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A theory of non-linear stretch vibrations of hydrogen bonds

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Abstract. A non-linear vibration of the stretch of hydrogen bonds has been studied theoretically. We have used the potential $V(r) = Ar^2 - Br^3$, where A and B are constants, to describe approximately the H-bond energy. We have obtained analytical solutions of the motion equation for a particle moving in this potential field. The theoretical results have been applied to some realistic physics systems, including water molecules, the DNA double helix and the α -helix protein. It is shown that the calculated vibration frequencies are in agreement with experimental data observed by the Raman scattering and other techniques. The asymmetry of the H-bond energy is also discussed.

1. Introduction

The importance of hydrogen bonds in the conformational stability of biological macromolecules is widely recognized. The H bond is also a key factor in keeping water in a liquid state at normal temperature. The vibration modes of the H-bond stretch in the molecules mentioned above have been observed in many experiments. The linear vibration theory of the H-bond stretch has been studied frequently (see, e.g., [1, 2]). However, the H bond is essentially non-linear. So far as we know, the theory of non-linear vibration of the H-bond stretch has not yet been studied sufficiently. It is the aim of this paper to perform such a study. To do this, it is important to use a suitable form of the H-bond potential. Up to now, three forms of the potential have been frequently used to describe the H-bond energy. They are

(i) the Toda lattice potential $V(r) = a[\exp(-br) - 1]/b + ar$, where $a = 0.31 \text{ eV } \text{\AA}^{-1}$, $b = 4.0 \text{ \AA}^{-1}$ [3–6],

(ii) the Lennard-Jones potential $V(r) = 4\varepsilon[(\sigma/R)^{12} - (\sigma/R)^6]$, where $\varepsilon = 0.22 \text{ eV}$, $\sigma = 4.01 \text{ \AA}$ and $R = 4.50 \text{ \AA} + r$ [7] and

(iii) the 2–3-power potential $V(r) = Ar^2 - Br^3$, where $A = 0.62 \text{ eV } \text{\AA}^{-2}$ and $B = 0.83 \text{ eV } \text{\AA}^{-3}$ [8].

It should be noted that the three potential forms are all approximate in describing the H bond. If we expand the Toda and Lennard-Jones potentials into a Taylor series with respect to r , we find that the first and second terms are exactly the same as a 2–3-power potential. Therefore, in order to simplify the theoretical study, it is reasonable to study the 2–3-power potential first in this paper.

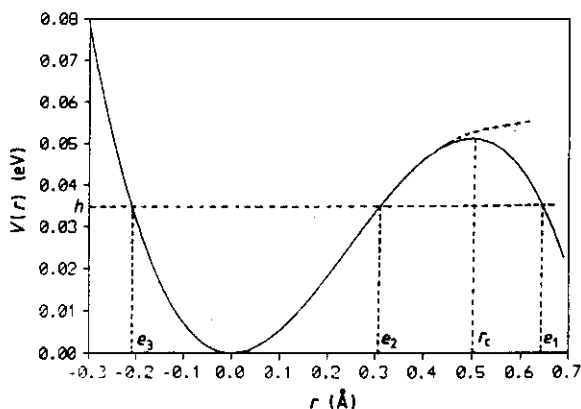


Figure 1. The curve of $V(r) = Ar^2 - Br^3$, with $A = 0.62 \text{ eV } \text{Å}^{-2}$ and $B = 0.83 \text{ eV } \text{Å}^{-3}$.

This paper is organized as follows. In section 2 the 2–3-power potential is studied in some detail. In section 3 the theory of non-linear stretch vibration of the H bond is established. Then the application of the theoretical results to some realistic physics systems including water molecules, the DNA double helix and the α -helix protein is performed in section 4. In the last section, section 5, some discussion is given and conclusions are drawn.

2. The study of the 2–3-power potential form of the H bond

When studying the molecular mechanism in the process of muscle contraction, Yomosa [8] used the 2–3-power potential $V(r) = Ar^2 - Br^3$ to describe the H-bond energy approximately. This form of the potential really reflects some of the main character of the H bonds. For example, we may use this potential to explain some of the character of liquid water molecules. An H bond exists between the oxygen atom of one H_2O molecule and the hydrogen atom of another H_2O molecule. Let the displacement of the hydrogen atom from its equilibrium position along the direction of the H bond be denoted by r . If the hydrogen atom is far from the oxygen atom, r is positive; otherwise, it is negative.

The curve of $V(r)$ is shown in figure 1. There are two points, $r = 0$ and $r = r_c = 2A/3B$ satisfying $dV(r)/dr = 0$. When $r < r_c$, the curve conforms to the real H bond very well. When $r > r_c$, the upper broken curve represents the real H-bond energy. However, in the vicinity of r_c , the H bond has been broken. So only when $r < r_c$ is the 2–3-power potential valid.

Let us imagine that there is a particle with mass m moving in this potential field. At the point $r = r_c$, its potential energy is $V(r_c) = h_c = 4A^3/27B^2$. When its total energy h is less than h_c , there are three points, $r = e_1$, $r = e_2$ and $r = e_3$ which satisfy $V(r) = h$, where $e_1 > r_c$, $0 < e_2 < r_c$ and $e_3 < 0$ (see figure 1). In this discussion we neglect the range $r > r_c$. The particle will vibrate between the points e_3 and e_2 . From the shape of the curve, we see that $e_2 > |e_3|$. This may explain why the H bonds are easier to extend than to compress. We define $|e_2/e_3|$ as the extension–compression ratio (ECR). Since the ECR is greater than unity, this implies that the existence of the H bonds is an important reason why it needs more energy to compress liquid water than to expand it. We thus explain

qualitatively the incompressibility of liquid water and some biological macromolecules by the 2-3-power potential of the H bond.

3. Theory of non-linear stretch vibration of the H bond

In this section, we shall study the motion of a particle with mass m (the particle is denoted by m hereafter) moving in this potential field. The following two cases will be studied later.

3.1. Harmonic vibration

When the energy is very small, m will oscillate in the vicinity of the point $r = 0$. In this condition, the potential can be reduced to $V(r) = Ar^2$. The equation of motion can be written as

$$d^2r/dt^2 = -\omega^2r \quad (3.1)$$

where $\omega^2 = 2A/m$. The solution of equation (3.1) is

$$r = L \cos(\omega t) \quad (3.2)$$

where ω is the frequency of the harmonic vibration, L is the amplitude and we have assumed that the initial phase of this motion is zero.

3.2. Non-linear vibration

When the energy h is neither very small nor larger than h_c , the non-linear term r^3 of $V(r)$ cannot be neglected. In this case, we have

$$V(r) = Ar^2 - Br^3 \quad (3.3)$$

and the Hamiltonian of the system is

$$H = \frac{1}{2}m(dr/dt)^2 + Ar^2 - Br^3. \quad (3.4)$$

The corresponding equation of motion is

$$m d^2r/dt^2 + 2Ar - 3Br^2 = 0. \quad (3.5)$$

Integrating (3.5) and letting $2A/m = \omega^2$, $B/m = Q$, we obtain

$$(dr/dt)^2 = -\omega^2r^2 + 2Qr^3 + 2QC \quad (3.6)$$

where C is an integral constant and $\sqrt{2QC}$ is the velocity of m at the position $r = 0$. The total energy of m can be written as

$$h = \frac{1}{2}m(2QC) = BC. \quad (3.7)$$

Then, we have

$$0 < BC < 4A^3/27B^2 \quad \text{or} \quad 0 < C < 4A^3/27B^3. \quad (3.8)$$

The particle m will vibrate periodically, but its solution of motion is not simply a sine or cosine function.

Let $R(r) = -\omega^2r^2 + 2Qr^3 + 2QC$. Under the condition (3.8), the equation $R(r) = 0$ has three real roots. They are $r = e_1$, $r = e_2$ and $r = e_3$, where $e_1 > e_2 > e_3$, and

we have mentioned that $e_1 > r_c$, $0 < e_2 < r_c$ and $e_3 < 0$. The particle m will move in the range $r \in [e_3, e_2]$.

Expanding the equation $R(r) = (r - e_1)(r - e_2)(r - e_3)$, we get

$$e_1 + e_2 + e_3 = \omega^2/2Q = A/B \quad (3.9a)$$

$$e_1e_2 + e_1e_3 + e_2e_3 = 0 \quad (3.9b)$$

$$e_1e_2e_3 = -C. \quad (3.9c)$$

Integrating equation (3.6) and assuming that, when $t = t_0$, the particle is at the position $r = e_3$, we have

$$\int_{e_3}^r \frac{dr}{\sqrt{r^3 - (\omega^2/2Q)r^2 + C}} = \int_{t_0}^t \sqrt{2Q} dt \quad r \in [e_3, e_2]. \quad (3.10)$$

Let

$$r = e_3 + (e_2 - e_3)u \quad u \in [0, 1]. \quad (3.11)$$

Substituting (3.11) into (3.10) and introducing

$$k^2 = (e_2 - e_3)/(e_1 - e_3) \quad k \in (0, 1) \quad (3.12)$$

we get another corresponding integral equation

$$\int_0^u \frac{du}{\sqrt{(1-u^2)(1-k^2u^2)}} = \int_{t_0}^t \sqrt{(B/2m)(e_1 - e_3)} dt \quad (3.13)$$

where we have already considered that $Q = B/m$. The solution of equation (3.13) can be expressed in terms of a Jacobian elliptic function with the mode k :

$$u = \text{sn}[\sqrt{(B/2m)(e_1 - e_3)}(t - t_0); k^2 = (e_2 - e_3)/(e_1 - e_3)]. \quad (3.14)$$

Then

$$r = e_3 + (e_2 - e_3) \text{sn}^2[\sqrt{(B/2m)(e_1 - e_3)}(t - t_0); k^2 = (e_2 - e_3)/(e_1 - e_3)]. \quad (3.15)$$

In order to facilitate the following computations, we introduce the dimensionless quantities

$$e'_i = (B/A)e_i \quad (i = 1, 2, 3) \quad h' = (B^2/A^3)h \quad t' = \sqrt{(A/m)} t. \quad (3.16)$$

According to (3.9a)–(3.9c) and (3.12), we obtain the following expressions:

$$e'_1 = [1 - (2 - k^2)e'_3]/(1 + k^2) \quad (3.17a)$$

$$e'_2 = [k^2 + (1 - 2k^2)e'_3]/(1 + k^2) \quad (3.17b)$$

$$e'_3 = \frac{1}{3}[1 - \sqrt{1 + k^2 + k^6 + k^8}/(1 - k^2 + k^4)] \quad (3.17c)$$

$$h' = -e'_1e'_2e'_3. \quad (3.18)$$

These formulae reveal the relations between h , k^2 and (e_1, e_2, e_3) .

We know that the period of the function $\text{sn } u$ is $4K$, and the period of $\text{sn}^2 u$ is $2K$, where K is the total elliptic integral:

$$K = \int_0^1 \frac{du}{\sqrt{(1-u^2)(1-k^2u^2)}} \quad (3.19)$$

When $k < 1$, K can be expanded with respect to k^2 :

$$K = (\pi/2)(1 + k^2/4 + 9k^4/64 + \dots) = \pi/2 + O(k^2). \quad (3.20)$$

When $k^2 < 0.04$ (or $h < 4 \times 10^{-4}A^3/B^2$), the terms in $O(k^2)$ can be neglected, i.e. $K \approx \pi/2$. Under this condition, according to the properties of $\text{sn } u$, we have $\text{sn } u \rightarrow \sin u$, $e_1 \gg e_2$, $e_2 \rightarrow 0^+$, $e_3 \rightarrow 0^-$ and $e_2 \approx -e_3$. Equation (3.15) reduces to the following form:

$$\begin{aligned} r &= (e_2 + e_3)/2 - (e_2 - e_3)/2 \cos[\sqrt{(2B/m)(e_1 - e_3)}(t - t_0)] \\ &\approx -e_2 \cos[\omega(t - t_0)] \end{aligned} \quad (3.21)$$

where we have used $B = A/(e_1 + e_2 + e_3)$ and $\omega^2 = 2A/m$. We can see that (3.21) is just consistent with (3.2).

In short, the particle m will vibrate harmonically in the vicinity of $r = 0$ when $k \rightarrow 0$ (here we consider $k^2 < 0.04$); when $k^2 > 0.04$ and the energy h is not large enough to break the H bond, the particle will vibrate anharmonically.

4. Application to some realistic physics systems

We have mentioned that the H bond occurs frequently in nature as a form of binding energy. It is the H bonds that join water molecules together and make the H_2O exist in a liquid state rather than in a gaseous state at normal temperatures. In the DNA double-helix chain, there are two H bonds between an adenine-thymine base pair and three H bonds between a guanine-cytosine base pair. The stretch of the H bonds may be an important reason for the existence of open states in DNA. In a superstructure of myosin molecules, there are two α -helical polypeptides, and in each helix there are three one-dimensional chains of peptide groups joined together by H bonds which stabilize the α -helix structure.

In this section, we shall study the vibrational properties of the H bonds in the three cases mentioned above.

First, we expand the solution (3.15) into a Fourier series

$$\begin{aligned} r &= A_0 + A_1 \cos[(\pi/K)\sqrt{(B/2m)(e_1 - e_3)}(t - t_0)] \\ &\quad + A_2 \cos[(2\pi/K)\sqrt{(B/2m)(e_1 - e_3)}(t - t_0)] + \dots \end{aligned} \quad (4.1)$$

where

$$A_0 = \frac{A}{B} \left[e_3' + 2 \left(\frac{\pi}{Kk} \right)^2 (e_2' - e_3') \sum_{l=0}^{\infty} \frac{q^{2l+1}}{(1 - q^{2l+1})^2} \right] \quad (4.2a)$$

$$A_1 = \frac{2A}{B} \left(\frac{\pi}{Kk} \right)^2 (e_2' - e_3') \left(\sum_{l=0}^{\infty} \frac{2q^{2(l+1)}}{(1 - q^{2l+3})(1 - q^{2l+1})} - \frac{q}{(1 - q)^2} \right) \quad (4.2b)$$

Table 1. The ranges of the fundamental frequencies for the three molecules.

	ω_1 (10^{13} s^{-1})	$\tilde{\nu}_1$ (cm^{-1})
H ₂ O	7.08–10.9	376–578
DNA	0.403–0.621	21–33
α -helix protein	0.663–1.02	35–54

$$A_2 = \frac{4A}{B} \left(\frac{\pi}{Kk} \right)^2 (e'_2 - e'_3) \left(\sum_{l=0}^{\infty} \frac{q^{2l+3}}{(1-q^{2l+5})(1-q^{2l+1})} - \frac{q^2}{(1-q)(1-q^3)} \right) \dots \quad (4.2c)$$

where the relation between q and k is

$$k^2 = 16q(1 + q^2 + q^6 + \dots)^4 / (1 + 2q + 2q^4 + \dots)^4. \quad (4.3)$$

The fundamental frequency of the system is

$$\omega_1 = (\pi/K) \sqrt{(B/2m)(e_1 - e_3)} = \sqrt{(A/2m)} \omega'_1 \quad (4.4)$$

where

$$\omega'_1 = (\pi/K) \sqrt{e'_1 - e'_3}. \quad (4.5)$$

The relation between ω_1 and the energy h is shown in figure 2. When h is larger than $0.14A^3/B^2$ (i.e. h is close to h_c), the curve drops down quickly. We think that the system will be unstable when $h \rightarrow h_c$. In fact, the 2–3-power potential does not conform to the real H-bond energy in the vicinity of the point r_c . So we shall only consider the range $h \in (0, 0.143A^3/B^2)$ and the corresponding frequency range $\omega_1 \in (1.3\sqrt{A/2m}, 2\sqrt{A/2m})$.

The coefficients A and B have been estimated in [8]:

$$A = 0.62 \text{ eV } \text{\AA}^{-2} \quad B = 0.83 \text{ eV } \text{\AA}^{-3}. \quad (4.6)$$

So

$$r_c = 2A/3B = 0.5 \text{ \AA} \quad h_c = 4A^3/27B^2 = 0.051 \text{ eV}. \quad (4.7)$$

That is to say, when the energy of m is larger than 0.051 eV (or the corresponding displacement is larger than 0.5 \text{\AA}), the H bond will be broken.

In table 1, we list the fundamental frequency ranges and the corresponding ranges of the wavenumber $\tilde{\nu}_1$ of H-bond vibrations in water, DNA and α -helix protein. Where the mass m_p of the hydrogen proton in water is 1.6726×10^{-27} kg, the average mass of bases in DNA is $308m_p$ and the average mass of a small unit cell in α -helix protein is $114m_p$.

The frequency values that we have obtained all belong to the range of infrared absorption. We know that the vibration modes of H-bond stretch in B-DNA at 10–120

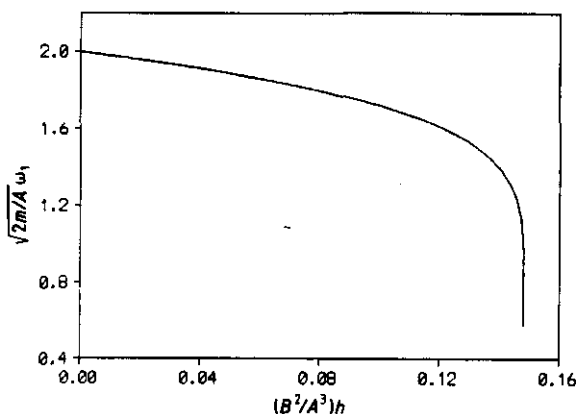


Figure 2. The curve describing the fundamental frequency as a function of energy.

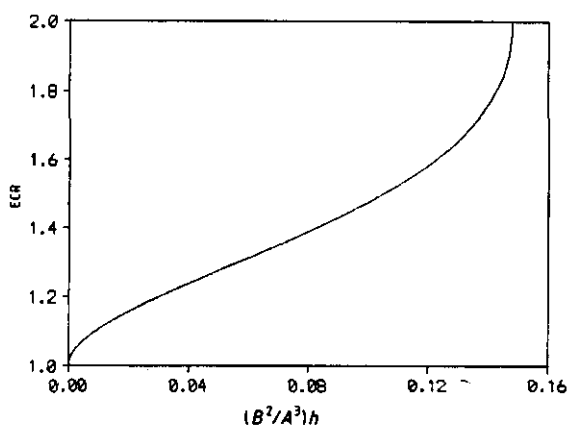


Figure 3. The curve describing the ECR as a function of energy.

cm^{-1} have been observed in both low-frequency Raman scattering [9, 10] and Fourier-transform infrared absorption [11]. The laser Raman measurements on living cells published by Webb [12] indicated that there exist small Raman shifts of $0\text{--}200\text{ cm}^{-1}$ in α -helix proteins. It is seen that our results are exactly within these ranges. In particular, our calculated range of the vibration frequencies in DNA includes the value of 30 cm^{-1} which has been observed to occur in Raman scattering by Painter *et al* [10]. We think that the anharmonicity in the stretch of the H bonds plays a major role in explaining the Raman shifts observed in experiments on biological macromolecules.

5. Discussion and conclusions

We have already mentioned that the ECR defined in section 2 reveals the asymmetry of the curve of H-bond energy (figure 3). The higher the energy, the larger is the ratio. When the energy approaches h_c , the ratio is close to 2. That is to say, with the same

Table 2. The ranges of the secondary frequencies for the three molecules.

	ω_2 (10^{13} s^{-1})	$\tilde{\nu}_2$ (cm^{-1})
H ₂ O	14.1–19.6	751–1040
DNA	0.807–1.12	42–60
α -helix protein	1.32–1.84	70–97

energy h_c , the distance that the particle is pulled out of its equilibrium position is twice that when it is compressed inwards. Therefore, the H bond is easier to extend than to compress. In the case of liquid water, this implies that the incompressibility of water is closely related to the character of the H bonds. For the same reason it is difficult to compress the α -helix protein along the helical axis. Similarly, the diameter of the DNA double helix is about 20 Å; it is also difficult to reduce this value.

We know that the Lennard-Jones potential is more suitable for describing the H bond in the whole range $R \in (0, \infty)$ than are the Toda and 2–3-power potentials. We assume that the particle m is moving in the Lennard-Jones potential field. When $r = e_2 = 0.5 \text{ \AA}$, we have $e_3 = -0.28 \text{ \AA}$. In this case, $|e_2/e_3| \approx 1.8$. This value is approximately equal to the corresponding value in the case of the 2–3-power potential. It seems that our conclusion on the incompressibility of the liquid water is independent of the potential that we use. We can reach a similar conclusion for the three potentials mentioned above. Consequently, the non-linearity of the H-bond potential is a key factor in the incompressibility of the water.

In section 4, we have calculated the ranges of fundamental frequencies in the case of water, DNA and α -helix protein. However, we have not considered the secondary frequencies yet. When the energy $h = 0.08A^3/B^2$, we have $q = 0.05$, $A_1 = 0.29 \text{ \AA}$ and $A_2 = 0.025 \text{ \AA}$. A_2 is about 10% of A_1 . So, in the case of $h > 0.08A^3/B^2$, the secondary frequency $\omega_2 = 2\omega_1$ cannot be neglected.

In table 2, we list the ranges of ω_2 (and its corresponding wavenumber $\tilde{\nu}_2$) for the three cases. These values also belong to the ranges of low-frequency Raman shifts which we mentioned in section 4.

We have only considered the stretch vibrations of a single H bond in this paper. In fact, it is the pure ideal case. It must be noted that real cases are much more complicated. Many H bonds exist in liquid water. These H bonds interact with each other and form many H-bond networks. The number of H bonds in one H-bond network is different from that in another network, and the number varies with conditions such as the temperature. In DNA and α -helix proteins, the stacking energy and other interactions also affect the vibrations of H bonds. It is difficult to calculate the vibration frequencies of H bonds in real cases, and the methods of statistics are required to achieve this. We shall not carry out any further calculations here.

In conclusion, we have used the 2–3-power potential to describe the H-bond energy approximately and have calculated the frequency ranges of the stretch vibration of H bonds, which are consistent with the observed values. Further experimental data are needed in order to examine the theory presented here.

Acknowledgments

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