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A Mathematical Theory for Vibrational Levels Associated with Hydrogen Bonds

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Abstract. We describe recent work in which we propose an alternative to the usual time independent Born-Oppenheimer approximation that is specifically designed to describe molecules with Hydrogen bonds. In our approach, the masses of the Hydrogen nuclei are scaled differently from those of the heavier nuclei, and we employ a specialized form for the electron energy level surface. Consequently, anharmonic effects play a role in the leading order calculations of vibrational levels for symmetric molecules. For non-symmetrical molecules, the different vibrational modes appear at different orders of approximation.

1 Introduction

The standard time-independent Born-Oppenheimer (BO for short) approximation [1] takes advantage of the large masses of the nuclei relative to the mass of the electrons. With mass unit given by the mass of the electrons, the masses of the nuclei are of order ϵ^{-4}, with ϵ small. It allows one to compute the low-lying vibrational states of the nuclear motion from knowledge of the ground state electron energy surface near its minimum, under the following two assumptions: the ground state is isolated from the other energy surfaces near its minimum and the minimum is non-degenerate. To leading order, as is well known, the vibrational energy levels are those of a harmonic oscillator (HO for short) associated with the non-degenerate minimum, see [3] for a recent review and references.

Despite its many successes, this approximation may fail to give accurate results when applied to molecules that contain hydrogen bonds. The binding energy of such bonds is typically very small, and the mass of the Hydrogen nucleus is an order of magnitude smaller than that of other nuclei such as Carbon. Moreover, the experimental vibrational spectra of some tri-atomic molecules with hydrogen bonds, such as $F\text{-}H\text{-}F^-$ and $F\text{-}H\text{-}Cl^-$, display significant deviations from the approximate harmonic spectrum, see [2].

In [4, 6], we revisit the BO approximation in order to propose an alternative taking into account the specificities of simple molecules that contain hydrogen bonds. Our approach differs from the standard BO approximation in the following way. First, we scale the masses of the Hydrogen nuclei as ϵ^{-3} while keeping the heavier nuclei scale as ϵ^{-4}. Note that for $\epsilon \simeq 0.082$ corresponding to the mass of the Carbon nucleus, the mass of the Hydrogen nucleus is approximately equal to $1.015\epsilon^{-3}$ times that of the electrons. Second, we model the electron energy surface in a special way that depends on ϵ. This takes into account the smallness of some coefficients of the harmonic potential associated with the hydrogen bond. The case of symmetric linear tri-atomic molecules in which bending is ignored is dealt with in [4], whereas [6] is devoted to asymmetric tri-atomic molecules in which rotations are included. Note that the local behaviour of the ground state energy surface around a minimum is enough to describe the low energy vibrational levels because the corresponding wave packets are strongly localized close to this minimum, as $\epsilon \to 0$. We describe these two model cases in an informal way below.

In order to keep things simple, we only discuss here the scalar Hamiltonians obtained by reducing the molecular Hamiltonian to kinetic energy plus smooth potential given by the ground state energy surface, E_{GS}. Extensions of these results to the full molecular Hamiltonians are provided in [4, 6].

2 The symmetric case

We consider here a tri-atomic molecule of the form A-H-A, where the A's are nuclei of masses ϵ^{-4} and H is a Hydrogen nucleus of mass ϵ^{-3}. The nuclei are constrained to move on a fixed axis. The reduced scalar Hamiltonian reads

$$H_S(\epsilon) = -\frac{\epsilon^4}{2}\Delta_W - \frac{\epsilon^3}{2}\Delta_Z + E_{GS}(\epsilon, W, Z) \tag{1}$$

where the Jacobi coordinates $(W, Z) \in \mathbb{R}^2$ give the distance between the two nuclei A and the location of the H nucleus w.r.t. the center of mass of the two A's, see Fig. 1. Some inessential factors coming from reduced masses are

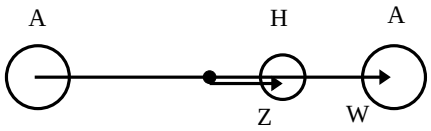

Figure 1. Coordinate system for A-H-A

simplified by a trivial rescaling of the variable Z. At equilibrium, we assume the molecule is symmetrical so that the minimum of the ground state energy surface lies at $(W_0, 0)$, with $W_0 > 0$. Numerics on the ion F-H-F^- suggest the expansion

$$\begin{aligned} E_{GS}(\epsilon, W, Z) &= E_0 + a_1(W - W_0)^2 + (a_2\epsilon - a_3(W - W_0))Z^2 + a_4 Z^4 + \cdots \\ &\equiv E_1(\epsilon,\, W,\, Z) + O((W - W_0)^\alpha Z^{2\beta}), \quad \alpha, \beta \in \mathbb{N},\ \alpha + \beta \geq 3, \end{aligned} \tag{2}$$

where the ϵ dependence only enters in the coefficient of Z^2, which is much smaller than the other coefficients. Note that symmetry implies an expansion in Z^2 and

$E_1(\epsilon, W, Z)$ is bounded below in case the following condition holds:

$$a_1, a_3, a_4 > 0, \quad \text{and either} \quad a_3^2 < 4a_1a_4, \quad \text{or} \quad a_3^2 = 4a_1a_4 \quad \text{and} \quad a_2 \geq 0. \tag{3}$$

Keeping only the leading term E_1 in the expansion defines the approximation $H_1(\epsilon) = -\frac{\epsilon^4}{2}\Delta_W - \frac{\epsilon^3}{2}\Delta_Z + E_1(\epsilon, W, Z)$. By rescaling the variables according to $w = (W - W_0)/\epsilon$, $z = Z/\epsilon^{1/2}$, $H_1(\epsilon)$ is equivalent to $E_0 + \epsilon^2 H_{NF}$, where the ϵ-independent, anharmonic, normal form Hamiltonian reads

$$H_{NF} = -\frac{1}{2}\Delta_w - \frac{1}{2}\Delta_z + a_1w^2 + (a_2 - a_3w)z^2 + a_4z^4. \tag{4}$$

It is proven in [4] that under condition (3) the spectrum of H_{NF} is discrete and that it is related to the spectrum of $H_S(\epsilon)$, $\sigma(H_S(\epsilon))$, in the following sense: *For any eigenvalue $\mathcal{E}_{NF}^{(j)}$ of H_{NF}, there exists $\mathcal{E}_S(\epsilon)$ in $\sigma(H_S(\epsilon))$ such that*

$$\mathcal{E}_S(\epsilon) = E_0 + \epsilon^2\mathcal{E}_{NF}^{(j)} + O(\epsilon^3), \quad \textit{as} \quad \epsilon \to 0. \tag{5}$$

Such results hold for more mass scales and other ϵ-dependent potentials, see [5].

3 The non-symmetric case

Here a tri-atomic molecule of the form *A-H-B* is considered, in a full three dimensional setting. Again, we start from the reduced scalar Hamiltonian in Jacobi coordinates. They are defined as in Fig. 2: $\boldsymbol{X}$ is the vector from the heavy nucleus A to the Hydrogen nucleus H whereas $\boldsymbol{Y}$ links the center of mass of AH to the other heavy nucleus B. We express $\boldsymbol{Y}$ by means of spherical coordinates with respect to the center of mass frame of reference as $\boldsymbol{Y} = (Y, \theta, \phi)$. For $\boldsymbol{X}$, we use a moving frame with third axis z' parallel to $\boldsymbol{Y}$ and first axis parallel to $\boldsymbol{Y} \wedge z$, z being the third axis of the fixed frame. Using cylindical coordinates in the moving frame, we get $\boldsymbol{X} = (R, \gamma, X)$. In these variables, the ground state

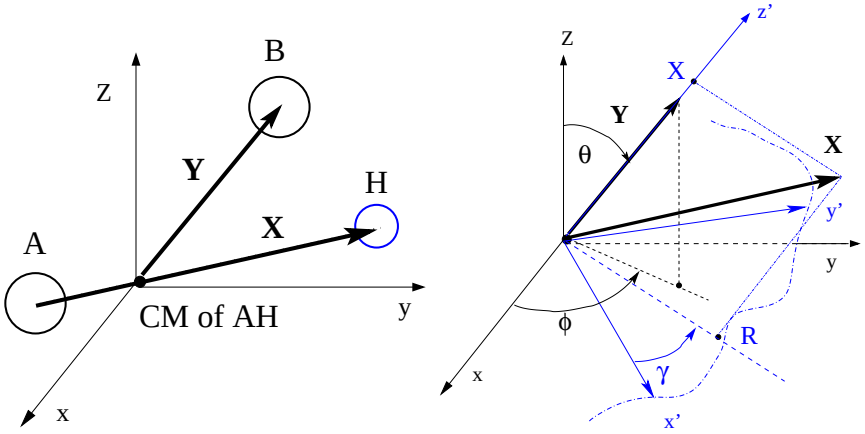

Figure 2. Coordinate system for *A-H-B*

energy surface does not depend on the angles, but the kinetic energy becomes messy. Taking mass scales as above, the scalar Hamiltonian reads

$$H_S(\epsilon) = -\frac{\epsilon^3}{2\mu_1(\epsilon)}\Delta_{\boldsymbol{X}} - \frac{\epsilon^4}{2\mu_2(\epsilon)}\Delta_{\boldsymbol{Y}} + E_{GS}(\epsilon, X, R, Y), \tag{6}$$

where $\mu_j(\epsilon)$ are reduced masses that are regular in ϵ. The molecule is assumed to be linear, *i.e.* at equilibrium, $\boldsymbol{X}$ and $\boldsymbol{Y}$ are colinear, so that $R_{\rm eq} = 0$.

The behaviour of the ground state close to the equilibrium point $(X_0, 0, Y_0)$ is modelled after comparisons with numerics on a typical case, here F-H-Cl^-, and taking into account the symmetries. We consider

$$\begin{aligned} E_{GS}(\epsilon, X, R, Y) &= V_1(X) + \epsilon V_2(X, R, Y), \qquad \text{with} \\ V_1(X) &= a_0 + a_2(X - X_0)^2 + \cdots \\ V_2(X, R, Y) &= b_{0,2,0}R^2 + b_{1,0,1}(X - X_0)(Y - Y_0) + b_{0,0,2}(Y - Y_0)^2 + \cdots \end{aligned} \tag{7}$$

The decomposition (7) reflects the fact that the molecule behaves like a compound AH interacting weakly with B, depending on the "proton affinities" of A and B. Also, the quadratic term in $(X - X_0)$ in V_2 is incorporated in V_1.

Making explicit the kinetic energy, expanding $H_S(\epsilon)$ in powers of $\epsilon^{1/4}$ and taking into account the scales of the quantum fluctuations leads to

$$\begin{aligned} H_S(\epsilon) &= a_0 - \frac{\epsilon^3}{2\mu_1}\left(\frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\,\frac{\partial^2}{\partial \gamma^2}\right) + \epsilon b_{0,2,0}R^2 \\ &- \frac{\epsilon^3}{2\mu_1}\frac{\partial^2}{\partial X^2} + a_2(X - X_0)^2 - \frac{\epsilon^4}{2\,\mu_2}\frac{\partial^2}{\partial Y^2} + \epsilon b_{0,0,2}(Y - Y_0)^2 + \cdots \end{aligned} \tag{8}$$

where the remaining terms can be safely neglected. This leading term is the sum of a one dimension HO describing the A-H streching modes, a two dimensional HO corresponding to degenerate bending modes and a one dimensional HO associated with the AH-B streching modes. The corresponding eigenvalues appear at different orders in ϵ and are given by

$$\begin{aligned} \mathcal{E}_X^{(n_1)}(\epsilon) &= \epsilon^{3/2}\sqrt{2a_2/\mu_1}(n_1 + 1/2), \qquad \mathcal{E}_{R,\gamma}^{(n_2)}(\epsilon) = \epsilon^{4/2}\sqrt{2b_{0,2,0}/\mu_1}(n_2 + 1), \\ \mathcal{E}_Y^{(n_3)}(\epsilon) &= \epsilon^{5/2}\sqrt{2b_{0,0,2}/\mu_2}(n_3 + 1/2). \end{aligned} \tag{9}$$

It is shown in [6] that these HO approximate $H_S(\epsilon)$ in the sense that:
For any choice of eigenvalue (9), there exists $\mathcal{E}_S(\epsilon)$ in $\sigma(H_S(\epsilon))$ such that

$$\mathcal{E}_S(\epsilon) = a_0 + \mathcal{E}_X^{(n_1)}(\epsilon) + \mathcal{E}_{R,\gamma}^{(n_2)}(\epsilon) + \mathcal{E}_Y^{(n_3)}(\epsilon) + O(\epsilon^3), \quad \textit{as} \quad \epsilon \to 0. \tag{10}$$

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