential energy $V(R)$ can be estimated through the Bohr-Sommerfeld-Wilson quantization condition [4]. This formula was postulated by Wilson and by Sommerfeld to give the quantization of elliptic orbits within the Bohr model of the hydrogen atom. With the advent of quantum mechanics, the formula was derived in the "semiclassical" approximation of large quantum numbers by Wentzel, Kramers, and Brillouin (WKB) [5,6]. The formula relates the energy E to an integer quantum number n through the phase-space integral:

$$2\pi(n+\tfrac{1}{2})\hbar = 2\int_{R_{\min}}^{R_{\max}} \sqrt{2\mu[E-V(r)]}\,dR , \tag{5}$$

where the limits of integration are defined through the turning point conditions $V(R_{\min}) = V(R_{\max}) = E$. To determine the total number N of bound (i.e., negative-energy) states, we set $E=0$ in (5) and replace $(n+\frac{1}{2})$ by N to obtain

$$\pi N \hbar = \int_{R_0}^{\infty} \sqrt{-2\mu V(R)}\,dR , \tag{6}$$

where now $V(R_0)=0$ and we replace $R_{\max}$ by infinity, assuming a long-range potential. Equation (6) is valid in an arbitrary system of units (such as mks), but we can simplify it if we express distances r and energies $v(r)$ in atomic units:

$$R = \frac{\hbar}{mc\alpha} r = a_0 r , \tag{7a}$$

$$V(R) = mc^2\alpha^2 v(r) = \frac{e^2}{a_0} v(r) , \tag{7b}$$

where a_0 is the unit of length, the Bohr radius. In these units Eq. (6) has the form

$$N = \left[\frac{1}{\pi} \left[\frac{2\mu}{m} \right]^{1/2} \right] \int_{r_0}^{\infty} \sqrt{-v(r)}\,dr = \left[\frac{1}{\pi} \left[\frac{2\mu}{m} \right]^{1/2} \right] I , \tag{8}$$

where I defined the dimensionless integral I as

$$I = \int_{r_0}^{\infty} \sqrt{-v(r)}\,dr \tag{9}$$

with v and r in atomic units. The lower limit of integration r_0 satisfies $v(r_0)=0$. It is now easy to see that the finite number of levels in a vibrational band is due to the integral (9) being convergent, which in turn is due to the long-range behavior of $v(r)$. Typically $v(r) \sim r^{-6}$ if the molecule dissociates into neutral atoms, and the integral converges. However if the molecule dissociates into ions, or for an atom which dissociates into an ion and electron, $v(r) \sim r^{-1}$ and the integral diverges, so there is an infinite number of states.

As will be discussed below the estimate (8) is very accurate for getting the number N of energy levels. But we still need knowledge of the potential energy $v(r)$ for the specific molecule in the specific state. This is available quite often. The estimate (1) is obtained by *assuming that the integral I is equal to 1.* It is clear that both the size of the integrand $\sqrt{-v}$ and the "range" where it is significant are of order unity in atomic units, since they are obtained from an electronic Hamiltonian at a fixed distance r. But clearly the assumption (or guess) $I \simeq 1$ is too general to be good for all molecules and all their excited states. In special cases we can evaluate I since we know $v(r)$, or alternatively we can infer the value of I from the experimental data on N. We shall do this in the next section. It should also be noted that (due to the square root) formula (9) is rather insensitive to errors in $v(r)$; as the integrand is everywhere positive, cancellations cannot occur.

III. COMPARISON WITH EXPERIMENT

For hydrogen H_2, the approximate estimate (1a) is

$$N = \frac{1}{\pi} \left[\frac{M}{m} \right]^{1/2} \simeq \sqrt{1836} \simeq 13.6 , \tag{10}$$

where M is the proton mass. The estimate (10) is in reasonable agreement with the actual number of vibrational states of hydrogen H_2, which is known from precise experiments of Herzberg and collaborators [7] to be 15 bound states for a rotationless ($J=0$) molecule. This suggests $I \simeq 1.103$. But one can use the very accurate computations of Kolos and Wolniewicz [8] to evaluate the integral (9) more precisely. I obtained $I = 1.108$, which shows that for H_2 the guess $I=1$ is very fortuitous. The exact number $N=15$ has also been known from numerical integrations [9] of the vibrational Schrödinger equation, which of course give precise values of all the energy levels E_n, much more information than is contained in N. It is remarkable how good the WKB approximation [or the Bohr-Sommerfeld-Wilson formula (8)] is in this molecular case. As states, the agreement of (1) or (10) with the data is somewhat fortuitous, since we do not know *a priori* that the guess $I \simeq 1$ will be good for hydrogen. Nevertheless the simple estimate (10) indicates that the "natural" number of states in a vibrational band of H_2 is about 13–14 and so helps us comprehend the facts.

It is trivial to scale the estimates (1) and (8) for various isotopes of hydrogen D_2, HD, DT, HT, and T_2 which are

TABLE I. Number of vibrational states for hydrogenic molecules ($J=0$).

Molecule	Formula (1)	Formula (8) (with $I=1.108$)	Data[a]
H_2	13.6	15.1	15
HD	15.7	17.4	17
HT	16.7	18.5	18
D_2	19.3	21.3	21
DT	21.1	23.4	23
T_2	23.6	26.1	26
$p\mu p$	0.95		1
$d\mu d$	1.34		2

[a] For H_2, HD, and D_2 the experimental data are from Ref. [7], while for the other isotopes we quote the computation of Ref. [10] and for $p\mu p$ the computations reviewed in Ref. [11].

all given in Table I. It is also amusing to consider the molecule-ion $H_2{}^+$, for which I found by numerical integration that the integral (9) is also close to unity in the ground electronic state. I found $I(H_2{}^+)\simeq 1.06$. Therefore the estimate (10) should also hold for $H_2{}^+$. Similarly for the muonic hydrogen ion $(p\mu p)^+$ we can use formula (10) with the muon mass replacing the electron mass. This gives $N\simeq 0.95$ in agreement with numerical computations which find a single bound state for muonic molecules [11]. It is somewhat surprising that the simple formula (1), based on the semiclassical Bohr-Sommerfeld-Wilson (large-N) approximation, should work even for N as small as unity.

For heavier molecules N is larger than for hydrogen H_2. But we should recall that there is no obligation for the integral (9) to be close to unity. We were lucky for H_2. Therefore we should expect deviations, and this is indeed the case. There is no intention to give a large survey in this paper, but a few cases will be discussed. For example, for chlorine Cl_2 where $M=35$ formula (1) predicts 80 levels, while the ground electronic state of Cl_2 has [12] only 59 vibrational states. Therefore we conclude that the integral (9) is about 0.73 for the ground electronic state of Cl. A similar value holds for iodine I_2, where with $M=127$ formula (1) predicts 153 states, but only 114 states are found in the ground electronic state [13]. This corresponds to the integral $I(I_2)\simeq 0.745$, surprisingly close to that of chlorine. While the absolute discrepancy is large, the percentage error is only about 25%. For the alkali-metal molecules the integrals are also within 10% of unity [15].

Dressler and Wolneiwicz have kindly pointed out that the integral I is large in some excited states of H_2 which have double minima. For example, in the EF electronic state the integral I is 2.41, and correspondingly there are 34 vibrational states (at $J=0$) in this electronic state [14], compared to 32.8 predicted by formula (8), which is still pretty good. But the guess $I\simeq 1$ is very inaccurate in this case and other excited states which result from the "crossing" of two electronic states.

IV. DISCUSSION AND SUMMARY

The literature on bound states contains *exact* results on the number of bound states in a potential. For example, Jost, Pais, Bargmann, and Schwinger have proven an upper bound [16]:

$$N\le\left[\frac{2\mu}{\hbar^2}\right]\int_{R_{\min}}^{\infty}R\,|V(R)|dR\equiv\left[\frac{2\mu}{m}\right]\int_{r_{\min}}^{\infty}r|v(r)|dr\ .$$

As seen from the second expression, this inequality shows that in the case of hydrogen $N\lesssim 1836$. This is true but useless, because N is large [17]. The formula (1) is not exact, so it is violated, but not by so very much.

There are two comments to add here. It would clearly be very interesting to compare formula (1) with a much larger number of examples than in this paper. A second comment concerns the parametrization of empirical potentials, used to represent the vibrational motion of diatomic molecules. It is customary to label them via equilibrium distance R_e and dissociation energy D_e, which are indeed directly available from experiment. The integral I of Eq. (9) is just as accessible from experiment via Eq. (8), and ought to be determined for each empirical potential, together with R_e and D_e.

In summary, this paper provides an estimate, Eq. (1), for the number N of states in a vibrational band. The estimate is sometimes a poor approximation, but it improves by a factor of π, a related previous estimate due to Bron and Oppenheimer.

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