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DIATOMIC MOLECULES AS PERTURBED MORSE OSCILLATORS AND THE EFFECT OF THE BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

The University of Oklahoma Ph.D. 1981

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DIATOMIC MOLECULES AS PERTURBED MORSE OSCILLATORS AND THE EFFECT OF THE BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
LAILA AMIN EL-KHARADLY
Norman, Oklahoma
1981

DIATOMIC MOLECULES AS PERTURBED MORSE OSCILLATORS AND THE EFFECT OF THE BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF PHYSICS AND ASTRONOMY

BY

J Neal Huffaker

David E Golden

Harold

DEDICATION

This dissertation is dedicated to my parents, Mr. Amin El-Kharadly and Mrs. Attiat Khalifa, and to my children, Khalid and Mona El-Ibiary.

ACKNOWLEDGEMENT

I want to express my deepest appreciation to Dr. Neal Huffaker for suggesting this topic and his patient help and guidance throughout the completion of this work. I also wish to thank Dr. David Golden, Dr. Helmut Fischbeck and Dr. Harold Huneke for reading the manuscript and for giving me helpful suggestions.

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ABSTRACT

The perturbed Morse oscillator is modified by adding a velocity-dependent term to allow for the nonadiabatic correction due to the breakdown of the Born-Oppenheimer approximation. A recurrence formula for this velocity-dependent term is derived. This formula is then used to derive - via a perturbation calculation - explicit expressions for the Dunham coefficients which include the nonadiabatic corrections.

Values of the PMO parameters (including the velocity-dependent parameter) are obtained for the ground state of the three isotopic molecules H_2, HD, and D_2 using two approaches. In the first approach, iteration computations are used to evaluate the different parameters from the experimentally derived Dunham coefficients. In the second approach, the PMO parameters are obtained by fitting the experimental energies directly in terms of the model parameters. The second approach is preferred to the first due to inaccuracies in the empirical Dunham coefficients.

The nonadiabatic corrections calculated using the present method for H_2 and D_2 are in agreement with those obtained using alternative methods. Moreover the present method proves very successful in predicting eigenvalues for HD which are in a very good agreement with the experimental ones.

DIATOMIC MOLECULES AS PERTURBED MORSE OSCILLATORS AND THE EFFECT OF THE BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

CHAPTER I

INTRODUCTION

The Born-Oppenheimer approximation [1] based on the fact that electrons move thousands of times faster than the heavy nuclei in a diatomic molecule, involves a complete separation between electronic and nuclear motion. One assumes that the nuclei move so slowly that the electrons are not affected by the nuclear speed, while the electrons move so fast that the nuclei observe only an effective vibrational potential energy due to the electronic motion. In this approximation, functions that describe the motion of the electrons are obtained by keeping the nuclei fixed in space, then the motion of the nuclei themselves are considered [2]. The stationary state wavefunction of the molecule is then the product of the electronic and nuclear wavefunctions. In this fashion, the nuclear motion (vibration and rotation) is reduced to a one-dimensional, one-particle problem in quantum mechanics solvable by analytical or numerical methods.

The radial Schroedinger equation for the rotating oscillator is given by

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 J(J+1)}{2\mu r^2}]\psi_{v,J}(r) = E_{v,J}\psi_{vJ}(r) \,, \qquad (1.1)$$

where r is the internuclear distance, μ is the reduced mass, and v and J are the vibrational and rotational quantum numbers, respectively. V(r) is the potential energy function of the nuclei and consists of two parts; the nuclear repulsion term $V_{nn}(r) = \frac{Z_1 Z_2}{r} e^2$ and the electronic energy $V_e(r)$ calculated by considering the nuclei fixed in space a distance r apart. The potential energy function V(r) is a complicated function of r and of the electronic quantum numbers and is not known exactly except for the simplest molecules.

Ideally, a model potential energy function for a vibrating diatomic molecule should have a simple, analytic form. The worth of that function is judged by the agreement between the eigenvalues it predicts and the spectroscopically observed term values. Several different potential models and approximation methods have been used with varying degrees of success. Empirical potential-energy curves for the bound states of diatomic molecules can be determined from experimental data for the vibrational levels G(v) and rotational constants B(v) by using the Rydberg-Klein-Rees method (RKR) [3]. In this method the turning points in the potential energy curve are given by

$$r_{\substack{max\\min}} = (f^2 + \frac{f}{g})^{\frac{1}{2}} \pm f \ .$$

The intermediate functions f and g which depend upon the term values G(v) and the rotational constants B(v) have the integral form:

$$f(v) = \frac{\hbar}{(2hc\mu)^{\frac{1}{2}}} \int_{v_{min}}^{v} [G(v) - G(v')]^{-\frac{1}{2}} dv'$$

and

$$g(v) = \frac{(2hc\mu)^{\frac{1}{2}}}{\hbar} \int_{v_{min}}^{v} B(v')[G(v) - G(v')]^{-\frac{1}{2}} dv'$$

where μ is the reduced mass. The lower limit of integration v_{min} is that value of v for which the quantity $E_{(v,J=0)} = Y_{00} + G(v)$ vanishes. The functions G and B in the above equations are polynomials that have been fitted to experimental data.

Another approach is the Morse potential [4] given by:

$$V(q) = V_e(1 - e^{-aq})^2 ,$$

where $q = r - r_e$, r_e is the equilibrium internuclear separation, V_e and a are constants determined from molecular properties. While this potential has analytic solutions and is probably the best three parameter model for actual molecules, it fails to describe the fine spectroscopic details and it is difficult to include the effect of rotation in the potential function.

One of the standard potentials for describing the vibrational motion of a diatomic molecule is the Dunham potential [5]. Dunham applied a version of the WKB approximation to a perturbed harmonic oscillator. The Dunham potential is given by

$$V(r) = hca_0\xi^2(1 + a_1\xi + a_2\xi^2 + \ldots) ,$$

where the leading term here is a harmonic oscillator potential with $a_0 = \omega_e^2/4B_e$ where ω_e is the classical frequency, $B_e = h/(8\pi^2\mu r_e^2 c)$, $\xi=(r-r_e)/r_e$, μ is the nuclear reduced mass and r_e is the value of the internuclear distance r at equilibrium. This potential has poor convergence properties and does not produce analytic wavefunctions. Dunham expressed the eigenvalues $E_{v,J}$ of equation (1.1) as a double power series in vibrational and rotational quantum numbers $(v+\frac{1}{2})$ and J as follows:

$$E_{v,J} = \sum_{j,k} Y_{jk}(v + \tfrac{1}{2})^j [J(J+1)]^k \ . \tag{1.2}$$

The term values $G(v)$ and the rotational constants $B(v)$ are related to the empirical coefficients by:

$$G(v) = \sum_{j=1} Y_{j0}(v + \tfrac{1}{2})^j \quad , \tag{1.3}$$

and

$$B(v) = \sum_{j=0} Y_{j1}(v + \tfrac{1}{2})^j \ . \tag{1.4}$$

Coefficients with $k>1$ are the centrifugal distortion constants D_v and H_v ..., etc.

$$D(v) = -\sum_{j=0} Y_{j2}(v + \tfrac{1}{2})^j \quad , \tag{1.5}$$

$$H(v) = \sum_{j=0} Y_{j3}(v + \tfrac{1}{2})^j \quad , \tag{1.6}$$

and the energy eigenvalues can be rewritten as:

$$E_{v,j} = G(v) + B(v)[J(J+1)] + D(v)[J(J+1)]^2 + H(v)[J(J+1)]^3 + \ldots \tag{1.7}$$

Among analytic potentials, the one currently exhibiting the greatest capacity for accuracy is the perturbed Morse oscillator (PMO) potential [6], defined by:

$$V(r) = V_e[y^2 + \sum_{n=4} b_n y^n] \ ,$$

where $y = 1 - \exp[-a(r - r_e)]$. This potential converges for all values of r except for a singularity at $r = 0$. Its parameters are related to the dissociation energy D_e by

$$D_e = V_e(1 + b_4 + b_5 + \ldots) \ .$$

The leading term of the PMO potential is a Morse potential [4]. Formulas have been given in [6] for calculating the three Morse parameters $\rho = ar_e$, $\sigma = (2\mu V_e)^{\frac{1}{2}}/a\hbar$, and $\tau = V_e/hc$. Here, σ is approximately the number of bound states of the Morse oscillator, roughly $\sigma \simeq \omega_e/2\omega_e x_e$. Formulas for the PMO coefficients up through b_{12} were given by Huffaker [6,7]. The expressions obtained for the energy levels via perturbation [6] were found to be mathematically equivalent to those obtained by Dunham [5]. The Dunham coefficients in the PMO model are expressed in terms of the modified Dunham coefficients as:

$$Y_{jk} = Y_{jk}^{(0)} + Y_{jk}^{(2)} + Y_{jk}^{(4)} + \dots ,$$

where

$$Y_{jk}^{(0)} \gg Y_{jk}^{(2)} \gg Y_{jk}^{(4)} \gg \quad \text{etc.}$$

and where $Y_{jk}^{(0)}/Y_{jk}^{(2\ell)} \simeq \sigma^{(2\ell)}$. In deriving the formulas for the various Dunham coefficients using the PMO model, the Born-Oppenheimer approximation was assumed to be valid. This should be accurate for molecules with large reduced masses. For light molecules however the validity of such an approximation is questionable.

The drawbacks of the Born-Oppenheimer approximation can be understood by considering the molecular Hamiltonian H which consists of the kinetic energy operators T of the nuclei and the electrons and the Coulomb interaction V between all particles:

$$\begin{aligned} H &= T + V \\ &= T_n + T_e + V_{nn} + V_{ne} + V_{ee} \end{aligned} \tag{1.8}$$

$$= \sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} - \sum_{i} \frac{1}{2}\nabla_{i}^{2} + \sum_{\alpha>B} \frac{z_{\alpha} z_{B}}{|\underset{\sim}{r}_{\alpha} - \underset{\sim}{r}_{B}|} - \sum_{\alpha,i} \frac{z_{\alpha}}{|\underset{\sim}{r}_{\alpha} - \underset{\sim}{r}_{i}|} + \sum_{i>j} \frac{1}{|\underset{\sim}{r}_{i} - \underset{\sim}{r}_{j}|} \tag{1.9}$$

where α refers to a nucleus with mass M_{α}, charge z_{α}, and position $\underset{\sim}{r}_{\alpha}$, and where i refers to an electron with position $\underset{\sim}{r}_{i}$.

[Atomic units ($m_e = \hbar = e = 1$) are used.]

Considering a diatomic molecule, where the Hamiltonian is relatively simple, Eq. (1.9) gives:

$$H = -\left[\frac{1}{2}\left(\frac{\nabla_1^2}{M_1} + \frac{\nabla_2^2}{M_2} + \sum_i \nabla_i^2\right)\right] + V \text{ ,} \tag{1.10}$$

where the positions of each particle are relative to a laboratory frame. Referring all coordinates to the nuclear center of mass, Eq. (1.10) yields [8]

$$H = T_{CM} - \frac{1}{2}\left(\frac{1}{\mu} \nabla_r^2 + \frac{1}{M_1+M_2} \sum_{i,j} \underset{\sim}{\nabla}_i \cdot \underset{\sim}{\nabla}_j + \sum_i \nabla_i^2\right) + V(r;\underset{\sim}{r}_i) \tag{1.11}$$

and the exact Schroedinger equation is

$$H\psi = E\psi \text{ ,} \tag{1.12}$$

where r is the relative position of M_1 with respect to M_2, $\underset{\sim}{r}_i$ are the position vectors of the electrons relative to the nuclear center of mass, and M_1 and M_2 are the nuclear masses. Since T_{CM} depends only on the molecular center of mass and V is a function of r and $\underset{\sim}{r}_i$, Eq. (1.12) is separable into center-of-mass motion and relative particles (internal) motion. The exact Schroedinger equation for the internal motion is

$$\left[-\frac{1}{2}\left(\frac{1}{\mu} \nabla_r^2 + \sum_i \nabla_i^2 + \frac{1}{M_1+M_2} \sum_{i,j} \underset{\sim}{\nabla}_i \cdot \underset{\sim}{\nabla}_j\right) + V(r \cdot \underset{\sim}{r}_i) - E\right]\psi = 0 \tag{1.13}$$

In the Born-Oppenheimer approximation, one assumes that the molecular wavefunction ψ is given by:

$$\psi(r;\underset{\sim}{r}_i) = \psi_n^e\,(\underset{\sim}{r}_i;r)\chi(r) \ , \tag{1.14}$$

where $\psi_n^e\,(\underset{\sim}{r}_i;r)$ is the electronic wavefunction and $\chi(r)$ is the nuclear function. Substituting Eq. (1.14) into Eq. (1.13) and neglecting the terms $1/(M_1+M_2)\,\sum_{i,j}\,\underset{\sim}{\nabla}_i\cdot\underset{\sim}{\nabla}_j$ and $(1/2\mu)\nabla_r^2\psi_n^e$, which couple electronic and nuclear motion, we obtain the equation:

$$\chi(r)\,[-\frac{1}{2}\sum_i\nabla_i^2 + V(\underset{\sim}{r}_i,r)]\psi_n^e\,(\underset{\sim}{r}_i;r)] - \psi_n^e\,(\underset{\sim}{r}_i;r)\frac{1}{2\mu}\,\nabla_r^2(r)$$

$$= E^{BO}\psi_n^e\,(\underset{\sim}{r}_i;r)\chi(r) \tag{1.15}$$

for the Born-Oppenheimer approximation. Defining $W_n^{BO}(r)$ through the equation:

$$[-\frac{1}{2}\sum_i\nabla_i^2 + V(\underset{\sim}{r}_i,r) - W_n^{BO}(r)]\psi_n^e\,(\underset{\sim}{r}_i;r) = 0 \tag{1.16}$$

we obtain by substituting into Eq. (1.15)

$$[-\frac{1}{2\mu}\,\nabla_r^2 + W_n^{BO}(r) - E^{BO}]\chi(r) = 0 \tag{1.17}$$

which is the equation for nuclear motion. The quantity $W_n^{BO}(r)$, the electronic energy as a function of nuclear coordinates, plays now the role of the potential [V in Eq. (1.1)] in which the nuclei move.

For light molecules, the Born-Oppenheimer approximation fails to predict some experimental features. For example electronic isotope shifts have been observed for diatomic hydrides [9,10], although according to the Born-Oppenheimer approximation, the potential curve of each electronic state of the molecule should be invariant to isotopic substitution. The isotope effects must be due to the small terms involving the coupling between electronic and nuclear motion, neglected in the Born-Oppenheimer approximation.

To allow for the effects of those small terms, a more rigorous treatment of Eq. (1.13) is needed. For that purpose we rewrite the Hamiltonian of Eq. (1.13) as the sum of two terms:

$$H = H_e^0 + H' \tag{1.18}$$

where

$$H_e^0 = -\frac{1}{2}\sum_i \nabla_i^2 + V(\underset{\sim}{r}_i;r) \tag{1.19}$$

and

$$H' = -\frac{1}{2\mu}\nabla_r^2 - \frac{1}{2(M_1+M_2)}\sum_{i,j} \underset{\sim}{\nabla}_i\cdot\underset{\sim}{\nabla}_j \ . \tag{1.20}$$

We expand the molecular wavefunction as a sum of the product terms

$$\psi(\underset{\sim}{r}_i;r) = \sum_n \chi_n(r)\psi_n(\underset{\sim}{r}_i;r) \ , \tag{1.21}$$

where the basis electronic states are eigenstates of the Born-Oppenheimer equation:

$$H_e^0\psi_n(\underset{\sim}{r}_i;r) = W_n^{BO}(r)\psi_n(\underset{\sim}{r}_i;r) \ , \tag{1.22}$$

and the sum is over all states. To determine the nuclear motion we must solve

$$[H_e^0 + H' - E]\sum_n \chi_n(r)\psi_n(\underset{\sim}{r}_i;r) = 0 \ . \tag{1.23}$$

Multiplying Eq. (1.23) on the left by the complex conjugate of one of the complete set of eigenstate of H_e^0, e.g. ψ_m^*, and integrating over the electron coordinates we obtain the following rigorous set of equations for the functions $\chi_n(r)$:

$$[-\frac{1}{2\mu}\nabla_r^2 + W_n^{BO}(r) + H'_{nn}(r) - E]\chi_n(r) = -\sum_{m\neq n} H'_{mn}(r)\chi_m(r) \qquad (1.24)$$

where

$$H'_{mn} = \int\psi_m^*(\underset{\sim}{r}_i;r)H'\psi_n(\underset{\sim}{r}_i,r)dr_i \ . \qquad (1.25)$$

By neglecting the off-diagonal elements of H' (i.e. considering $H'_{mn}=0$) we get the adiabatic approximation $\psi=\chi_n\psi_n$ and a Schroedinger-type equation for the nuclear motion:

$$[-\frac{1}{2\mu}\nabla_r^2 + U_n^{ad} - E]\chi(r) = 0 \qquad (1.26)$$

where the potential energy $U_n^{ad}(r)$ is given by:

$$\begin{aligned} U_n^{ad}(r) &= W_n^{BO}(r) + H'_{nn}(r) \\ &= W_n^{BO}(r) - \frac{1}{2(M_1+M_2)} \langle n|\sum_{i,j}\nabla_i\cdot\nabla_j|n\rangle - \frac{1}{2\mu}\langle n|\nabla_r^2|n\rangle \end{aligned} \qquad (1.27)$$

where the latter two terms are the adiabatic corrections to the Born Oppenheimer approximation, which partially correct for the coupling between electronic and nuclear motion. The term "adiabatic" refers to the fact that the simple product nature of the wavefunction is still preserved by the terms giving rise to the corrections. In the ground state the matrix element $\langle 0|\nabla_r^2|0\rangle$ is given by

$$\int \psi_0^*\nabla_r^2\psi_0 dr = -\frac{1}{r^2}\int \psi_0^*(L_x^2 + L_y^2)\psi_0 d\underline{r}_i + \int \psi_0^* \frac{d^2\psi_0}{dr^2} d\underline{r}_i \qquad (1.28)$$

where L_x and L_y are the electronic angular momentum operators for rotation given by

$$L_x = -i \sum_i (y_i \frac{\delta}{\delta z_i} - z_i \frac{\delta}{\delta y_i})$$

and

$$L_y = -i \sum_i (z_i \frac{\delta}{\delta x_i} - x_i \frac{\delta}{\delta z_i}) \qquad (1.29)$$

Bunker [11] derived theoretical expressions for the isotope shift of a transition using the adiabatic potential. The theoretical results were found to be in good agreement with the observed isotope shifts of the Lyman bands of H_2, HD and D_2.

Nonadiabatic effects (i.e., nonvanishing H'_{mn}) mix different electronic states. In the nonadiabatic approximation, the wavefunction cannot be expressed as a simple product of electronic and nuclear wavefunctions. Herman and Asgharian [8] showed that only second-order energy corrections are produced as a result of including the nonadiabatic effects in the Hamiltonian. Both adiabatic H'_{nn} and nonadiabatic H'_{mn} terms contain inverse power of the reduced nuclear mass and should be unimportant for heavy molecules.

The use of ab initio variational calculations of the electronic eigenfunctions (where the wavefunction is expanded in terms of a suitable basis set and a variational method is employed for calculations) by Kolos and Wolniewicz [12,13,14] led to very accurate computations of the potential functions and the energy levels of H_2 and D_2. These computations include the adiabatic corrections.

Various techniques have been used to treat the nonadiabatic contributions to the Born-Oppenheimer approximation. In most of these calculations effective Hamiltonians were derived. Then different approximations and simplifications were used to estimate the nonadiabatic effects.

Fisk and Kirtman [15] derived a total effective potential for the nuclear vibration of a diatomic molecule in the ground state which upon simplification and approximation reduces to the form:

$$U_{eff} = E_0(r) - E_0^{eq} + W_{ad} + \frac{h^4}{\mu^2} <\Delta E>_{av}^{-1} \frac{d}{dr} B_{00}(r) \frac{d}{dr}$$

for a rotationless state (j=0) in the electronic ground state, where E_0^{eq} is the ground state electronic energy at equilibrium distance r_e. W_{ad} is the expectation value of the adiabatic correction terms in the electronic ground state. The last term in U_{eff}, namely

$$(\frac{h^2}{\mu})^2 <\Delta E>_{av}^{-1} \frac{d}{dr} B_{00}(r) \frac{d}{dr}$$

represents the nonadiabatic term which couples the ground electronic state with excited states. In this expression $B_{00} \equiv \int \psi_0^* \frac{d^2\psi_0}{dr^2} d\underline{r}_1$ and $<\Delta E>_{av}$ is the average excitation energy for the state in question. Using this effective potential, Fisk and Kirtman found that for H_2 in the ground state, the nonadiabatic effects raises the energy of the levels V=0 and V=1 by .23 and .67 cm^{-1} respectively.

Bunker [16,17] studied the effects of both the adiabatic and the nonadiabatic correction terms on the molecular constants and on the Dunham coefficients. In this study the adiabatic potential was given by

$$V(\xi)^{ad} = V(\xi) + A(\xi)$$

where $V(\xi)$ is the previously defined Dunham potential and $A(\xi)$ is the adiabatic correction given by

$$A(\xi) = <n|H'|n> = B_e(K_0 + K_1\xi + K_2\xi^2 + \ldots)$$

where B_e and ξ are as defined before, $|n>$ is the ground state electronic wavefunction and the coefficients K_i are mass-independent. Both the equilibrium distance r_e and the force constant K_e are changed as a consequence of adding $A(\xi)$. The change in the force constant is of the order of (B_e^2/ω_e^2) times the force constant. The equilibrium distance r_e^{ad} changes according to the equation

$$r_e^{ad} = [1 - (\frac{B_e^2}{\omega_e^2})2K_1]r_e \ .$$

Nonadiabatic corrections were determined from the discrepancies between the adiabatic energies and the experimental values. Both adiabatic and nonadiabatic terms were found to change the Dunham coefficients. The resultant changes are of the same order of magnitude as the higher order modified coefficients $Y_{10}^{(2)}$, $Y_{01}^{(2)}$, ... etc. [16]. The general expressions and the mass dependence of the coefficients Y_{jk} after allowing for the breakdown of the Born-Oppenheimer approximation are discussed in details in [18].

Adiabatic and nonadiabatic corrections were also found to change the dipole moment U_v of the vibrational levels of the ground electronic state of heteronuclear diatomic molecule as well as the nuclear quadrupole coupling constant eQq [19] where Q is the quadrupole moment of the nucleus and q is the electric field gradient function.

More investigations of the effects of the breakdown of the Born-Oppenheimer approximation led Bunker et al. [20] to derive an effective vibration-rotation Hamiltonian for the ground electronic states of diatomic molecules. The Hamiltonian contains an effective internuclear potential and two effective reduced masses, one for the vibrational and one for the rotational kinetic energy. From this Hamiltonian, the vibration-rotation equation is found to satisfy:

$$\left\{-\frac{\hbar^2}{2\mu_v}\frac{d^2}{dr^2} + [\omega(r) + \Delta\omega(r) + \frac{\hbar^2}{2\mu_r r^2} J(J+1) - E_{vJ}]\right\}\psi_{vJ}^{(r)} = 0$$

where $\omega(r)$ is the relativistically and adiabatically corrected internuclear potential function. The reason for using μ_v and μ_r instead of the nuclear reduced mass μ or the atomic reduced mass μ_{atomic} is to account for the fact that, while the electrons move with the nuclei as they vibrate or rotate, there is some non-adiabatic lag of electrons behind the nuclear motion. Thus using an effective vibrational or rotational reduced mass is more appropriate than using nuclear or atomic reduced mass where

$$\mu < \mu_v < \mu_{atomic} \quad \text{and} \quad \mu < \mu_r < \mu_{atomic} .$$

As a result of the non-adiabatic lag of electrons the instantaneous electrostatic potential is modified to an effective internuclear potential function $\omega(r) + \Delta\omega(r)$. A least-squares optimization of μ_v and μ_r was made [20] by fitting the eigenvalues of the above equation to the experimental energies of the electronic ground state of H_2 and D_2 molecules. Satisfactory fits were achieved using the usual nuclear reduced mass for the rotational term, but a different reduced mass for the vibrational term.

In contrast to the results of Fisk and Kirtman [15], Bunker concluded that the nonadiabatic correction should lower the energies of the vibrational levels. This lowering agrees with the measured difference between experimental results [22,23] and *ab initio* adiabatic calculations [12,14].

Bishop and Shih [24] proposed an effective Schroedinger equation for H_2 and D_2 to take into account the nonadiabatic effects. For a rotationless state, this equation is given by

$$\{-[1-\alpha(R)](2u)^{-1}\frac{d^2}{dR^2} + U(R)\}\psi(v,0;R) = E(v,0)\psi(v,0;R)$$

where R is the internuclear distance, U(R) is the Born-Oppenheimer potential corrected by the adiabatic terms, α(R) is the nonadiabatic correction factor and is given by

$$\alpha(R) = Kf(R) = -\frac{K}{2\mu}<\psi_0\,\frac{\partial^2\psi_0}{\partial R^2}>$$

where K is a flexible parameter. Bishop and Shih gave heuristic arguments for their choice of the function f(r). That effective Schroedinger equation was then simplified into two alternative forms. In the first form the correction factor α(R) was held constant at $\alpha(R_e)$ to give the equation:

$$\{-[1-\alpha(R_e)](2u)^{-1}\frac{d^2}{dR^2} + U(R)\}\psi(v,0;r) = E(v,0)\psi(v,0;R).$$

In the second form, the effective Schroedinger equation is multiplied by [1-α(R)] to give (after neglecting small terms)

$$\{-(2u)^{-1}\frac{d^2}{dR^2} + U(R) + \alpha(R)[U(R) - E(v,0)]\}\psi(v,0;R)$$

$$= E(v,0)\psi(v,0;R)\ .$$

This equation was solved individually for each vibrational level v by replacing the E(v,0) on the left hand side by the appropriate adiabatic value. Both approaches were successful in predicting nonadiabatic corrections which agree with the observed ones (the difference between experimental and calculated eigenvalues). However the second approach was found to give smaller root-mean-square deviations between theoretical and experimental values than the first approach. The first approach is entirely equivalent to the method used by Bunker [20].

The ab initio adiabatic calculation described above works well for light homonuclear diatomic molecules and improves the agreement between calculated and experimental eigenvalues for H_2 and D_2. The situation is different for a heteronuclear diatomic molecule such as HD. Difficulties arise in the adiabatic approximation because the center of mass does not coincide with the center of charge and the molecular Hamiltonian takes on a more complicated form. In regard to nonadiabatic corrections Bishop and Shih [24] pointed out that their effective Schroedinger equation is not applicable to heteronuclear molecules. Also Bunker [20] discussed the difficulties associated with heteronuclear molecules which arise from the presence of additional series of perturbations not present in the case of homonuclear molecules. Thus for HD mixing could occur between the ground state and excited states which could not mix for H_2 or D_2.

In the present work we use the PMO potential as an approximation to the actual molecular vibrational potential (including adiabatic effects) and allow for the nonadiabatic effects by adding a velocity-dependent term to the PMO potential, treating it as another perturbation. Thus we can study the nonadiabatic effects without the need for an ab initio calculation in the adiabatic approximation. We hoped that by applying that rather simple perturbation approach to hydrogen and its isotopes, we could obtain a qualitative as well as quantitative agreement with the results obtained for H_2 and D_2 molecules by Bunker et al. [21] and by Bishop and Shih [24]. If our approach proved to be successful for H_2 and D_2, we would then apply it to the HD molecule where the application of the previous approaches [20,24] was questionable. We hoped to achieve a better understanding of both the adiabatic and nonadiabatic breakdown of the Born-Oppenheimer approximation.

In Chapter II a recursion relation for a velocity-dependent interaction term is derived. Such relations make perturbation calculations of any desired order much easier.

In Chapter III the perturbation interaction with various undetermined parameters for the velocity-dependent effects as well as the usual velocity-independent PMO parameters were used to find first, second, and third-order corrections to the energy eigenvalues of the Morse oscillator. Explicit expressions for the various Dunham coefficients Y_{jk} with $j + k \leq 4$ in terms of the various parameters are derived.

In Chapter IV the numerical values of the PMO parameters are determined for the isotopic molecules H_2, HD, and D_2. Discussion of the effects of the accuracy of the Dunham coefficients on the resultant PMO parameters is included. The dependence of the new nonadiabatic correction term on the reduced mass is discussed.

In Chapter V, a least-squares optimization of the PMO parameters is made (starting with the PMO parameters obtained in Chapter IV) by fitting the eigenvalues given by Eq. (1.2) to the experimental energies. The values of the PMO parameters which give the best fit are obtained. For each molecule two sets of parameters were found to give an excellent fit with the experimental data. One of these sets was found to give a positive nonadiabatic correction, the other gives a negative nonadiabatic correction in agreement with Bunker's results [21]. These two sets of parameters are discussed and the calculated eigenvalues are compared with experiment using these two sets.

In Chapter VI we discuss the accuracy of our results and examine the mass dependence of both the adiabatic and nonadiabatic correction terms for the three isotopic molecules H_2, HD, and D_2. The nonadiabatic correction effects are compared with those obtained for H_2 and D_2 using a different approach [24]. The validity of our approach to heteronuclear molecules is discussed. The usefulness of this approach is discussed along with some of the disadvantages of using the PMO potential as an approximation of the adiabatic Born-Oppenheimer approximation at high vibrational levels.

CHAPTER II

THEORETICAL FORMALISM

The Schroedinger equation for a non-rotating Morse oscillator is

$$\frac{d^2\psi}{du^2} + \frac{2\mu}{\hbar^2}\left\{E - D_e[\exp(-2au) - 2\exp(-au)]\right\}\psi = 0 . \qquad (2.1)$$

Infeld and Hull [25] showed that Eq. (2.1) could be written in the form

$$\frac{d^2R(x)}{dx^2} + [-n^2 - \tfrac{1}{4}\exp(2x) + (s + \tfrac{1}{2})\exp(x)]R(x) = 0 \qquad (2.2)$$

with the definitions

$$(s + \tfrac{1}{2}) = (2\mu D_e)^{\frac{1}{2}}/(a\hbar) , \qquad (2.3a)$$

$$n^2 = -2\mu E/(a\hbar)^2 , \qquad (2.3b)$$

and

$$x = -au + \ln 2(s+\tfrac{1}{2}) . \qquad (2.3c)$$

Equation (2.2) is recognizable as type B factorization.

Huffaker and Dwivedi [26] have shown that by transforming the Morse oscillator from type B to type F factorization, it is possible to obtain raising and lowering operators for n or v (the vibrational quantum number) which when applied to the physically normalized solutions R_n^s give

$$\mathcal{G}_s^{+}(n)R_n^s = R_{n-1}^s \tag{2.4a}$$

$$\mathcal{G}_s^{-}(n)R_{n-1}^s = R_n^s \tag{2.4b}$$

where

$$\mathcal{G}_s^{\pm} = \left(\frac{4(n - \frac{1}{2} \mp \frac{1}{2})\ (n - \frac{1}{2})^2}{(n - \frac{1}{2} \pm \frac{1}{2})(s + n)(s - n + 1)}\right)^{\frac{1}{2}} \times \\ \left[(n - \tfrac{1}{2} \pm \tfrac{1}{2})e^{-x} - \frac{s + \frac{1}{2}}{2n - 1} \pm e^{-x}\frac{d}{dx}\right] \tag{2.4c}$$

where for a particular Morse oscillator, the parameter s is a constant and is given by the equation:

$$(s + \tfrac{1}{2}) = \sigma \approx \tfrac{1}{2}\,\frac{\omega_e}{\omega_e x_e}$$

while n takes the values

$$n = s, s-1, \ldots n_0 \qquad 0 < n_0 \leq 1.$$

The vibrational quantum number is $v = s - n$ and thus takes the values $0,1,2,\ldots,s-n$, and the function $R_n^s = \psi_{s-n} = \psi_v$. Substituting (2.4c) into (2.4a) and (2.4b) yields

$$R_{n-1}^s = \left[\frac{4(n-1)(n-\frac{1}{2})}{n(s+n)(s-n+1)}\right]^{\frac{1}{2}}\left[ne^{-x} - \frac{s+\frac{1}{2}}{(2n-1)} + e^{-x}\frac{d}{dx}\right]R_n^s \tag{2.5a}$$

and

$$R_{n+1}^s = \left[\frac{4(n+1)(n+\frac{1}{2})}{n(s+n+1)(s-n)}\right]^{\frac{1}{2}}\left[ne^{-x} - \frac{s+\frac{1}{2}}{(2n+1)} - e^{-x}\frac{d}{dx}\right]R_n^s. \tag{2.5b}$$

Equations (2.5a) and (2.5b) can be rewritten as:

$$\left[\frac{n(s+n)(s-n+1)}{4(n-1)(n-\frac{1}{2})}\right]^{\frac{1}{2}}R_{n-1}^s = \left[ne^{-x} - \frac{s+\frac{1}{2}}{(2n-1)} + e^{-x}\frac{d}{dx}\right]R_n^s \tag{2.5c}$$

and

$$\left[\frac{n(s+n+1)(s-n)}{4(n+1)(n+\frac{1}{2})}\right]^{\frac{1}{2}}R_{n+1}^s = \left[ne^{-x} - \frac{s+\frac{1}{2}}{(2n+1)} - e^{-x}\frac{d}{dx}\right]R_n^s. \tag{2.5d}$$

Subtracting (2.5d) from (2.5c), we obtain

$$\left[\frac{n(s-n)(s+n+1)}{4(n+1)(n+\frac{1}{2})^2}\right]^{\frac{1}{2}}R^s_{n+1} - \left[\frac{n(s+n)(s-n+1)}{4(n-1)(n-\frac{1}{2})^2}\right]^{\frac{1}{2}}R^s_{n-1}$$

$$= \left[\frac{(s+\frac{1}{2})}{(2n-1)} - \frac{s+\frac{1}{2}}{(2n+1)} - 2e^{-x}\frac{d}{dx}\right]R^s_n \, . \tag{2.6a}$$

Rearranging, Eq. (2.6a) becomes

$$e^{-x}\frac{d}{dx}R^s_n = \frac{1}{4(n-\frac{1}{2})}\left[\frac{n(s+n)(s-n+1)}{(n-1)}\right]^{\frac{1}{2}}R^s_{n-1}$$

$$+ \frac{(s+\frac{1}{2})}{4(n^2-\frac{1}{4})}R^s_n \tag{2.6b}$$

$$- \frac{1}{4(n+\frac{1}{2})}\left[\frac{n(s-n)(s+n+1)}{(n+1)}\right]^{\frac{1}{2}}R^s_{n+1} \, .$$

With $x = -au + \ell n2(s+\frac{1}{2})$ and $y = 1 - e^{-au}$, Eq. (2.6b) becomes

$$\frac{d}{dy}R^s_n = -\frac{(s+\frac{1}{2})}{2(n-\frac{1}{2})}\left[\frac{n(s+n)(s-n+1)}{(n-1)}\right]^{\frac{1}{2}}R^s_{n-1}$$

$$- \frac{(s+\frac{1}{2})^2}{2(n-\frac{1}{2})(n+\frac{1}{2})}R^s_n \tag{2.7}$$

$$+ \frac{(s+\frac{1}{2})}{2(n+\frac{1}{2})}\left[\frac{n(s-n)(s+n+1)}{(n+1)}\right]^{\frac{1}{2}}R^s_{n+1} \, .$$

In terms of ψ_v Eq. (2.7) becomes

$$\frac{d}{dy}\psi_v = -\frac{1}{2}\frac{\sigma}{(\sigma-v-1)}\left[\frac{(\sigma-v-\frac{1}{2})(2\sigma-v-1)(v+1)}{(\sigma-v-\frac{3}{2})}\right]^{\frac{1}{2}}\psi_{v+1} - \frac{1}{2}\frac{\sigma^2}{(\sigma-v)(\sigma-v-1)}\psi_v$$

$$+ \frac{1}{2}\frac{\sigma}{(\sigma-v)}\left[\frac{(\sigma-v-\frac{1}{2})(2\sigma-v)v}{(\sigma-v+\frac{1}{2})}\right]^{\frac{1}{2}}\psi_{v-1} \tag{2.8}$$

Defining

$$C_v = -\frac{\sigma^2}{2}\frac{1}{(\sigma-v)(\sigma-v-1)} \tag{2.9a}$$

and

$$D_v^{\pm} = \mp \frac{\sigma}{2(\sigma - v)} \left[\frac{v(\sigma - v \pm \tfrac{1}{2})(2\sigma - v)}{(\sigma - v \mp \tfrac{1}{2})}\right]^{\frac{1}{2}}, \tag{2.9b}$$

substituting in Eq. (2.8), we obtain the recursion relation

$$\frac{d}{dy} |\psi_v> = C_v\psi_v + D_{v+1}^{+}\psi_{v+1} + D_v^{-}\psi_{v-1} . \tag{2.10}$$

Since we are interested in the kinetic energy operator, a repeated application of Eq. (2.10) yields the following:

$$\begin{aligned} \frac{d^2}{dy^2} |\psi_v> = {} & D_{v+1}^{+}D_{v+2}^{+}\psi_{v+2} + D_{v+1}^{+}(C_v + C_{v+1})\psi_{v+1} \\ & + (C_v^2 + D_{v+1}^{+}D_{v+1}^{-} + D_v^{-}D_v^{+})\psi_v \\ & + D_v^{-}(C_v + C_{v-1})\psi_{v-1} + D_v^{-}D_{v-1}^{-}\psi_{v-2} . \end{aligned} \tag{2.11}$$

Using the binomial expansion, D_{v+1}^{+}, D_v^{-} and C_v are expanded in the form:

$$D_{v+1}^{+} = -\sqrt{\frac{\sigma}{2}(u + \tfrac{1}{2})} \left\{1 + \frac{3u + 7/2}{4\sigma} - \frac{4u^2 + (u - 1)}{8\sigma^2} + \ldots\right\} \tag{2.12a}$$

$$D_v^{-} = \sqrt{\frac{\sigma}{2}(u - \tfrac{1}{2})} \left\{1 + \frac{3u - 7/2}{4\sigma} - \frac{4u^2 - (u + 1)}{8\sigma^2} + \ldots\right\} \tag{2.12b}$$

and

$$C_v = - \left\{\tfrac{1}{2} + \frac{u}{\sigma} + \frac{3u^2 + \tfrac{1}{4}}{2\sigma^2} + \ldots\right\} \tag{2.12c}$$

where $u = v + \frac{1}{2}$. Substituting Eqs. (2.12) into Eq. (2.11), we obtain

$$\begin{aligned} \frac{d^2}{dy^2} |\psi_v> = {} & -\left\{u\sigma + (\frac{3}{2} u^2 + \frac{1}{8}) + \sigma^{-1}(2u^3 + \frac{u}{2}) + \sigma^{-2}(\frac{5}{2} u^4 + \frac{5}{4} u^2 + \frac{1}{32}) + \ldots\right\}\psi_v \\ & \pm P_{\pm1}\left\{\sigma + (\frac{11u \pm 15/2}{4} + \frac{\sigma u^2 \pm 10u + 7/2}{4\sigma}\right\}\psi_{v\pm1} \\ & + P_{\pm2}\left\{\sigma^2 + (\frac{3u \pm 5}{2})\sigma + \frac{-7u^2 \pm 10u + 67/4}{16}\right\}\psi_{v\pm2} \end{aligned} \tag{2.13}$$

where

$$P_{\pm m} = \left[\frac{(u \pm \frac{1}{2})(u \pm \frac{3}{2}) \ldots (u + m \mp \frac{1}{2})}{2^{|m|} \sigma^{|m|}}\right]^{\frac{1}{2}} . \qquad (2.14)$$

The kinetic energy operator d^2/dr^2 can be derived using the relation

$$y = (1 - e^{-aq}) \qquad (2.15)$$

where $q = r - r_e$. Upon differentiation Eq. (2.15) yields

$$\frac{d}{dr} = \frac{d}{dy}\frac{dy}{dr} = ae^{-aq}\frac{d}{dy} . \qquad (2.16)$$

A second differentiation gives:

$$\frac{d^2}{dr^2} = a^2\left\{(1 - y)^2 \frac{d^2}{dy^2} - (1 - y)\frac{d}{dy}\right\} . \qquad (2.17)$$

Defining

$$z = e^{aq} - 1 \qquad (2.18)$$

Eq. (2.17) becomes

$$\frac{d^2}{dr^2} = a^2\left\{\frac{1}{(1 + z)^2}\frac{d^2}{dy^2} - \frac{1}{(1 - z)}\frac{d}{dy}\right\} . \qquad (2.19)$$

Expanding $(1 + z)^{-2}$ and $(1 + z)^{-1}$Eq. (2.19) becomes:

$$\frac{d^2}{dr^2} \simeq a^2\left\{(\frac{d^2}{dy^2} - \frac{d}{dy}) - z(\frac{2d^2}{dy^2} - \frac{d}{dy}) + z^2(\frac{3d^2}{dy^2} - \frac{d}{dy}) + \ldots\right\} . \qquad (2.20)$$

Substituting Eqs. (2.10) and (2.13) and the expansions of powers of z from [19] into Eq. (2.20) we obtain the recursion relation:

$$\frac{d^2}{dr^2}|\psi_v> \cong [-u\sigma - \frac{3}{2}u^2 - \sigma^{-1}34\mu]\psi_v + P_{\pm 1}\left\{(u+\tfrac{1}{2})\sigma - \frac{23u^2 \pm 16\mu + \frac{121}{4}}{4}\right\}\psi_{v\pm 1}$$

$$
\begin{aligned}
&+ P_{\pm2}\left\{\sigma^2 - \frac{10u \pm 58}{4}\sigma + \frac{18u^2 \pm 130u + 156}{4}\right\}\psi_{v\pm2}\\
&+ P_{\pm3}\left\{2\sigma^2 + \frac{11u \pm \frac{79}{2}}{2}\sigma + \frac{36u \pm 26}{4}\right\}\psi_{v\pm3}\\
&+ P_{\pm4}\left\{3\sigma^2 + (18u \pm 30)\sigma\right\}\psi_{v\pm4}\\
&+ P_{\pm5}\left\{4\sigma^2 + (6u \pm 10)\sigma\right\}\psi_{v\pm5} \;.
\end{aligned}
\tag{2.21}
$$

By using the recursion relation (2.21) as a perturbation to the perturbed Morse oscillator (which has been proven to be a good approximation for actual heavy molecules) we can still maintain the approximate separation of nuclear and electronic motion without assuming, as in the Born-Oppenheimer approximation, fixed nuclei of infinite masses.

CHAPTER III

PERTURBATION CALCULATION

The perturbed Hamiltonian used in the present calculation is

$$H = H_0 + H_1 + H_2 \tag{3.1}$$

where H_0 is the unperturbed Hamiltonian satisfying the Schroedinger equation

$$H_0\psi_m^{(0)} = E_0\psi_m^{(0)} . \tag{3.2}$$

H_1 consists of two parts: (a) perturbation to the Morse oscillator (anharmonic effects) with the form [6],

$$hcT \sum_{n=4} b_n(1 - e^{-aq})^n = hc\tau \sum_{n=4} c_n(e^{aq} - 1)^n , \tag{3.3}$$

where the coefficients c_n are related to b_n by

$$\begin{aligned} c_n &= \sum_{m=1}^{n-3} c_{n,m} b_{n-m+1} , \\ c_{n,m} &= -c_{n,m-1}\left(\frac{n-m+1}{m-1}\right) \end{aligned} \tag{3.4}$$

and

$$c_{n,1} = 1 \text{ , and}$$

(b) perturbation due to the inclusion of the nonrigid rotational energy term, shown by Huffaker [6] to have the form

$$\frac{h^2J(J+1)}{2hc\mu r^2} \simeq K \sum_{\ell} P_{\ell}(\rho)(e^{aq} - 1)^{\ell} \simeq A_{rot}(e^{aq} - 1) + B_{rot}(e^{aq} - 1)$$

$$+ C_{rot}(e^{aq} - 1)^3 + D_{rot}(e^{aq} - 1)^4 + E_{rot}(e^{aq} - 1)^5 \qquad (3.5)$$

$$+ F_{rot}(e^{aq} - 1)^6 + \ldots$$

where

$$K = \frac{\tau J(J+1)}{\rho^2\sigma^2} \qquad (3.6)$$

where J is the rotational quantum number. The polynomials $P_{\ell}(\rho)$ are defined in [6]. The rotational coefficients A_{rot}, ... F_{rot} are related to the quantum number J or K as follows:

$$A_{rot} = -hc\,\frac{2K}{\rho}\,,$$

$$B_{rot} = hc\,\frac{K}{\rho^2}\,(\rho + 3)\,,$$

$$C_{rot} = -hc\,\frac{K}{\rho^3}\,(\frac{2}{3}\,\rho^2 + 3\rho + 4)\,,$$

$$D_{rot} = hc\,\frac{K}{\rho^4}\,(\frac{\rho^3}{2} + \frac{11}{4}\,\rho^2 + 6\rho + 5)\,, \qquad (3.7)$$

$$E_{rot} = -hc\,\frac{K}{\rho^5}\,(\frac{2}{5}\,\rho^4 + \frac{5}{2}\,\rho^3 + 7\rho^2 + 10\rho + 6)\,,$$

$$F_{rot} = hc\,\frac{K}{\rho^6}\,(\frac{\rho^5}{3} + \frac{137}{60}\,\rho^4 + \frac{15}{2}\,\rho^3 + \frac{85}{6}\,\rho^2 + 15\rho + 7)\,.$$

The combined effects of (a) and (b) give

$$H_1 = A(e^{aq} - 1) + B(e^{aq} - 1)^2 + C(e^{aq} - 1)^3 + D(e^{aq} - 1)^4$$

$$+ E(e^{aq} - 1)^5 + F(e^{aq} - 1)^6 + \ldots \qquad (3.8)$$

where A, B, and C are purely rotational, while D, E, ... etc. combine rotational and anharmonic effects, i.e.,

$$\begin{aligned} A &= A_{rot} , \\ B &= B_{rot} , \\ C &= C_{rot} , \\ D &= D_{rot} + hc\tau c_4 , \\ E &= E_{rot} + hc\tau c_5 , \\ F &= F_{rot} + hc\tau c_6 . \end{aligned} \tag{3.9}$$

The expansion of powers of [exp(au)-1] needed for perturbation are listed in [27].

The second perturbation term H_2 is the velocity dependent term and is proportional to the operator (d^2/dr^2) for which a recursion formula was derived in the previous chapter. First, second and third-order perturbation calculations were performed to study the effect of the Born-Oppenheimer-violating term on the energy eigenvalues and on the modified Dunham coefficients. The results of the perturbation calculation due to the total perturbation H_1+H_2 are listed in Table I grouped by the order of perturbation and then alphabetically; also, the correction due to H_1 [6] is written before the contribution resulting from the velocity-dependent term.

In the calculation we made use of the fact that the vibrational wavefunctions are orthogonal, and of the common formulas of perturbation [28] where the shift in energy due to first order perturbation is

$$\Delta E^{(1)} = \langle v|H_2|v'\rangle , \tag{3.10}$$

the energy correction $\Delta E^{(2)}$ due to second order correction is given by

$$\Delta E^{(2)} = \sum_{v'} \frac{\langle v|H_2|v'\rangle\langle v'|H_2|v\rangle}{[E_v^{(0)} - E_{v'}^{(0)}} , \tag{3.11}$$

and the energy shifts $\Delta E^{(3)}$ due to third order correction is

$$\Delta E^{(3)} = \sum_{v',v''} \frac{<v|H_2|v'><v'|H_2|v''><v''|H_2|v>}{[E_v^{(0)} - E_{v'}^{(0)}][E_v^{(0)} - E_{v''}^{(0)}]} - \sum_{v'} \frac{|<v|H_2|v'>|^2<v|H_2|v>}{E_v - E_{v'}} . \qquad (3.12)$$

The energy difference between the vibrational levels of the Morse oscillator are expressed in the form

$$[E_v^{(0)} - E_{v+n}^{(0)}]^{-} = - \frac{\sigma}{2n\nu_e} \left\{1 + \frac{\omega}{\sigma} + (\frac{\omega}{\sigma})^2 + \dots\right\} \qquad (3.13)$$

where $\omega = v + \frac{1}{2}(n + 1)$.

Table I. Perturbation Terms Contributing to the Dunham Coefficients Y_{jk} .

First-order Perturbation Terms

$$A[(2u/\sigma) + \sigma^{-2}(3u^2 + ½) + \sigma^{-3}(4u^3 + u)]$$

$$+ B[\frac{u}{\sigma} + \sigma^{-2}(\frac{15u^2}{2} + \frac{7}{8}) + \sigma^{-3}(20u^3 + \frac{29u}{4})]$$

$$+ C[\sigma^{-2}(6u^2 + 1) + \sigma^{-3}(38u^3 + 19u)]$$

$$+ D[\sigma^{-2}(\frac{3u^2}{2} + \frac{3}{8}) + \sigma^{-3}(\frac{69u^3}{2} + \frac{187u}{8})]$$

$$+ E[\sigma^{-3}(15u^3 + \frac{55u}{4}) + \sigma^{-4}(\frac{415u^4}{2} + \frac{1405u^2}{4})]$$

$$+ F[\sigma^{-3}(\frac{5u^3}{2} + \frac{25u}{8}) + \sigma^{-4}(\frac{465u^4}{4} + \frac{1005u^2}{4})]$$

$$+ G[\sigma^{-4}(35u^4 + \frac{385u^2}{4})] + H[\sigma^{-4}(\frac{35u^4}{8} + \frac{245u^2}{16})]$$

$$- \lambda[u\sigma + (\frac{3}{2} u^2)]$$

Second-order Perturbation Terms

$$-(2\nu_e)^{-1}\Big\{A^2[½ + \frac{9u}{2\sigma} + \sigma^{-2}(\frac{75u^2}{4} + \frac{27}{16})] + AB[\frac{8u}{\sigma} + \sigma^{-2}(72u^2 + 8)]$$

$$+ AC[\frac{3u}{\sigma} + \sigma^{-2}(72u^2 + \frac{21}{2})] + AD[\sigma^{-2}(36u^2 + 7) + \sigma^{-3}(584u^3 + 358u)]$$

$$+ AE[\sigma^{-2}(\frac{15u^2}{2} + \frac{15}{8}) + \sigma^{-3}(355u^3 + 280u)]$$

$$+ AF\sigma^{-3}(120u^3 + 120u) + AG\sigma^{-3}(\frac{35u^3}{2} + \frac{175u}{8})$$

$$+ B^2[\frac{u}{2} + \sigma^{-2}(30u^2 + \frac{7}{2})] + BC\sigma^{-2}(27u^2 + \frac{15}{4})$$

$$+ BD[\sigma^{-2}(3u^2 + \frac{3}{4}) + \sigma^{-3}(286u^3 + 175u)]$$

$$+ BE\sigma^{-3}(80u^3 + 65u) + BF\sigma^{-3}(\frac{15u^3}{2} + \frac{75u}{8})$$

$$+ C^2\sigma^{-2}(\frac{15u^2}{4} + \frac{7}{16}) + CD\sigma^{-3}(104u^3 + 65u)$$

$$+ CE\sigma^{-3}(35u^3 + \frac{95u}{8}) + D^2[\sigma^{-3}(\frac{17u^3}{4} + \frac{67u}{16}) + \sigma^{-4}(\frac{9595u^4}{16} + \frac{29103u^2}{32})]$$

$$+ DE\sigma^{-4}(\frac{1125u^4}{4} + \frac{4025u^2}{8}) + DF\sigma^{-4}(\frac{165u^4}{8} + \frac{885u^2}{16})$$

$$+ E^2\sigma^{-4}(\frac{315u^4}{16} + \frac{1085u^2}{32})$$

$$+ \lambda^2[\sigma^3\frac{u}{2} + \sigma^2(3u^2 + \frac{3}{4}) + \sigma(4u^3 + \frac{7}{2}u)]$$

$$+ A\lambda[2u\sigma + \tfrac{1}{2} + \sigma^{-1}\frac{19}{4}\mu + \sigma^{-2}(\frac{99}{8}u^2 + \frac{33}{32})]$$

$$- B\lambda[u\sigma + (\frac{17}{2}u^2 + \frac{27}{8}) + \sigma^{-1}(10u^3 + \frac{35u}{4})]$$

$$+ C\lambda[(\frac{51}{8}u^2 + \frac{9}{4}) + \sigma^{-1}(30u^3 + \frac{105}{4}u)]$$

$$+ D\lambda[(\frac{3}{2}u^2 + \frac{3}{4}) - \sigma^{-1}(\frac{1153}{2}u^3 + \frac{35}{4}u)]$$

$$- E\lambda[(50u^3 + 45u)\sigma^{-1}]$$

$$+ F\lambda[\frac{75}{2}u^3 + \frac{15}{2}u)\sigma^{-1}]\Big\}$$

Third-order Perturbation Terms

$$+(2v_e)^{-2}\Big\{A^3\Big(1 + \frac{17u}{\sigma}\Big) + A^2B\Big(1 + \frac{99u}{2\sigma}\Big) + A^2C\Big(\frac{27u}{\sigma}\Big)$$

$$+ A^2D\Big[\frac{6u}{\sigma} + \sigma^{-2}\Big(\frac{795u^2}{2} + \frac{555}{8}\Big)\Big]$$

$$+ A^2E\sigma^{-2}\Big(\frac{285u^2}{2} + \frac{245}{8}\Big) + A^2F\sigma^{-2}\Big(\frac{45u^2}{2} + \frac{45}{8}\Big)$$

$$+ AB^2\Big(\frac{21u}{\sigma}\Big) + ABC\Big(\frac{9u}{\sigma}\Big) + ABD\sigma^{-2}\Big(222u^2 + \frac{79}{2}\Big)$$

$$+ ABE\sigma^{-2}\Big(30u^2 + \frac{15}{2}\Big) + ACD\sigma^{-2}\Big(39u^2 + \frac{23}{4}\Big)$$

$$+ AD^2\sigma^{-3}\Big(\frac{985u^3}{2} + \frac{2683u}{8}\Big) + ADE\sigma^{-3}\Big(\frac{225u^3}{2} + \frac{715u}{8}\Big)$$

$$+ B^3\Big(\frac{u}{2\sigma}\Big) + B^2D\sigma^{-2}\Big(6u^2 + \frac{3}{2}\Big) + BD^2\sigma^{-3}\Big(\frac{85u^3}{4} + \frac{335u}{16}\Big)$$

$$+ D^3\sigma^{-4}\Big(\frac{375}{16}u^4 + \frac{1707}{32}u^2\Big) - \lambda^3\Big[\frac{\sigma^2}{8} + \frac{9}{4}u\sigma + \Big(\frac{15}{8}u^2 + \frac{15}{32}\Big)\Big]$$

$$- A^2\lambda\sigma\Big(\frac{7}{2}u^3 - \frac{19}{8}u\Big) + \lambda^2A\Big[u\sigma^3 + \frac{15}{2}\sigma^2\Big(u^2 + \frac{1}{4}\Big)\Big]$$

$$+ B^2\lambda\Big[\sigma\frac{u}{2} + \Big(16u^4 + \frac{57}{4}u^2 + \frac{37}{16}\Big)\Big]$$

$$- \lambda^2B\Big[\Big(\frac{3}{2}u^2 + \frac{3}{8}\Big)\sigma^2 + \Big(\frac{3}{2}u^3 + \frac{25}{8}u\Big)\sigma\Big]$$

$$+ C^2\lambda\Big(\frac{13}{16}u^4 - \frac{81}{16}u^2 + \frac{7}{8}\Big) + \lambda^2C\Big(\frac{145}{8}u^3 + \frac{1797}{96}\Big)\sigma^{-1}$$

$$+ D^2\lambda\Big(\frac{19}{4}u^3 + \frac{89}{16}u\Big)\sigma^{-1} + \lambda^2D\Big(43u^2 + \frac{15}{2}\Big) + \lambda^2E\Big(\frac{35}{2}u^3 - \frac{105}{8}u\Big)\sigma$$

$$+ AB\lambda\Big(2u^3 + \frac{27}{2}u\Big)\sigma + AC\lambda\Big(\frac{3}{2}u^3 + \frac{39}{4}u\Big)\sigma$$

$$+ AD\lambda\Big(u^3 - \frac{47}{2}u\Big)\sigma - AE\lambda\Big(\frac{185}{12}u^2 - \frac{381}{64}\Big)\Big\}$$

where λ is a constant for a given molecule and will be determined by fitting the theoretically derived Dunham coefficients to the experimental values.

Making the necessary substitutions for A, B, ... and replacing $c_4, \ldots, c_8$ with $b_4, \ldots, b_8$ according to equations (3.9) and (3.47) then collecting the coefficients of various powers of $u = v + \frac{1}{2}$ and $J(J+1)$, expressions for the modified Dunham coefficients $Y_{jK}^{(2\ell)}$ as functions of ρ, σ, τ, λ, $b_4 \ldots b_8$ are obtained. The results are listed in Table II.

Table II

Dunham Coefficients of the Perturbed Morse Oscillator

$$Y_{00}^{(0)} = 0 \ ,$$

$$Y_{00}^{(2)} = \frac{T}{\sigma^2}\left[\frac{3}{8} b_4 - \frac{3}{4} b_4\Delta\right] .$$

$$Y_{10}^{(0)} = \omega_e^{(0)} = \frac{2\tau}{\sigma} \left(1 - \Delta - \frac{\Delta^2}{2}\right) ,$$

$$Y_{10}^{(2)} = \omega_e^{(2)} = \frac{\tau}{8\sigma^3} \left[-3b_4-15b_5+25b_6 - \frac{67}{4} b_4^2 - 56\Delta^2 - 70b_4\Delta - 60b_5\Delta - 60b_6\Delta\right] .$$

$$Y_{01}^{(0)} = B_e^{(0)} = \frac{\tau}{\rho^2\sigma^2} \ ,$$

$$Y_{01}^{(2)} = B_e^{(2)} = \frac{\tau}{8\sigma^4\rho^6}\left[- \frac{5}{6} \rho^3 + \frac{21}{4} \rho^2 - 14\rho + 15 - \rho^2(7\rho + 9)b_4 \right.$$
$$\left. + 15\rho^3 b_5 + \Delta\left(-10\rho^3 - \frac{87}{2} \rho^2 + 36\rho - 30\right)\right] .$$

$$Y_{20}^{(0)} = -\omega_e x_e^{(0)} = - \frac{T}{\sigma^2}\left[1 - \frac{3b_4}{2} + 2\Delta\left(1 - \frac{3}{2} b_4\right)\right] ,$$

$$Y_{20}^{(2)} = -\omega_e x_e^{(2)} = \frac{5}{16\sigma^4}\left[9b_5 - 15b_6 - 35b_7 + 49b_8 + \frac{237}{20} b_4^2 \right.$$
$$\left. + \frac{143}{2} b_4 b_5 - \frac{177b_4b_6}{2} - \frac{217}{4} b_5^2\right] .$$

$$Y_{02}^{(0)} = -D_e^{(0)} = - \frac{T}{\rho^6\sigma^4} \ ,$$

$$Y_{02}^{(2)} = -D_e^{(2)} = \frac{\tau}{8\sigma^6\rho^{10}}\left[- \frac{59}{18} \rho^4 + \frac{111}{4} \rho^3 - \frac{623}{6} \rho^2 + 199\rho \right.$$
$$- 163 + \rho^2\left(\frac{16}{3} \rho^2 - 27\rho + 119\right)b_4 - 10\rho^3(\rho+9)b_5 + 45\rho^4 b_\beta - 46\rho^4 b_4^2$$

$$+ \left(\frac{2687}{90}\rho^4 + \frac{3617}{16}\rho^3 + \frac{11203}{24}\rho^2 + \frac{2241}{4}\rho + \frac{1367}{4}\right)\Delta] \ .$$

$$Y_{11}^{(0)} = -\alpha_e^{(0)} = -\frac{3T}{\rho^4\sigma^3}[(\rho - 1) + \Delta(\sigma - 1)] \ ,$$

$$Y_{11}^{(2)} = \frac{T}{8\sigma^5\rho^8}[\frac{-3\rho^5}{2} + \frac{43}{3}\rho^4 - \frac{411}{6}\rho^3 + \frac{1135\rho^2}{8} - 285\rho + 175$$

$$- \rho^2\left(\frac{13\rho^3}{12} - \frac{103\rho^2}{8} - 79\rho + \frac{335}{2}\right)b_4 + 5\rho^3\left(\frac{29\rho^2}{\sigma} - 15\rho + 38\right)b_5$$

$$- 15\rho^4(17\rho + 15)\frac{b_6}{2} + 175\rho^5 b_7 + \rho^4(1043\rho + 1005)\frac{b_4^2}{8} - 715\rho^5 b_4 \frac{b_5}{2}$$

$$+ \Delta[91\rho^5 + \frac{1251\rho^4}{2} - 2550\rho^3 + 2400\rho^2 + 1260\rho - 420]$$

$$- \Delta^2[\frac{837\rho^5}{12} + \frac{1047\rho^4}{4} - 136\rho^3 - 1050\rho^2 - 630\rho] \ .$$

$$Y_{30}^{(0)} = \omega_e y_e^{(0)} = \frac{T}{2\sigma^3}[-b_4 + 5b_5 + 5b_6 - \frac{17}{4}b_4^2 + 3b_4\Delta] \ .$$

$$Y_{03}^{(0)} = H_e^{(0)} = \frac{\tau}{\rho^{10}\underset{3\tau}{\sigma^4}}(-\rho + 3) \ .$$

$$Y_{12}^{(0)} = -B_e^{(0)} = \frac{3\tau}{4\rho^8\sigma^5}[-13\frac{\rho^2}{3} + 18\rho - 19 + 8\rho^2 b_4 + \frac{13}{3}\rho^2\Delta] \ .$$

$$Y_{21}^{(0)} = \gamma_e^{(0)} = \frac{3\tau}{2\sigma^4\rho^6}[\frac{-7\rho^3}{6} + \frac{23\rho^2}{4} - 10\rho + 5 + 3\rho^2(\rho-1)b_4 + 5\rho^3 b_5$$

$$+ \frac{7}{3}\rho^3\Delta] \ .$$

$$Y_{31}^{(0)} = \delta_e^{(0)} = \frac{5\tau}{4\sigma^5\rho^8}[-\rho^5 + \frac{109}{15}\rho^4 - 25\rho^3 + \frac{139}{3}\rho^2 - 42\rho + 14$$

$$+ \rho^2\left(\frac{13}{\rho}\rho^3 - \frac{71\rho^2}{4} + 34\rho - 17\right)b_4$$

$$+ \rho^3\left(\frac{5\rho^2}{3} - 30\rho + 28\right)b_5 + 9\rho^4(\rho - 1)b_6$$

$$+ 14\rho^5 b_7 - 51\rho^4(\rho - 1)\frac{b_4^2}{4} - 45\rho^5 b_4 b_5 + 3\Delta\rho^5] \ .$$

$$Y_{22}^{(0)} = \pi_e^{(0)} = \frac{T}{2\sigma^6\rho^{10}}\left[\frac{-73\rho^4}{6} + \frac{351\rho^3}{4} - \frac{529\rho^2}{2} + 375\rho - 195\right.$$

$$+ 3\rho^2 (32 \frac{\rho^2}{3} - 57\rho + 61)b_4 + 30(\rho - 3)b_5$$

$$\left. + 45\rho^4 b_6 - 78\rho^4 b_4^2 + \frac{73}{3} \rho^4\Delta\right] .$$

$$Y_{40}^{(0)} = \omega_e z_e^{(0)} = \frac{5T}{8\sigma^4}\left[-3b_5 - 3b_6 + 7b_7 + 7b_8 + \frac{13}{4} b_4^2 - 33b_4 \frac{b_5}{2} - 33b_4 \frac{b_5}{2}\right.$$

$$\left. - \frac{63}{4} b_5^2 + \frac{75}{8} b_4^3 + 12b_5\Delta\right] .$$

$$Y_{04}^{(0)} = L_e^{(0)} = \frac{T}{\sigma^8\rho^{14}}\left[-5 \frac{\rho^2}{3} + 9\rho - 13 + \rho^2 b_4\right] .$$

where $\Delta = \frac{\lambda\sigma^2}{2T}$. (3.14)

Discussion of Formulas

If we examine the formulas in Table II we find that to a first approximation the change in the Dunham coefficients $Y_{jk}^{(0)}$ due to the inclusion of the Born-Oppenheimer violating term can be expressed by the following simple relation:

$$\delta Y_{jk}^{(0)} = -\Delta j Y_{jk}^{(0)} \tag{3.15a}$$

From (3.15a) it is clear that the new velocity-dependent perturbation term does not affect the coefficients $Y_{00}^{(0)}$ or $Y_{0K}^{(0)}$. Generally the changes in $Y_{jk}^{(2\ell)}$ for $\ell \neq 0$ are small and can be neglected without affecting the accuracy of the results, as they are at most $1/\sigma^2$ of the biggest changes in $Y_{jk}^{(0)}$.

From Eq. (3.15a) we see that the Dunham coefficients in the nonadiabatic approximation Y_{jk}^{nad} are related to those in the adiabatic approach [6] Y_{jk} by the following simple relation

$$Y^{nad}_{jk} \approx Y_{jk}(1 - j\Delta) \qquad (3.15b)$$

and

$$Y^{nad}_{0k} \approx Y_{0k} \qquad (3.15c)$$

Since the Dunham coefficients Y_{j0} (which are related to the vibrational energies) are proportional to σ^{-j} where σ is given by

$$\sigma = \frac{[2\mu V_e]^{\frac{1}{2}}}{ah} ,$$

we can see that Eq. (3.15a) is in fact equivalent to

$$(\mu^{-j/2})^{nad} = (\mu^{-j/2})(1 - j\Delta) , \qquad (3.15d)$$

where μ^{nad} is the reduced mass in the nonadiabatic approximation. Rearranging Eq. (3.15c) yields

$$\mu^{nad} = \mu(1 + 2\Delta) \qquad (3.15e)$$

i.e. the nonadiabatic corrections can be looked at as using an effective reduced mass for the vibrational energies which is different from the reduced mass used in the adiabatic approximation by $2\mu\Delta$. By the same argument we can see from Eq. (3.15c) that the reduced mass involved in calculating the rotational energies is not changed by the nonadiabatic corrections. This conclusion agrees with Bunker et al. [20], who found that the nonadiabatic corrections can be accounted for by solving an effective Hamiltonian which contains two different reduced masses: one μ_v for the vibrational kinetic energy operator and one μ_r for the rotational energy operator. Satisfactory fit to the experimental vibrational, rotational energies of the ground state of H_2 and D_2 were obtained when μ_r was kept equal to the nuclear reduced mass μ while μ_v which gives the best fit was found to satisfy the relation $\mu_v = \mu/(1+B)$ where μB was found to be the same for both isotopes.

Ignoring higher-order modified Dunham coefficients, we use the experimental values of ω_e, B_e, D_e and α_e to find the new parameter Δ and the three Morse parameters ρ, σ and τ as follows:

$$\Delta \approx [1 - (\omega_e/2B_e)(D_e/B_e)^{\frac{1}{2}}] \,, \tag{3.16a}$$

$$\rho = 1 + \frac{\alpha_e\omega_e}{6B_e^2(1 - \Delta)^2} \,, \tag{3.16b}$$

$$\sigma \approx \frac{1}{\rho^2} (B_e/D_e)^{\frac{1}{2}} \,, \tag{3.16c}$$

$$\tau \approx \sigma B_e(B_e/D_e)^{\frac{1}{2}} \,. \tag{3.16d}$$

If we set the velocity dependent term Δ in Eq. (3.16a) equal to zero the equations for the three Morse parameters, ρ, σ, τ become equivalent to those obtained from the PMO model [6]. With similar approximation the first three parameters of the PMO model, b_4, b_5, and b_6, can be determined from $\omega_e x_e$, γ_e, and $\omega_e y_e$ using the following equations:

$$b_4 = \frac{2}{3} [1 - \frac{\sigma^2\omega_e x_e}{\tau(1 - 2\Delta)}] \,, \tag{3.17a}$$

$$\begin{aligned} b_5 = \frac{1}{5\rho^3}[&\frac{2\gamma_e\sigma^4\rho^6}{3\tau} + \frac{7\rho^3}{6} - \frac{23\rho^2}{4} + 10\rho - 5 + 3\rho^2(\rho^2 - 1)b_4 \\ &- \frac{7}{3}\Delta\rho^3] \,, \end{aligned} \tag{3.17b}$$

$$b_6 = \frac{1}{5} [\frac{2\sigma^3}{\tau}\omega_e y_e + b_4 - 5b_5 + \frac{17b_4^2}{4} - 3b_4\Delta] \,. \tag{3.17c}$$

In a similar fashion if $Y_{31} = \delta_e$ and $Y_{40} = \omega_e z_e$ are known, appropriate values of b_7, b_8 can be determined from the following equations:

$$\begin{aligned} b_7 = {} & + \frac{1}{14\rho^5}[(\frac{4\sigma^5\rho^8}{5T})\delta_e + \rho^5 - \frac{109}{15}\rho^4 + 25\rho^3 - \frac{139}{3}\rho^2 + 42\rho - 14 \\ & - \rho^2(\frac{13}{\sigma}\rho^3 - \frac{71}{4}\rho^2 + 34\rho - 17)b_4 \\ & - \rho^3(\frac{5\rho^2}{3} - 30\rho + 28)b_5 - 9\rho^4(\rho - 1)b_6 \\ & + 51\rho^4(\rho - 1)\frac{b_4^2}{4} + 45\rho^5 b_4 b_5 - 3\Delta\rho^5] , \end{aligned} \tag{3.17d}$$

$$\begin{aligned} b_8 = {} & [\frac{8\sigma^4}{35T}\omega_e z_e + \frac{3}{7}b_5 + \frac{3}{7}b_6 - b_7 - \frac{13}{28}b_4^2 + \frac{33}{14}b_4 b_5 + \frac{33}{14}b_4 b_6 \\ & + \frac{63}{28}b_5^2 - \frac{75}{56}b_4^3 - \frac{12}{7}b_5\Delta] . \end{aligned} \tag{3.17e}$$

The error in such a process is cumulative as Eqs. (3.16) represent the near cancellation of large terms. Also the loss of precision in calculating the various Dunham coefficients affects the accuracy of the various model parameters. With these two factors in mind we developed an iterative procedure where the available Dunham coefficients were used as an input to calculate approximate values of the various parameters which in turn are used to calculate higher order correction $Y_{10}^{(2)}$, $Y_{01}^{(2)}$... etc., then a comparison between the resultant Dunham coefficients and the corresponding experimental values is made. Iteration computation is continued until the desired degree of self consistency is achieved.

CHAPTER IV

ITERATION CALCULATION OF THE PMO PARAMETERS FOR H_2, HD, AND D_2

We chose to study the hydrogen molecule and its isotopic species HD and D_2 because they have the smallest reduced masses and thus should have the largest violation of the Born-Oppenheimer approximation. Evidence of violation of the Born-Oppenheimer approximation for H_2 and D_2 was pointed out by Bunker [11].

H_2, HD, and D_2 molecules have been extensively investigated experimentally. The Raman scattering by Stoicheff [29] provides precise rotational data on v=0,1 for the electronic ground state of H_2 which when combined with the infrared quadrupole spectrum [30,31] and with the electronic emission spectrum [22] provides rotational and vibrational data for higher levels up to v=14. For HD, Raman scattering [29] and the infrared rotation vibration spectrum (1-0, 2-0, 3-0, 4-0 bands) [32,33] provide rotational and vibrational data up to v=4. The electronic absorption spectrum by Dabrowski and Herzberg [34] provides accurate rotational constants and vibrational intervals of the ground state of HD up to the dissociation limit. For D_2 both analysis of the high resolution work of Lyman and Werner bands by Bredohl and Herzberg [23] and the Raman data [29] provide precise values of rotational and vibrational energies up to the last vibrational level v=21 which lies only 2 cm^{-1} below dissociation. It is worthwhile here to mention that in all the above investigations, the values of the Dunham coefficients obtained by forced or least square fitting depend fairly strongly on the number of vibrational levels v and the degree of the polynomials used. Thus, they are not uniquely determined, and as Bredohl et al. [23] have pointed out, it is impossible to establish from experimental data which particular Y_{jk} is closest to the true value. This point has also been emphasized by Cashion [35]. For the H_2 molecule one set of data based on a three-term formula to fit the first three levels was given by Stoicheff [29]. Another set of coefficients were given by Herzberg et al. [22], who found that a good representation of their experimental data is obtained by retaining Stoicheff's values for Y_{10}, Y_{20} and Y_{30} but using a four-term formula to fit the first eight levels. For HD two sets of coefficients based on 10 and 5 level fits were found to represent the experimental data [34]; on the other hand three sets of coefficients based on 19, 10 and 5 level fits were given [23] for D_2. We used the different sets of coefficients for the three isotopes as an input to our program to obtain the various PMO parameters. The results of calculation along with the corresponding Dunham coefficients are listed in Tables III, IV and V for H_2, HD and D_2 respectively.

From Tables III-V we see that, although different sets of coefficients for a particular molecule yield PMO parameters which differ only slightly, yet the change in the new perturbation parameter Δ is relatively large and depends strongly on the particular set of data used as an input. Moreover the sign of Δ is reversed when Y_{02} changes

Table III

The Dunham coefficients Y_{jK} and PMO Parameters of the Ground State $X^1\Sigma_g^+$ of H_2

Y_{jK}	8 level fit [22]	3 level fit [29]
Y_{10}	4400.39	4400.39
Y_{20}	-120.815	-120.815
Y_{30}	0.7242	0.7242
Y_{01}	60.864	60.841
Y_{11}	-3.07638	-3.0177
Y_{21}	0.06017	0.0285
Y_{02}	-0.04657	-0.04684
PMO parameters		
ρ	1.60905	1.598405
σ	13.96924	14.11779
τ	30756.12	30986.03
b_4	0.15541280	0.14245260
b_5	0.05632070	0.04726374
b_6	0.02145786	0.02038393
Δ	$0.6088775\text{x}10^{-4}$	$-0.3390600\text{x}10^{-2}$

Table IV

The Dunham coefficients Y_{jK} and PMO Parameters of the Ground State $X^1\Sigma^+$ of HD

Y_{jK}	10 level fit	5 level fit
Y_{10}	3813.15	3813.55
Y_{20}	-91.65	-92.01
Y_{30}	0.723	0.862
Y_{01}	45.6554	45.6430
Y_{11}	-1.9860	-1.9615
Y_{21}	0.03146	0.02027
Y_{02}	0.026051	0.026322
PMO parameters		
ρ	1.627131	1.548189
σ	16.0383	16.318151
τ	31097.81	31046.83
b_4	0.15105530	0.13559800
b_5	0.05005741	0.0530612
b_6	0.04328541	0.0341543
Δ	0.2296507×10^{-2}	-0.260286×10^{-2}

Table V

The Dunham coefficients Y_{jK} and PMO Parameters of the Ground State $X^1\Sigma_g^+$ of D_2

Y_{jK}	19 level fit	10 level fit	5 level fit
Y_{10}	3116.08	3115.50	3115.78
Y_{20}	-62.40	-61.82	-62.04
Y_{30}	0.812	0.562	0.618
Y_{01}	30.4558	30.4436	30.4338
Y_{11}	-1.1009	-1.0786	-1.0690
Y_{21}	0.02237	0.01265	0.007877
Y_{02}*	0.011655	0.011655	0.011655
PMO parameters			
ρ	1.615758	1.6037720	1.598195
σ	19.58761	19.874890	20.0095
τ	30505.79	30932.05	31130.20
b_4	0.1421837	0.1382988	0.13218360
b_5	0.080262	0.0580003	0.0479549
b_6	0.04447317	0.0413803	0.05476411
Δ	-0.0759507×10^{-2}	-0.117475×10^{-2}	-0.1748395×10^{-2}

*Y_{02} is obtained approximately by linear extrapolation of the constants D_v for $v=0$ and $v=1$ using the relation $B_e \approx D_1 - D_0$.

by as little as 0.006% as in the case of H_2 and by about 0.01% for HD. The strong dependence of Δ on the coefficients Y_{02} is clear from Eq. (3.16a). In the case of D_2, although the value of Δ depends on the particular set of coefficients used, yet the change is not so dramatic as it is for H_2 and HD; obviously this is because we used the same Y_{02} for the three data sets. We can summarize the results in Tables III-V as follows:

(1) Positive values of Δ resulted when we used inaccurate set of coefficients, e.g. for H_2 positive Δ resulted when we used the set of data [22] for which some of the coefficients are based on the 8 level fit and some based on the 3 level fit. For HD the positive value of Δ resulted when we used data based on the 10 level fit. In that set the Dunham coefficient Y_{02} has a larger standard deviation than the Y_{02} in the set of data resulting in negative values of Δ.

(2) The Dunham coefficients are obtained by fitting observed term values to the double power series given by Eq. (1.2) which are essentially expansions in powers of $(v + 1/2)/\sigma$. As v increases, the convergence of the series becomes less rapid and affects the accuracy of the derived coefficients. For that reason we believe that the coefficients derived using a smaller number of vibrational levels v are more reliable and that we should exclude the value obtained from the 8 and 10 level fits for H_2 and HD respectively. Also the small values of Δ resulting from the 10 and 19 level fits for D_2 are considered inaccurate.

(3) A positive value of Δ implies a decrease in the leading term of the Dunham coefficients, i.e. Y_{10} as can be seen from Eq. (3.15).

This in turn leads to an energy decrease. A negative nonadiabatic correction is in agreement with Bunker's results [21] and with those of Bishop and Shih [24]. On the other hand negative Δ means positive nonadiabatic corrections which agrees with the earlier results obtained by Fisk and Kirtman [15]. It should be recalled that Fisk and Kirtman made an ab initio estimate, while the results of Bunker and of Bishop and Shih were semi-empirical and in good agreement with differences between experimental values and very accurate ab initio adiabatic calculations.

Since it appears that the data based on lower level fits should give the most reasonable results, we repeated the calculation of the various parameters when $\Delta=0$ (i.e. without non-adiabatic Born-Oppenheimer violation) using sets based on the 3 level fit for H_2 and 5 level fits for both HD and D_2. The results are listed in Table VI for the two cases ($\Delta=0$ and $\Delta\neq0$) along with the reduced mass for each molecule. As we expected, the velocity-dependent term is mass-dependent and the correction coefficient Δ is inversely proportional to the reduced mass μ. The Morse parameters ρ and τ are nearly the same for the three isotopic molecules, but the parameters b_4, b_5 and b_6 are not exactly the same for the three isotopic species. This is in part due to the inaccuracy of the raw data and to the fact that in our calculation the series has been truncated at b_6. In order to get higher PMO model parameters, we need more accurate data and formulas for more Dunham coefficients. Huffaker [7] studied the effect of truncation of the series on the various parameters for CO, HF and HCl molecules and concluded that truncation does not have serious effects on mole-

Table VI

Comparison of the PMO Parameters and Δ for H_2, HD and D_2

mol	ρ	σ	τ	b_4	b_5	b_6	Δ	μ
H_2	1.594831	14.17005	31079.30	0.1462035	0.0393670	0.03456199	0.00	0.504066
	1.598405	14.11779	30986.03	0.1424526	0.0472637	0.02038393	-0.3390600×10^{-2}	
HD	1.595355	16.36822	31127.51	0.1388348	0.0462374	0.0464899	0.00	0.671917
	1.598257	16.31851	31049.22	0.1357093	0.0528603	0.3449859	-0.260286×10^{-2}	
D_2	1.596670	20.04284	31176.73	0.1340681	0.0439908	0.0619413	0.00	1.007363
	1.598195	20.00950	31130.20	0.1321836	0.0479549	0.0547641	-0.1748395×10^{-2}	

cules with large number of bound states σ. However, even for CO with $\sigma \simeq 77$, b_{10} was found to be larger than b_8 and b_9 [39] even when the series was truncated at b_{12}. From that point of view it is clear that in order to make better evaluation of b_n's for molecules with small σ as in the present case, we would need more precise data. For HD, $Y_{31} = \delta_e$ and $Y_{40} \simeq \omega_e z_e$ are given for both 10 and 5 level data. We used equations (3.17d) and (3.17e) to calculate b_7 and b_8. For D_2 the calculation of b_7 and b_8 were only possible for the 19 and 10 level fits. For H_2, b_7 and b_8 were not calculated owing to the lack of sufficient data. The effect of truncating the series at b_8 instead of b_6 for HD and D_2 are shown in Table VII.

From Table VII it is clear that the effects of stopping at a given number of parameters for HD and D_2 are not serious.

Assuming the validity of the Born-Oppenheimer approximation (Δ=0) we recalculated the eight parameters for HD obtaining the values $\rho = 1.5964$, $\sigma = 16.346$, $\tau = 31085\text{cm}^{-1}$, $b_4 = 0.14092$, $b_5 = 0.0456$, $b_6 = 0.047903$, $b_7 = 0.026048$, $b_8 = 0.016902$.

Table VII

The Effect of Truncation on PMO Parameters for HD and D_2

PMO Parameter	HD		D_2	
	Series truncated at b_6	Series truncated at b_8	Series truncated at b_6	Series truncated at b_8
ρ	1.59818	1.5996	1.603772	1.6046
σ	16.318151	16.289	19.87489	19.855
τ	31046.83	30990.00	30932.05	30900.00
b_4	0.135598	0.13762	0.1382988	0.13973
b_5	0.0530612	0.052416	0.058003	0.057552
b_6	0.0341543	0.035479	0.0413803	0.042329
b_7		0.034002		0.028187
b_8		0.0036692		0.014829
Δ	$-0.260286\text{x}10^{-2}$	$-0.26832\text{x}10^{-2}$	$-0.0995635\text{x}10^{-2}$	$-0.10014\text{x}10^{-2}$

CHAPTER V

EVALUATION OF THE PMO PARAMETERS BY LEAST SQUARES FITS

The results obtained in the previous chapter are rather unsatisfactory. First, they are based on empirical values of Dunham coefficients which are quite sensitive to the number of levels fitted. Second, the negative values of Δ obtained in Chapter IV mean positive nonadiabatic corrections which contradicts the results obtained by Bunker et al. [20]. They found that a satisfactory fit could be achieved if the reduced mass μ for the vibrational kinetic energy in the adiabatic approximation was replaced by $\mu_V = \mu/(1+B) \approx u(1-B)$. μB was found to be the same for H_2 and D_2 and is given by $\mu B = -0.0002537$. This implies an increase in the vibrational reduced mass which in turn leads to an energy decrease as a result of using the nonadiabatic approach. Moreover by comparing Eq. (3.15e) with Bunker's vibrational reduced mass [16] given by $u/(1+B)$ we found that our velocity dependent parameter Δ should be approximately equal to $(B/2) \approx (0.0002537/2\mu)$. We suspected that the differences between our results and those of Bunker might be due to inaccuracies in the empirical Dunham coefficients from which we evaluated the PMO parameters.

Ideally, Dunham coefficients are the coefficients of the double power series expansion for $E_{v,J}$:

$$E_{v,J} = \sum_{j,k} Y_{jk}(v + \tfrac{1}{2})^j [J(J + 1)]^k . \qquad (1.2)$$

Empirically, these coefficients are obtained by fitting techniques involving choices of where to truncate the two sums in the above equation, and of which empirical energy eigenvalues to fit. As shown by the entries in Tables III-V, the empirical Dunham coefficients for H_2, HD, and D_2 depend rather sensitively on these choices.

In order to avoid the difficulties involved in the use of semi-empirical Dunham coefficients, we decided to determine the best set of PMO parameters (including Δ) directly from the empirical energy levels. For this purpose we combined a multivariable minimization program developed by Huffaker with our program for energy calculation using Eq. (1.2) and formulas from Table II. We started with two sets of PMO parameters for each molecule, one obtained in Chapter IV via the iteration program with the negative value of Δ, the other using the same values for all parameters except for Δ, which we replaced by the value $\Delta \approx (B/2) \approx (0.0002573/2\mu)$. These parameters were then varied through the program so as to minimize the weighted square error

$$\sum_{v,J} (E_{vJ}^{exp} - E_{vJ}^{calc})^2/W_{vJ} \qquad (5.1)$$

where E_{vJ}^{exp} and E_{vJ}^{calc} are experimental and calculated values of $E_{vJ}-E_{00}$, and where W_{vJ} is a weighting factor. Since it is known that the PMO model is less accurate for higher values of v or J, the weight factor W_{vJ} can make square errors for large v or J less important than those for small v or J. At first we used a weighting function of the form

$(E_{vJ}^{exp})^2(v + .3J)^2$. Huffaker then suggested that another form given by $(E_{vJ}^{exp})^2\exp[\ln 2(v + .3J)]$ might be a better representation of the accuracy of the PMO model. We found that the two forms of W_{vJ} mentioned above yield slightly different results. We preferred to use the second form to the first one.

In carrying out the calculations the series expansions (1.2) were cut off at $j \leq 4$ and $k \leq 3$ up to $j + k \leq 4$. For each molecule the fitting procedure was carried out up to $v \approx \frac{1}{2}\sigma$ and $J = 4$. As experimental data we used the same data used by Bunker et al. [21] for H_2. Those data were calculated from constants obtained by them through private communications and we found it slightly different from those given earlier by Dieke [36]. For HD and D_2 we used the data given in [37] and [23] respectively.

In Tables VIII-X we give the observed minus the calculated values for H_2, HD and D_2 molecules respectively. In each of these tables there are two numbers for each (v,j): the upper one is the difference between the observed and the best fit energy when Δ is negative while the lower number is that difference when Δ is positive. The two sets of PMO parameters which produced the best fit energies for H_2, HD and D_2 are listed in Table XI.

From Tables VIII-X we notice the following:

(1) There is very little difference between the best fit energies calculated using either a positive nonadiabatic correction factor Δ or negative one and since the positive values of Δ have much smaller absolute values than the negative values and agree with Bunker's values in magnitude as well as in sign we tend to believe that the minimum obtained using the negative Δ is a false one.

Table VIII

The observed minus calculated vibration-rotation energies in cm^{-1} relative to the v = j = 0 energy for H_2. The upper number is when $\Delta = -0.0027708$. The lower number is when $\Delta = 0.00025996$.

v	j = 0	j = 1	j = 2	j = 3	j = 4
0	0.00	0.00	-0.01	-0.02	0.07
	0.00	0.00	-0.00	-0.02	0.04
1	0.04	-0.08	-0.02	-0.04	0.03
	0.05	-0.06	0.01	-0.02	0.05
2	0.12	0.10	0.07	-0.02	-0.01
	0.10	0.09	0.07	-0.01	-0.02
3	0.03	-0.07	0.05	-0.04	0.12
	0.08	-0.11	0.07	-0.04	0.13
4	0.08	-0.12	-0.09	-0.01	0.05
	0.12	-0.15	0.09	-0.01	0.05
5	0.09	0.02	0.05	0.11	0.28
	-0.11	0.05	0.09	0.15	0.28
6	0.01	0.04	0.12	0.17	0.12
	0.06	0.10	0.17	0.19	0.05
7	-0.02	-0.03	-0.05	0.18	0.52
	-0.01	-0.04	-0.10	0.32	0.84

Table IX

The observed minus calculated vibration-rotation energies in cm^{-1} relative to the $v = j = 0$ energy, for HD. The upper number is when $\Delta = -0.0023948$. The lower number is when $\Delta = 0.00018714$.

v	j = 0	j = 1	j = 2	j = 3	j = 4
0	0.00	0.00	0.02	-0.04	0.08
	0.00	0.00	0.05	0.00	0.12
1	0.04	0.04	0.03	-0.23	0.02
	0.09	0.08	0.05	-0.26	0.10
2	0.07	-0.13	0.03	-0.21	0.00
	0.11	-0.10	0.03	-0.16	0.12
3	0.13	-0.06	0.00	-0.05	0.00
	0.12	-0.06	-0.01	-0.08	0.08
4	-0.08	-0.17	-0.05	-0.13	0.00
	-0.10	-0.17	-0.05	-0.11	-0.01
5	0.06	-0.15	0.04	-0.03	0.09
	0.03	-0.15	0.08	-0.06	0.17
6	0.05	-0.02	0.13	0.06	0.17
	0.03	0.00	0.21	0.11	0.28
7	0.26	0.16	0.27	0.18	0.21
	0.15	0.17	0.34	0.27	0.22
8	-0.09	-0.22	-0.19	-0.45	-0.55
	0.00	0.25	-0.23	0.56	-0.89

Table X

The observed minus calculated vibration-rotation energies in cm^{-1} relative to the v = j = 0 energy for D_2. The upper number is when $\Delta = -0.0012600$. The lower number is when $\Delta = 0.0001313$.

v	j = 0	j = 1	j = 2	j = 3	j = 4
0	0.00	0.02	-0.02	0.01	0.06
	0.00	0.02	-0.01	0.02	0.06
1	-0.08	-0.06	0.11	0.09	0.06
	0.02	0.00	0.06	0.06	0.05
2	0.21	0.18	0.14	-0.06	0.11
	0.24	0.20	0.13	-0.10	0.02
3	-0.08	-0.08	-0.02	0.02	0.10
	-0.10	-0.11	-0.09	-0.10	-0.07
5	-0.15	-0.14	0.00	-0.01	0.11
	-0.16	-0.18	-0.07	-0.12	0.03
6	0.09	0.03	0.07	-0.04	-0.16
	0.17	0.13	0.21	0.17	0.17
7	0.30	0.23	0.15	-0.08	-0.37
	0.32	0.31	0.34	0.30	0.30
8	0.63	0.48	0.20	-0.30	-0.96
	0.30	0.27	0.22	0.09	-0.02
9	0.61	0.43	-0.13	-1.04	-2.19
	-0.54	-0.53	-0.70	0.99	-1.26

(2) This is the first time (to our knowledge) where a nonadiabatic correction is taken into account for a heteronuclear molecule such as HD and the agreement between theory and experiment is quite satisfactory.

(3) For D_2 and H_2 molecules the agreement between observed and calculated values are better than those obtained by Bunker et al. [21] except for a very few points. However in our approach we are unable to fit as many vibrational levels as in Bunker's approach since our PMO model was truncated after b_8, Y_{40}, Y_{31}, etc. and higher order coefficients become important for higher vibrational levels.

From Table XI we notice that in the second set Δ is positive and one order of magnitude smaller than Δ in the first set. Also although both values of Δ in the two sets are inversely proportional to the reduced mass for the three isotopic molecules yet we find that 2μΔ in the second set are equal to $\approx 0.260\text{x}10^{-3}$, $0.255\text{x}10^{-3}$ and $0.264\text{x}10^{-3}$ for H_2, HD and D_2 respectively which is very close to $0.2537\text{x}10^{-3}$ ±0.000012 estimated by Bunker et al. [21] for H_2 and D_2.

Table XI. The PMO parameters which give best fitted energies for H_2, HD and D_2.

	molecule	ρ	σ	τ	b_4	b_5	b_6	b_7	b_8	Δ
1st set	H_2	1.5983	14.124	31014.926	0.14012	0.05350	0.04766	0.02397	0.0205	$-0.2771\text{x}10^{-2}$
	HD	1.5997	16.284	30982.075	0.14176	0.05334	0.04628	0.02476	0.0198	$-0.2345\text{x}10^{-2}$
	D_2	1.5982	20.005	31124.60	0.14026	0.04396	0.05350	0.02554	0.01627	$-0.126\text{x}10^{-2}$
2nd set	H_2	1.6017	14.108	31072.533	0.13955	0.05256	0.04786	0.02362	0.02023	$0.2599\text{x}10^{-3}$
	HD	1.5966	16.393	31268.390	0.13732	0.04735	0.05058	0.02094	0.02058	$0.1871\text{x}10^{-3}$
	D_2	1.5990	20.003	31160.990	0.14094	0.04778	0.04644	0.02424	0.01845	$0.1312\text{x}10^{-3}$

CHAPTER VI

ANALYSIS OF NUMERICAL RESULTS AND CONCLUSIONS

In Chapter V we showed that the differences between experimental and calculated rovibronic energies in the adiabatic approximation were reduced by including a nonadiabatic correction term in the PMO potential. The mass dependence of this correction term for H_2, HD, and D_2 is consistent with the effects expected from the nonadiabatic interaction. For H_2 and D_2 our results agree quantitatively with Bunker's results [21] and with those obtained by Bishop and Shih [24]. In this chapter a more detailed analysis of the results obtained in Chapter V will be made.

First, we consider the errors which are probably present in our analysis because of our truncation of the PMO series. As we mentioned in Chapter V, we used only eight PMO parameters and consequently 14 Dunham coefficients. Truncation of the PMO series at b_8 and the Dunham coefficients Y_{jk} at $j+k\leq 4$ is certainly responsible for some of the differences between measured and calculated eigenvalues. This contribution increases rapidly with v. For example, neglecting the Y_{50} coefficient could be a major source of error at high v since it contributes $Y_{50}[(v+.5)^5-.5^5]$ to the energy eigenvalues. Also Y_{04} and Y_{41} could improve our calculated energies by $Y_{04}[J(J+1)]^4$ and $Y_{41}[(v+.5)^4-.5^4][J(J+1)]$ respectively. We can get a rough idea of the magnitude of the error resulting of the neglect of Y_{50} by plotting $\log|Y_{j0}|$ against j and extrapolating to j=5 to find the order of magnitude of Y_{50}. Fig. 1 shows the values of $\log|Y_{j0}|-N$ against j for the three isotopes where N=0,5,10 for H_2, HD and D_2 respectively. From the figure we found that $Y_{50} \simeq 0.0009$ cm^{-1} for H_2, 0.00055 cm^{-1} for HD and 0.00017 cm^{-1} for D_2. This means that the error resulting from that coefficient alone is about 21 cm^{-1} for H_2 at v=7. For HD at v=8 the error is about 24 cm^{-1}. For D_2 the error is about 13 cm^{-1} at v=9. Although this is only a rough estimate, and although part of this error is removed by the neglect of Y_{60} (since Y_{j0}'s alternate in sign) we feel that this is probably the largest source of error in our approach. The reason that we obtained a good agreement between theory and experiment up to v=7, 8 and 9 for H_2, HD, and D_2 respectively could be attributed to the fact that truncation of the series at low j has the effect of influencing the other coefficients, especially the smaller ones (Y_{30} and Y_{40}), to compensate for the effects of the coefficients not included in the calculation. This is in turn affects the accuracy of the PMO parameters, especially b_7 and b_8. Such effects were studied in detail by Huffaker [7]. Hopefully by combining Huffaker's program which takes into account higher order modified coefficients [37] with the minimization program used here we could diminish the effect of that error and obtain more accurate Dunham coefficients and more precise PMO parameters.

Next, we consider the implication of our results for the existence of adiabatic and nonadiabatic effects which violate the Born-Oppenheimer approximation. Recall that according to the Born-Oppenheimer

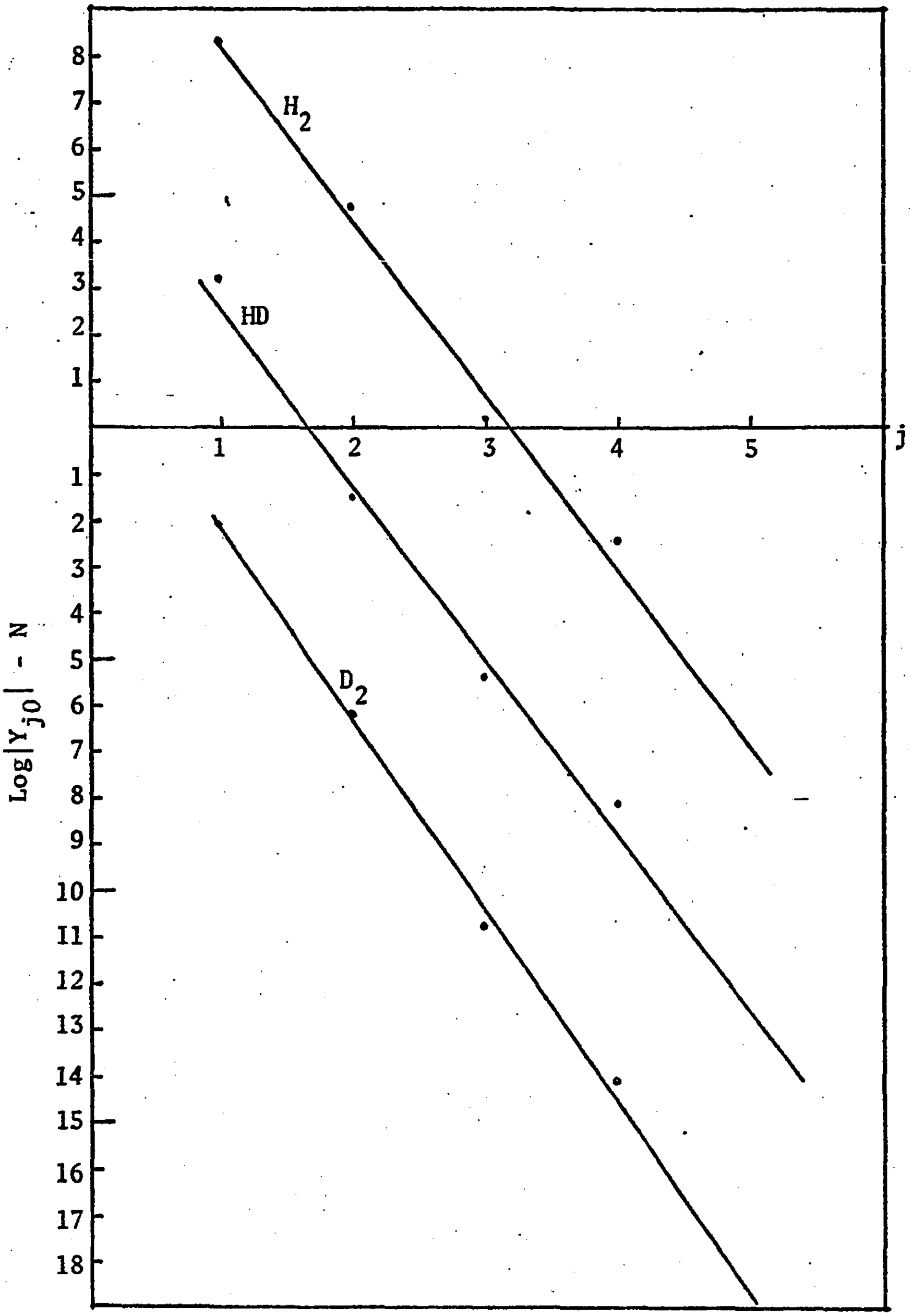

Figure 1. The plot of $\log|Y_{j0}| - N$ against j for H_2, HD and D_2.

approximation, the PMO parameters should be identical for different isotopic species. From Table XI it is clear that the PMO parameters ρ, τ, ... b_8 are different for the three isotopic molecules. This means that the potential curves are different for the three isotopes. Of course, difference in static potential curves for different isotopic species are an adiabatic correction to the Born-Oppenheimer approximation. Bunker [17] showed that including an adiabatic correction produces a mass-dependent term in the equilibrium distance as well as in the force constant; hence we think of the isotopic variation of the PMO parameters as a kind of adiabatic correction which should have some functional dependence on the reduced masses.

To examine the mass dependence of the equilibrium internuclear distance r_e we use the definitions

$$r_e = \frac{\rho}{a}, \quad \tau = \frac{V_e}{hc} \quad \text{and} \quad \sigma = \frac{(2\mu V_e)^{1/2}}{a\hbar}$$

and rearranging we find that

$$r_e \approx \frac{\rho\sigma}{0.243555\sqrt{\mu\tau}} .$$

Using the numerical values of ρ, τ and σ from the second set of Table X we found that the internuclear equilibrium distances r_e for H_2, HD and D_2 are 0.74134A°, 0.74139 A° and 0.74122 A° respectively. So there is no simple dependence of r_e on the reduced mass . The adiabatic force constant κ can be obtained using the definitions $\nu_{osc} = \frac{1}{2\pi}\sqrt{\kappa/\mu} \approx \omega_e c$ where $\omega_e \approx (2\tau/\sigma)(1+\Delta)$. Substituting the numerical values of τ, μ, σ, and Δ we found that $\kappa \approx 5.7765\text{x}10^5$, $5.7812\text{x}10^5$, and $5.7731\text{x}10^5$ dyne/cm for H_2, HD, and D_2 respectively. Here again there is no clear dependence on reduced mass. From Table XI it is also obvious that the PMO coefficients $b_4 \ldots b_8$ for HD do not lie half-way between for H_2 and D_2. It is certainly plausible to assume that adiabatic effects for HD should be intermediate between those for H_2 and D_2; indeed this was assumed by Kolos and Wolniewicz [14]. The results in Chapter V clearly contradict this assumption.

Theorists are careful to point out that various simplifying assumptions involved in ab initio adiabatic calculations hold only for homonuclear molecules, and they have not presented adiabatic results for HD. The reason is easy to understand: the trial electron functions are expressed in coordinates with origin at the center-of-charge of the nuclei, which provides natural symmetries. If the molecule is homonuclear, this origin is also the equilibrium value of the center-of-mass, and is thus very nearly an inertial system, except for small (adiabatic) effects when electrons move one way and nuclei the opposite way. On the other hand, if the molecule is heteronuclear, the center-of-mass is nowhere near the center-of-charge, and the latter is not an inertial system. Thus, our results for HD could be an indication of the corrections which are present because the center-of-charge and the center-of-mass do not coincide.

For H_2 and D_2 one can still assume that the adiabatic correction is proportional to $1/\mu$ and obtain the Born-Oppenheimer values of r_e^0 and κ^0, assuming the relation:

$$r_e = r_e^0 + \frac{\kappa_1}{\mu}$$

and

$$\kappa = \kappa^0 + \frac{c_1}{\mu}$$

where r_e^0 and κ^0 are the equilibrium internuclear distance and the force constant is the Born-Oppenheimer approximation. We find to a first order approximation that $r_e^0 = 0.74110$ A^0 and $\kappa_1 = 0.00012$. For the force constant we find that $\kappa^0 = 5.7697\text{x}10^5$ dyne/cm and $c_1 = 0.0034\text{x}10^5$.

We find that, unlike the adiabatic effects, the nonadiabatic effects for H_2, HD and D_2 are very nearly proportional to $1/\mu$. In a way this is surprising, since the nonadiabatic effects are thought of as second-order-perturbation corrections involving higher electronic states, and more excited states can mix with the ground state in HD than in H_2 or D_2 because of the nuclear-exchange symmetry of the latter. Obviously this additional mixing is not very important for the nonadiabatic correction.

We also felt we should compare the values of the non-adiabatic corrections with those obtained by other methods. The nonadiabatic effects E^{nad} can be calculated using the formula

$$E^{nad} = \sum_{j=K=0} j\Delta Y_{jK}(v + \tfrac{1}{2})^j [J(J+1)]^K \tag{6.1}$$

where Y_{jK} is the adiabatic Dunham coefficients and Δ is the nonadiabatic coefficient defined in Chapter III. Considering a rotationless state (J=0) Eq. (6.1) becomes

$$E^{nad} = \sum_{j=0} j\Delta Y_{j0}(V + \tfrac{1}{2})^j \ . \tag{6.2}$$

Using Eq. (6.2), we calculated the nonadiabatic effects relative to v=J=0 for the three isotopes. The results are listed in Table II. For comparison, we included the nonadiabatic correction calculated by Bishop and Shih [24] for H_2 and D_2 in the third and fifth columns of Table XII.

From the table it is clear that there is a very little difference between the nonadiabatic corrections obtained in the present approach and those obtained by Bishop and Shih [24] using Eq. (14). Though the nonadiabatic corrections were not calculated here for $J \neq 0$ they could in principle be calculated using Eq. (6.1). This is not done since the J dependence of the nonadiabatic correction is small and since we did not include high values of J in our calculations.

The nonadiabatic corrections calculated using Eq. (6.2) are plotted versus $u = v + 1/2$ in Figure 2 for H_2, HD and D_2.

The PMO parameters listed in Table XI (including positive values of Δ) reduced the weighted square errors given by Eq. (5.1) from 0.66×10^{-9} to 0.17×10^{-11} for H_2, from 0.12×10^{-9} to 0.40×10^{-11} for HD, and from 0.26×10^{-9} to 0.40×10^{-11} for D_2. Consequently the Dunham coefficients based on these PMO parameters should be more accurate and reliable than the set of coefficients we started with in Chapter IV to obtain the PMO parameters. In Tables XIII to XV we list the new Dunham coefficients which are calculated according to the formulas given in Table II using the second set of PMO parameters obtained in Table XI for the three isotopes. For comparison we listed the corresponding sets of coefficients obtained in references [22,29], [34] and [23] for H_2, HD, and D_2 respectively, noting that there are more than one set for each molecule depending on the number of vibrational levels included in the fitting procedure used in those references.

From the above analysis and the analysis in the previous chapters we conclude that the nonadiabatic breakdown of the Born-Oppenheimer approximation could be corrected for by adding a velocity dependent term

Table XII

Values of the Nonadiabatic Corrections E^{nad} in cm^{-1} for H_2 and D_2

(J = 0)

molecule	H_2		D_2	
V	a	b	a	b
0	0.00	0.00	0.00	0.00
1	-1.02	-0.97	-0.37	-0.36
2	-1.92	-1.83	-0.71	-0.69
3	-2.70	-2.58	-1.02	-0.99
4	-3.37	-3.21	-1.31	-1.26
5	-3.91	-3.74	-1.57	-1.50
6	-4.34	-4.14	-1.79	-1.72
7	-4.64	-4.42	-1.98	-1.90
8			-2.16	-2.06
9			-2.29	-2.19

a nonadiabatic correction obtained using Eq. (6.2)

b nonadiabatic correction obtained using Eq. (14) in Ref. [24]

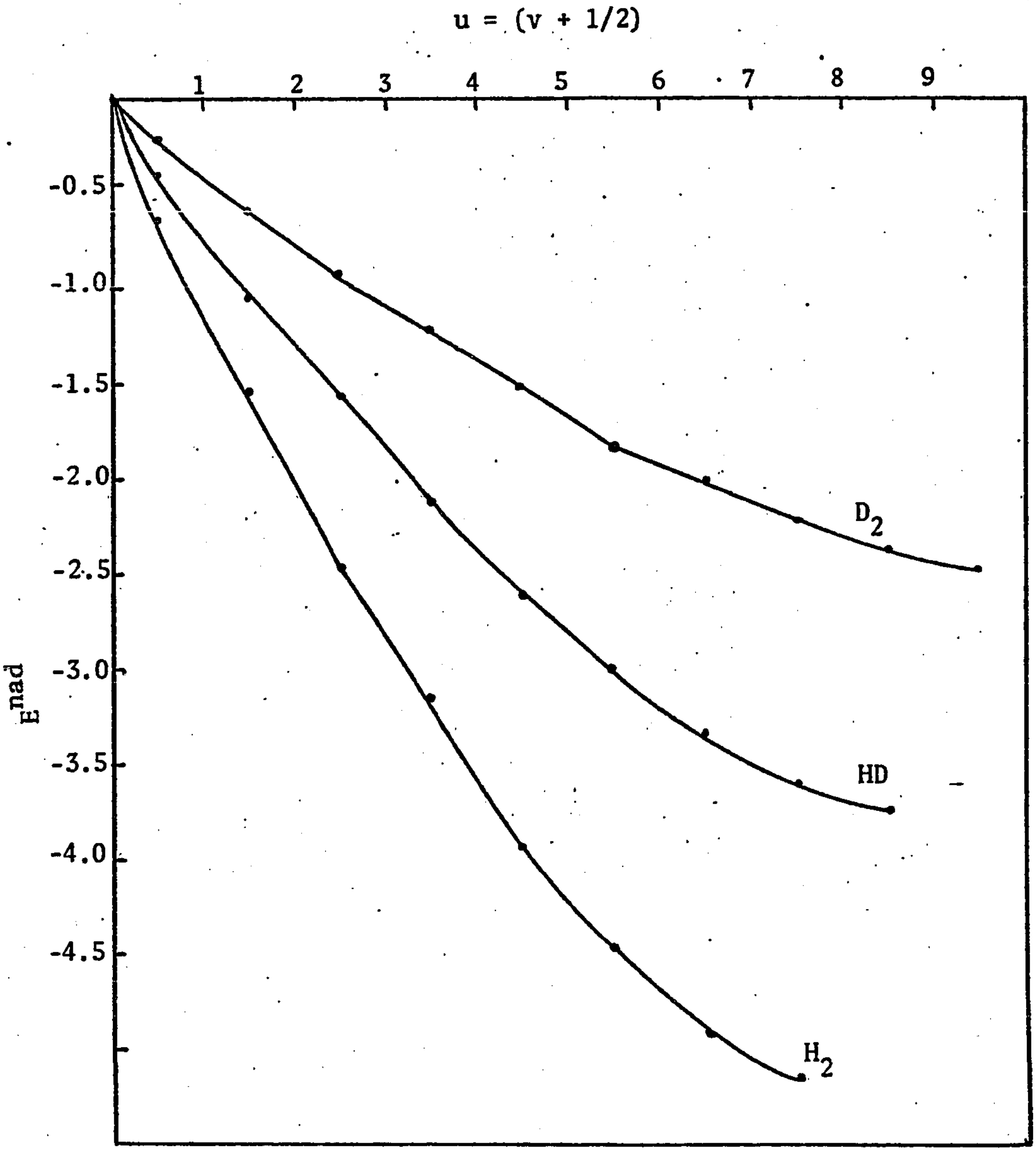

Figure 2. The nonadiabatic correction in cm^{-1} against v for H_2, HD and D_2.

Table XIII

The Dunham coefficients Y_{jK} in the ground state $X^1\Sigma_g$ of H_2 molecule

j	K	$Y^{(0)}_{jK}$	$Y^{(2)}_{jK}$	Y_{jK}	Y_{jK} (8 level fit) [22]	Y_{jK} (3 level fit) [29]
0	0	0.00	8.1695	8.1695		
0	1	60.85170	-0.00799	60.844	60.864	60.841
0	2	-0.04645	$-0.347\text{x}10^{-5}$	-0.04645	-0.04657	-0.04684
0	3	$0.4958\text{x}10^{-4}$	0.0	$0.4958\text{x}10^{-4}$		
1	0	4403.72	-0.4656	4403.26	4400.39	4400.39
1	1	-3.0341	-0.0036	-3.0376	-3.0763	-3.0177
1	2	0.00152	0.00	0.00152		
1	3	$-0.04564\text{x}10^{-5}$		$-0.04564\text{x}10^{-5}$		
2	0	-123.3167	0.0122	-123.355	-120.81	-120.81
2	1	0.0464	0.0	0.0464	0.0601	0.0285
2	2	$-0.809\text{x}10^{-5}$	0.00	$-0.809\text{x}10^{-5}$		
3	0	1.546		1.546	0.724	0.724
3	1	-0.03576	0.00	-0.03576		
4	0	-0.08829	0.00	-0.08829		

Table XIV

The Dunham Coefficients Y_{jK} in the ground state $x^1\Sigma$ of HD molecule.

j	K	$Y_{jK}^{(0)}$	$Y_{jK}^{(2)}$	Y_{jK}	Y_{jK} [10 level fit] [34]	Y_{jK} [5 level fit] [34]
0	0	0.00	5.9916	5.9916		
0	1	45.645	-0.005	45.640	45.655	45.643
0	2	-0.026	$0.325\text{x}10^{-5}$	-0.0261	-0.0261	-0.0263
0	3	$0.2100\text{x}10^{-4}$	0.00	$0.2100\text{x}10^{-4}$		
1	0	3814.02	-0.1537	3813.86	3813.15	3813.55
1	1	-1.9545	$-0.2618\text{x}10^{-2}$	-1.957	-1.9860	-1.9615
1	2	$0.7002\text{x}10^{-3}$	0.00	$0.7002\text{x}10^{-3}$		
1	3	$-0.1626\text{x}10^{-6}$	0.00	$-0.1626\text{x}10^{-6}$		
2	0	-92.35	$0.745\text{x}10^{-3}$	-92.35	-91.65	-92.01
2	1	0.0209	0.00	0.0209	0.03146	0.02027
2	2	$0.1288\text{x}10^{-4}$	0.00	$0.1288\text{x}10^{-4}$		
3	0	0.9655	0.00	0.9655	0.723	0.862
3	1	$-0.1352\text{x}10^{-2}$	0.00	-0.1352		
4	0					
4	0	-0.0473	0.00	-0.0473	0.0133	-0.0379

Table XV

The Dunham coefficients Y_{jK} in the ground state $x^1\Sigma_g$ of D_2

j	K	$Y_{jK}^{(0)}$	$Y_{jK}^{(2)}$	Y_{jK}	Y_{jK} [19 level fit] [23]	Y_{jK} [10 level fit] [23]	Y_{jK} [5 level fit] [23]
0	0	0.00	4.1161	4.1161			
0	1	30.441	-0.0025	30.439	30.458	30.440	30.434
0	2	-0.0116	$0.4876\text{x}10^{-6}$	-0.0116			
0	3	$0.6218\text{x}10^{-5}$	0.0	$0.06218\text{x}10^{-5}$			
1	0	3115.103	-0.1545	3114.95	3116.08	3115.50	3115.78
1	1	-1.0696	$-0.468\text{x}10^{-3}$	-1.0700	-1.1009	-1.0780	01.0690
1	2	$0.2707\text{x}10^{-3}$	0.00	$0.2707\text{x}10^{-3}$			
1	3	$-0.6114\text{x}10^{-7}$	0.0	$-0.6114\text{x}10^{-7}$			
2	0	-61.392	$-0.458\text{x}10^{-2}$		-62.40	-61.82	-62.04
2	1	$0.9941\text{x}10^{-2}$	0.00	$0.9941\text{x}10^{-2}$	0.02237	0.01265	0.007877
2	2	$-0.6652\text{x}10^{-6}$	0.00	$-0.6652\text{x}10^{-6}$			
3	0	0.4778	0.00	0.4778	0.812	0.562	0.618
3	1	$-0.4561\text{x}10^{-3}$	0.00	$-0.456\text{x}10^{-3}$			
4	0	-0.018	0.00	-0.018	-0.0764	-0.0228	-0.0274

$\Delta\, d^2/dr^2$ to the PMO potential and treating it as a perturbation correction.

We showed that the changes in the Dunham coefficients Y_{j0} (produced by including the new term) are equivalent to a change in the "vibrational" reduced mass of about $2\Delta\mu$ where μ is the reduced mass used in the adiabatic approximation. On the other hand the coefficients Y_{0k} are not - to first order - affected by including the nonadiabatic term. In terms of reduced masses this means that in both adiabatic and nonadiabatic approximation we use the same reduced mass to calculate the rotational kinetic energies.

Treating the PMO parameters and Δ as fitting parameters, we were able to achieve satisfactory fits to experimental vibronic energies of the ground state of H_2, HD, and D_2. Although several groups have attempted to perform ab initio nonadiabatic calculation for H_2 and D_2, none succeeded in fitting discrepancies between experimental and predicted adiabatic energies. The present results prove that our approach is as efficient - in predicting accurate eigenvalues - as that of Bunker [20]. Also we showed that there is a very little difference between our calculations and those obtained by Bishop and Shih [24]. Moreover our approach proved very successful for the case of a heteronuclear molecule in contrast to the other approaches [20, 24], which were developed only for homonuclear molecules.

In the present approach we do not need an ab initio calculation to find the adiabatic energies, but we need precise and reliable data for the energy levels. Care must be taken in fitting to avoid a "false minimum" with a value of Δ with the wrong sign. One can apply the rule that the nonadiabatic correction should lower the adiabatic energies since it is in principle a second-order correction term.

One advantage of allowing for the breakdown of the Born-Oppenheimer approximation while using the PMO model is that the formulas for the energy levels are still simple and can be easily computed and can be applied in principle to more complicated molecules other than H_2. The disadvantage of this approach is the fact that although the convergence properties of the perturbation series are good for moderate values of v, however we cannot study the nonadiabatic corrections for levels of high quantum number v. This is of course because the PMO model itself involves a perturbation expansion in the powers of $(v + 1/2)/\sigma$ and the accuracy of the calculated energies decreases rapidly as v increases. To handle higher vibrational levels accurately one needs higher-order PMO coefficients b_n and higher-order Dunham coefficients.

The wave functions for the PMO model including nonadiabatic effects can be calculated fairly easily (via perturbation theory) to the accuracy of the PMO functions of Dwivedi and Huffaker [38,39]. We would expect that these functions would give better representation of the vibration and rotation eigenfunctions of light diatomic molecules. Such functions would allow more accurate determination of the transition probabilities especially for hydrides and deuterides.

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