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# An Analytic Treatment of Adiabatic and Nonadiabatic Effects on the Vibration-rotational Energies of Diatomic Molecules

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By means of a quantitative analytic treatment, we have calculated the adiabatic and nonadiabatic effects on the vibration-rotational energies of diatomic **molecules**. We have proved that one can in principle determine independently one coefficient of each radial function representing the rotational nonadiabatic and adiabatic effects whereas because the remaining coefficients of the three radial functions representing the adiabatic, rotational and vibrational nonadiabatic effects appear in inextricable linear combinations they cannot be individually determined from experimental measurements of transition frequencies in the absence of external -electric and magnetic fields.

### I. INTRODUCTION

In his innovative algebraic treatment of the vibration-rotational motions of diatomic molecules,\* Dunham derived analytic relationships between the parameters in his flexible function for the internuclear potential energy and the molecular eigenenergies for the discrete states denoted by the vibrational and rotational quantum numbers v and J (in the absence of other contributions to the total molecular angular momentum) respectively. Using this mechanical theory during succeeding decades spectroscopists have determined these potential-energy functions for particular diatomic molecules; by this method they sought to achieve a reduction of many frequency and wavenumber data to relatively few molecular parameters in the form of coefficients in the potential-energy function that serve to reproduce the observed data. These data have during the course of time become more precise, primarily because of the relentlessly improving spectral resolution. The spectra of isotopic variants of a particular diatomic species have been routinely subjected to simultaneous analysis. In these circumstances Dunham's theory was found to become inadequate to describe quantitatively data of the available quality and quantity. Effects beyond those associated with the potential-energy function appeared not only to cause deviations from the expected mass-scaling factors relating the energies of isotopic variants but even to lead to systematic discrepancies in the energies of highly rotationally excited states of a

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single isotopic **species**.<sup>2</sup> The attribution of an internuclear potential-energy function implies the separate treatment of electronic and nuclear motions equivalent to the classical notion<sup>3</sup> of the atomic model of a molecule that Born and Oppenheimer introduced into quantum **mechanics**.<sup>4</sup> The deviations from the mechanical behaviour are attributed to adiabatic and nonadiabatic effects: adiabatic effects result from the dependence of internuclear potential energy of a particular isotopicvariant on not only the internuclear distance but also the relative nuclear momenta, thus within a particular electronic state, whereas nonadiabatic effects are attributed to the induction by vibrational and rotational motions of the nuclei of interactions with other electronic states.

During the several decades since the work of Born, Oppenheimer and Dunham, many researchers have considered, in progressively greater detail, these effects and have endeavoured to envisage their explicit consequences in relation to the energies of diatomic molecules. Van Vleck carried out a systematic analysis of the deviations from the Born-Oppenheimer behaviour of the vibration-rotational energies of a diatomic molecule related to isotopic effects,' whereas Townes and coworkers were primarily interested in the effects observable by means of pure rotational spectra.<sup>6</sup>. In their more nearly complete treatment of this problem, Herman and Asgharian produced an effective hamiltonian that takes into account the adiabatic and nonadiabatic effects up to second order in the ratio of electronic to nuclear masses.<sup>7</sup> Treating in detail the adiabatic potential energy, Bunker proposed the theoretical framework for the calculation of electronic isotope shifts and corrections to the Dunham coefficients  $Y_{0,1}$  and  $Y_{1,0}$ .<sup>8-10</sup> By means of a more rigorous method" based on the Van Vleck transformation, Bunker and Moss obtained essentially the same results as Herman and Asgharian. Besides rewriting the results of Bunker and Moss in terms of isotopically invariant functions, Watson concluded that the adiabatic and nonadiabatic effects are not separable.<sup>12</sup> Despite these and other investigations, there is still lacking a quantitative analytic treatment of the relation of identifiable theoretical effects to the parameters that one can experimentally determine in the process of a comprehensive analysis of abundant spectral lines due to pure rotational and vibration-rotational transitions of multiple isotopic variants of a particular diatomic molecular species within one electronic state; our present analysis arises from this objective. The empirical determination of adiabatic and nonadiabatic corrections is important because they can be accurately evaluated by means of quantum-mechanical calculations for only the simplest diatomic molecules. For this reason we have derived analytic expressions for the vibration-rotational energies in terms of the parameters in radial functions to represent the adiabatic effects and both the rotational and vibrational nonadiabatic effects as the basis of a quantitative decision whether these effects are entirely inseparable. The determination of these effects in the form of radial functions from vibration-rotational spectra not only generates the most compact and physically meaningful representation of the observable data<sup>13</sup> but also provides information about fundamental molecular properties that is difficult otherwise to acquire, even by means of ab initio quantum

computations for instance. Although to express adiabatic and-especially- nonadiabatic effects as functions of an internuclear distance may appear paradoxical, we assume that the electronic state of interest, commonly the electronic ground state, is sufficiently remote from other electronic states; because under these conditions these effects contribute only a small proportion of the energy of an eigenstate sufficiently far below the dissociation limit, to treat them as perturbations in the form of radial functions is appropriate.

We seek to account for adiabatic and nonadiabatic effects by means of an empirical effective hamiltonian. To this end we first outline the derivation of one commonly used hamiltonian." Then we consider the separability of the adiabatic and nonadiabatic effects. To calculate the concurrent consequences of such effects we apply perturbation theory in a quantitative analytic treatment invoking three further radial functions in the spirit of **Dunham**.<sup>1</sup> Finally we discuss the significance of these results in relation to the analysis of experimental spectra.

### II. THE EFFECTIVE VIBRATION-ROTATIONAL HAMILTONIAN

According to the analysis by Born and **Oppenheimer**,<sup>4</sup> the adiabatic and nonadiabatic corrections to the vibration-rotational energies of a molecule have as factor the ratio of the electronic mass to a selected nuclear mass to various powers. In terms of their expansion parameter  $\kappa$  this ratio is  $\kappa^4$ ; that the numerical value of this ratio is much less than unity,  $\kappa^4 \ll 1$ , bestows important properties on the ultimate results in our treatment of the adiabatic and non-adiabatic effects which requires the introduction of this ratio into the molecular hamiltonian. Of various ways to do this consistently, here we proceed by working in atomic units. Taking  $e^2/(4\pi\epsilon_0 a_0)$  and  $a_0 = 4\pi\epsilon_0 \hbar^2/(m_e e^2)$  to be the units of energy and length respectively, we write the nonrelativistic hamiltonian operator for a diatomic molecule as

$$H = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \frac{1}{2} \sum_{c} \frac{m_{e}}{M_{c}} \nabla_{c}^{2} - \sum_{c} \sum_{i} \frac{Z_{c}}{r_{ci}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} + \frac{Z_{a}Z_{b}}{R}, \qquad (1)$$

in which the first two terms represent the kinetic energies of the electrons and of the nuclei respectively; the remaining terms signify the coulombic potential energies successively of attraction between the two nuclei (having atomic numbers  $Z_a$  and  $Z_b$ ) and electrons and of repulsion between the electrons and between the nuclei;  $\mathbf{r}_{ci}$  and  $\mathbf{r}_{ij}$  are the distances between a nucleus c and an electron i and between two electrons respectively whereas R denotes the internuclear distance. Separating the motion of the molecule as a whole and placing the coordinate origin at the centre of nuclear mass we obtain the hamiltonian<sup>8</sup>

$$H = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{c} \sum_{i} \frac{Z_{c}}{r_{ci}} + \sum_{i} \sum_{j > i} \frac{1}{r_{ij}} + \frac{Z_{a}Z_{b}}{R} - \frac{m_{e}}{2M_{N}} \left(\sum_{i} \nabla_{i}\right)^{2} - \frac{m_{e}}{2\mu} \nabla_{R}^{2}, \qquad (2)$$

in which  $M_N = M_a + M_b$  is the total nuclear mass,  $\mu = M_a M_b / (M_a + M_b)$  is the reduced nuclear

mass and  $\nabla_{\mathbf{R}}$  is the gradient operator with respect to the components of  $\mathbf{R} = \mathbf{R}_{\mathbf{b}} - \mathbf{R}_{\mathbf{a}}$ . If on the other hand we place the coordinate origin at the geometrical centre of mass the resulting hamiltonian is<sup>8</sup>

$$H = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{c} \sum_{i} \frac{Z_{c}}{r_{ci}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} + \frac{Z_{a}Z_{b}}{R} - \frac{m_{e}}{8\mu} \left(\sum_{i} \nabla_{i}\right)^{2} - \frac{m_{e}}{2\mu} \nabla_{R}^{2} + \frac{m_{e}(M_{b} - M_{a})}{2M_{a}M_{b}} \nabla_{R} \cdot \sum_{i} \nabla_{i}.$$

$$(3)$$

To explain the idea underlying the construction of effective hamiltonians we express the **Schrödinger** equation for a **diatomic** molecule in the form  $H\Psi_{\rho k} = E_{\rho k}\Psi_{\rho k}$ . Hereafter greek letters denote electronic quantum numbers whereas roman ones denote vibration-rotational quantum numbers; hence  $|E_{\rho k}-E_{\nu j}| >> |E_{\rho m}-E_{\rho n}|$ . By means of a unitary operator T we transform the **Schrödinger** equation into  $\tilde{H}\Psi_{\rho k} = E_{\rho k}\tilde{\Psi}_{\rho k}$ , in which  $\tilde{H} = THT^+$  and  $\tilde{\Psi} = T\Psi$ . We expand  $\tilde{\Psi}_{\rho k}$  as a linear combination of a complete basis set in the conventional way:<sup>14</sup>

$$\tilde{\Psi} = \sum_{\sigma} \Phi_{\sigma} \chi_{\sigma k}.$$
(4)

Here  $\{\Phi_{\sigma}\}\$  is an orthonormal set of eigenfunctions of the Born-Oppenheimer electronic hamiltonian H<sub>0</sub>; we write  $H = H_0 + \lambda H'$  in which H' contains all the terms proportional to the ratio of the electronic mass to the selected nuclear mass. Application of  $\langle \Phi_{\rho} |$  from the left to the transformed S&r&linger equation (with integration over only the electronic coordinates) leads to

$$\sum_{\sigma} < \Phi_{\rho} |\tilde{H}| \Phi_{\sigma} > \chi_{\sigma k} = E_{\rho k} \chi_{\rho k}.$$
(5)

If we choose the unitary operator T such that  $\langle \Phi_{\rho} | \tilde{H} | \Phi_{\sigma} \rangle = \delta_{\rho\sigma} \langle \Phi_{\rho} | \tilde{H} | \Phi_{\rho} \rangle$ , we find that the functions  $\chi$  are eigenfunctions of the effective hamiltonian  $H_{eff}^{(\rho)} = \langle \Phi_{\rho} | \tilde{H} | \Phi_{\rho} \rangle$  with eigenvalues  $E_{\rho k}$ :

$$H_{eff}^{(\rho)}\chi_{\rho k} = E_{\rho k}\chi_{\rho k}.$$
(6)

When  $\lambda = 0$  this condition is satisfied by  $T = \hat{1}$ , the identity operator. In most problems of physical interest it is impracticable or even impossible to achieve the condition just mentioned. In that case one resorts to an approximation based on the expansion of  $\tilde{H}$  as a series in  $\lambda$  with powers of positive integers:

$$\tilde{H} = H_o + \sum_{p=1}^{\infty} \lambda^p \tilde{H}_p; \tag{7}$$

here the first term is a consequence of  $T(\lambda = 0) = \hat{1}$ . Making the simplest possible approximation

we choose  $\mathbf{T} = \mathbf{e}^{-i\lambda S}$  and determine the l-independent operator S so that  $\langle \Phi_{\rho} | \widetilde{H}_1 | \Phi_{\sigma} \rangle = \delta_{\rho\sigma} \langle \Phi_{\rho} | \widetilde{H}_1 | \Phi_{\rho} \rangle$ . The result is an approximate effective hamiltonian of the form

$$H_{eff}^{(\rho)} \cong \langle \Phi_{\rho} | (H_o + \lambda \tilde{H}_1 + \lambda^2 \tilde{H}_2) | \Phi_{\rho} \rangle,$$
(8)

in which

$$\tilde{H}_1 = H' + i[H_o, S],$$
 (9a)

$$\tilde{H}_2 = i[H', S] + \frac{1}{2}[S, [H_o, S]] = \frac{i}{2}[H' + \tilde{H}_1, S].$$
(9b)

If in addition we choose  $\langle \Phi_{\rho} | S | \Phi_{\rho} \rangle = 0$ , then  $\langle \Phi_{\rho} | \tilde{H}_1 | \Phi_{\rho} \rangle = \langle \Phi_{\rho} | H' | \Phi_{\rho} \rangle$ .

Bunker and Moss used this method to obtain an effective hamiltonian for a diatomic molecule in a  ${}^{1}\Sigma$  electronic state;<sup>11</sup> they chose

$$H_{o} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{c} \sum_{i} \frac{Z_{c}}{r_{ci}} + \sum_{i} \sum_{j > i} \frac{1}{r_{ij}} + \frac{Z_{a}Z_{b}}{R},$$
(10)

and

$$H' = -\frac{m_e}{2M_N} \left(\sum_i \nabla_i\right)^2 - \frac{m_e}{2\mu} \nabla_R^2.$$
(11)

Because H' fails to commute with the eigenvalues of  $H_0$ , the diagonalization of  $H_1$  requires an iterative procedure that eventually produces the operator S; the latter is necessary to construct  $\tilde{H}_2$ . The effective hamiltonian for the vibration-rotational energies of a diatomic molecule in a  ${}^{1}\Sigma$  state becomes

$$H_{eff} = -\frac{m_e}{2\mu} \frac{d}{dR} [1 + \beta(R)] \frac{d}{dR} + \dot{V}_{eff} + \frac{m_e}{2\mu R^2} [1 + \alpha(R)] J (J + 1),$$
(12)

in which a(R) and  $\beta(R)$ , which are intrinsically of order  $m_e/\mu$  by the nature of the electronic matrix elements that they represent, give rise to the rotational and vibrational nonadiabatic corrections;  $V_{eff}$  contains the Born-Oppenheimer potential energy plus adiabatic and further **non**-adiabatic corrections:

$$V_{eff}(R) = V^{BO}(R) + V^{AD}(R) + V^{NA}(R).$$
(13)

Here,  $V^{BO} = \langle 0 | H_0 | 0 \rangle$  and is of order  $(m_e/\mu)^0$ ,  $V^{AD} = \langle 0 | H' | 0 \rangle$  with order  $m_e/\mu$ , and  $V^{NA}$ , of order  $(m_e/\mu)^2$ , comes from  $\langle 0 | H_2 | 0 \rangle$  which also leads to the remaining nonadiabatic contributions; devoting our attention to the electronic ground state, we have set  $\rho = 0$  and  $| \Phi_0 \rangle = | 0 \rangle$ . According to custom, we express the effective hamiltonian (12) in SI or other macroscopic units; it is thus written

$$H_{eff} = -\frac{\hbar^2}{2\mu} \frac{d}{dR} [1 + \beta(R)] \frac{d}{dR} + V_{eff} + \frac{..\hbar^2}{2\mu R^2} [1 + \alpha(R)] J (J \cdot I 1).$$
(14)

## III. THE ADIABATIC AND NONADIABATIC VIBRATION-ROTATIONAL ENERGY CORRECI' IONS

Because the electronic coordinates are referred to the centre of nuclear mass which changes with isotopic substitution, the functions  $V^{AD}(R)$ ,  $V^{NA}(R)$ , a(R) and  $\beta(R)$  in the effective hamiltonian (14) are not isotopically invariant. To resolve this problem Watson replaced the electronic linear and angular momenta by appropriate linear combinations thereof.<sup>12</sup> The resulting expression is equivalent to that obtained by the use of the hamiltonian (3) instead of (2) in the construction of the effective hamiltonian. According to empirical precedent," the functions a(R) and  $\beta(R)$  thus take the forms

$$\alpha(R) = m_e \alpha_a(R)/M_a + m_e \alpha_b(R)/M_b, \beta(R) = m_e \beta_a(R)/M_a + m_e \beta_b(R)/M_b; \quad (15)$$

the reduced nuclear mass  $\mu$  becomes replaced by the reduced atomic mass  $\mu_c = M_a M_b / (M_a + M_b - Cm_c)$ , in which C is the net molecular charge  $Z_a + Z_b - N$  in units of the protonic charge with N being the number of electrons in the molecule. The form of equation 15 is consistent with the perturbation in the hamiltonian (3) that can be separated into contributions of each nucleus.

Watson also argued that the adiabatic and nonadiabatic contributions are not experimentally **separable**.<sup>12</sup> To test this we introduce a mock perturbation parameter  $\boldsymbol{\xi}$  into the effective hamiltonian (14)

$$H_{eff} = -\frac{\hbar^2}{2\mu} \frac{d}{dR} [1 + \xi \beta(R)] \frac{d}{dR} + V^{BO} + \frac{\hbar^2}{2\mu R^2} [1 + \xi \alpha(R)] J (J + 1) + \xi (V^{AD} + V^{NA});$$
(16)

we use equation A8 in appendix A with x = R,  $P(R) = -\hbar^2 [1 + \xi \beta(R)]/(2\mu)$ ,  $Q = V^{BO} + \xi (V^{AD} + V^{NA}) + \hbar^2 [1 + \xi \alpha(R)] J (J + 1)/(2\mu R^2)$ , W = 1 and E the vibration-rotational energies  $E_{vJ}$ , to obtain the energy shift

$$\Delta E_{vJ} = \frac{\partial E_{vJ}}{\partial \xi}\Big|_{\xi=0} = \langle F \frac{dV^{BO}}{dR} \rangle - \frac{\hbar^2}{4\mu} \langle \beta^{"} \rangle - \langle V^{AD} + V^{NA} \rangle - \frac{\hbar^2}{2\mu} J(J+1) \langle \frac{\alpha}{R^2} + 2\frac{F}{R^3} \rangle,$$
(17)

in which

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$$F(R) = -\frac{1}{2} \int_{R_o}^{R} \beta(t) dt + F(R_o),$$
(18)

according to equation A4. Because the value of the lower limit is arbitrary, one can choose it for maximum convenience. For instance, if one expands  $\beta(R)$  in a series of the dimensionless variable  $x = (R-R_e)/R_e$  to various positive powers, then the choice  $R_0 = R_e$ , the equilibrium internuclear separation, leads to simple expressions. Equations (17) and (18), analogous to those obtained by Watson,<sup>12</sup> appear superficially to indicate that the effects of the nonadiabatic function  $\beta(R)$  on the eigenenergies  $E_{vJ}$  prove experimentally inseparable from those of  $\alpha(R)$ ,  $V^{AD}$ and  $V^{NA}$ ; to investigate this possibility more profoundly we apply the following analytic treatment.

### **IV. PERTURBATION THEORY**

One can solve the eigenvalue equation for the vibration-rotational hamiltonian derived above according to various methods. We apply perturbation theory because we thereby generate analytic expressions of the energies in terms of the parameters in the potential-energy function. To facilitate this approximate procedure we write the mass-independent potential-energy function  $V^{BO}$  in the form V(x) adopted by Dunham<sup>1</sup>

$$V^{BO}(x) = h c a_o x^2 \left[ 1 + \sum_{i=1}^{N} a_i x^i \right].$$
 (19)

However, in the resulting expressions for the Dunham coefficients  $Y_{kl}$  we replace the potentialenergy coefficients  $a_i$  by those of a more convenient series.

We treat the Born-Oppenheimer vibration-rotational hamiltonian

$$H_{eff} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR} + U, \ U = V^{BO} + \frac{\hbar^2}{2\mu R^2} J(J+1),$$
(20)

and then add the adiabatic and nonadiabatic corrections that are much smaller. As previously,<sup>16</sup> we proceed to define the perturbation parameter  $\lambda = (2B_e/\omega_e)^{1/2}$  and the new variable  $q = x/\lambda$ . If we change variables from R to q and expand U in a power series of the latter we obtain an eigenvalue equation for the operator

$$\mathcal{H} = (hc\omega_e)^{-1} [H_{eff} - hcB_e J(J+1)]$$

$$= -\frac{1}{2} \frac{d^2}{dq^2} + \frac{1}{2} q^2 + \frac{1}{2} \sum_{i=1}^{\infty} a_i \lambda^i q^{i+2} + J_B \sum_{i=1}^{\infty} (-1)^i (i+1) \lambda^i q^i,$$
(21)

in which  $J_B = B_e J(J+1)/\omega_e$ . Then we use equation B4 in appendix B to obtain a recurrence relation for the moments  $Q^{(N)} \equiv \langle q^N \rangle$  and derive an additional relation between the energy and the moments from the Hellmann-Feynman theorem (B5).<sup>16</sup> At this stage we use perturbation theory and expand both the energy and the moments in series of  $\lambda$  to various non-negative powers,

$$\mathcal{E} = \sum_{p=0}^{\infty} \mathcal{E}_p \lambda^p, \quad Q^{(N)} = \sum_{p=0}^{\infty} Q_p^{(N)} \lambda^p.$$
(22)

The dimensionless energy  $\mathcal{E}$  is related to the vibration-rotational energy E according to  $E = hc\omega_e \mathcal{E} + hcB_e J(J + 1)$  and  $\mathcal{E}_0 = (v + 1/2)$ . The Hellmann-Feynman theorem (B5) provides an expression for the energy coefficients,

$$\mathcal{E}_{p} = \frac{1}{p} \sum_{i=1}^{p} i \left[ \frac{1}{2} a_{i} Q_{p-1}^{(i+2)} + J_{B} (-1)^{i} (i+1) Q_{p-i}^{(i)} \right],$$
(23)

and equation B6 becomes a recurrence relation for the perturbation corrections to the moments,

$$Q_{p}^{(N+1)} = \frac{1}{N+1} \left\{ \frac{1}{4} N(N-1)(N-2)Q_{p}^{(N-3)} + 2N\mathcal{E}_{o}Q_{p}^{(N-1)} + \sum_{i=1}^{p} \left[ 2N\mathcal{E}_{i}Q_{p-i}^{(N-1)} - (N + \frac{i+2}{2})a_{i}Q_{p-i}^{(N+i+1)} - (-1)^{i}(i+1)(2N+i)J_{B}Q_{p-i}^{(N+i-1)} \right] \right\}.$$
(24)

The starting point of the hierarchical procedure is the normalization condition  $Q_p^{(0)} = \delta_{p0}$ . Known generally by the name perturbation theory without wavefunctions or the hypervirial perturbative method, this procedure is practicable for both numerical and analytic calculation;<sup>16</sup> the latter is facilitated by symbolic manipulation on computers by means of processors such as Maple or Reduce. A direct consequence of the invariance of the operator  $\mathcal{H}$  with respect to the replacement of  $(\lambda, q)$  by  $(-\lambda, -q)$  is that  $\mathcal{E}_{2p} + 1 = 0$  and  $Q_p^{(N)} = 0$  if N + p is odd; the actual expansion parameter is hence  $\lambda^2$  instead of  $\lambda$ ; note that  $< x^N > = \lambda^N Q^{(N)}$ .

Because of the form of the recurrence relations 23 and 24 the perturbation coefficients  $\mathcal{E}_{2p}$  and  $\mathbf{Q_p}^{(N)}$  are polynomials in  $(\mathbf{v} + 1/2)$  and  $\mathbf{J_B}$ . The vibration-rotational energies are thus expressed as

$$E_{vJ} = hc \sum_{k=0} \sum_{l=0} Y_{kl} (v + \frac{1}{2})^{k} [J(J+1)]^{l},$$
(25)

in which the Dunham coefficients  $Y_{kl}$  (conventionally in wavenumber units) depend on the potential-energy coefficients  $a_i$ . Furthermore, the term coefficients  $Y_{kl}$  are also series in  $\lambda^2$  to

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various powers,

$$Y_{kl} = \sum_{p=0} Y_{kl}^{(p)} \lambda^{2p}.$$
 (26)

When we attempted the calculation of the coefficients  $Y_{kl}^{(p)}$  directly from equations 23 and 24, by expansion of the perturbation corrections  $\mathcal{E}_{2p}$  and  $Q_p^{(N)}$  in series of (v + 1/2) and [J(J + 1)] to various powers, we found the symbolic computation of this procedure to execute much less rapidly than that outlined above.

In order to add the adiabatic and nonadiabatic corrections to the perturbation calculation just described we expand them in series in q to non-negative powers:

$$V^{AD} + V^{NA} = hc \sum_{i=0} \eta_i \lambda^i q^i , \qquad (27)$$

$$\alpha = \sum_{i=0}^{\infty} \zeta_i \lambda^i q^i, \tag{28}$$

$$\beta = \sum_{i=0} \Xi_i \lambda^i q^i.$$
<sup>(29)</sup>

Direct expansion of  $\beta$  in the effective hamiltonian operator gives rise to unbound contributions of the form  $\mathbf{Dq^iD}$ , D being  $\mathbf{d/dq}$ . To circumvent this difficulty we assume that  $\beta$  is a sufficiently well behaved function; for instance we take  $\beta(\mathbf{x})$  to be the local representation near  $\mathbf{x} = 0$  or  $\mathbf{R} = \mathbf{R_e}$  of a function that possesses the correct asymptotic properties at  $\mathbf{R} = 0$  and as  $\mathbf{R} \rightarrow \infty$ . Thus we proceed to apply the generalized Hellmann-Feynman theorem (A7) for an arbitrary adjustable parameter  $\boldsymbol{\xi}$ . We use equation 29 and substitute  $\boldsymbol{\xi}$  for every  $\boldsymbol{\Xi_k}$  to obtain the contribution of each such term to the energy according to first-order perturbation theory. The treatment of the other contributions offers no difficulty; we estimate, to sufficient accuracy, the energy shifts that they produce by means of the Hellmann-Feynman theorem. Up to order P in  $\boldsymbol{\lambda}$  we have

$$\frac{\partial \mathcal{E}}{\partial \zeta_{k}} = J_{B} \sum_{i=0}^{P-k} (-1)^{i} (i+1) \lambda^{i+k} \sum_{m=0}^{P-k-i} Q_{m}^{(i+k)} \lambda^{m}, \qquad (30)$$

$$\frac{\partial \mathcal{E}}{\partial \eta_k} = -\frac{1}{\omega_e} \sum_{i=0}^{P-k} Q_i^{(k)} \lambda^{i+k}, \qquad (31)$$

$$\frac{\partial \mathcal{E}}{\partial \Xi_{k}} = -\frac{1}{2(k+1)} \left\{ \sum_{m=0}^{P-k} Q_{m}^{(k+2)} \lambda^{m+k} + \frac{1}{2} \sum_{i=1}^{P-k} (i+2) a_{i} \lambda^{i+k} \sum_{m=0}^{P-k-i} Q_{m}^{(i+k+2)} \lambda^{m} + J_{B} \sum_{i=1}^{P-k} (-1)^{i} i(i+1) \lambda^{i+k} \sum_{m=0}^{P-k-i} Q_{m}^{(i+k)} \lambda_{m} \right\} - \frac{k(k-1)}{4} \sum_{m=0}^{P-k} Q_{m}^{(k-2)} \lambda^{m+k}.$$
(32)

In all these equations the coefficients of  $\lambda$  to odd powers vanish. The energy shift to first order

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$$\mathbf{AE} = hc\omega_{e} \left( \sum_{k=0}^{\infty} \frac{\partial \mathcal{E}}{\partial \zeta_{k}} \zeta_{k} + \sum_{k=0}^{\infty} \frac{\partial \mathcal{E}}{\partial \eta_{k}} \eta_{k} + \sum_{k=0}^{\infty} \frac{\partial \mathcal{E}}{\partial \Xi_{k}} \Xi_{k} \right)$$
(33)

The combined effects of these three terms are presented in Table I. The expressions there for the quantities  $Z_{kl}$  (correspondingly also in wavenumber units) contain contributions to the vibration-rotational terms  $E_{kl}$  further to the coefficients  $Y_{kl}$  of the **functionals** of v and J in equation 25. We have previously determined the form of the coefficients  $Z_{kl}$  based on only the radial functions equivalent to those above containing the coefficients  $\zeta_j$  and  $\eta_j$ ; the present results derived according to a different algorithm and generated by means of a different computer processor confirm quantitatively the previous results.<sup>17</sup>

### **V. DISCUSSION**

Equations 12 and 13 are analogous to those derived by Bunker and Moss" except that they indicate, explicitly or implicitly, the order of each term in terms of the Born-Oppenheimer parameter  $\kappa^4$ ; the explanation by Bunker and Moss who expressed the dependence in terms of the reduced nuclear mass  $\mu$  to various non-positive powers is less clear, although equivalent because they assumed masses in units of the electronic mass.<sup>11</sup> All the nonadiabatic functions  $\alpha(\mathbf{R}), \beta(\mathbf{R})$  and  $\mathbf{V}^{\mathbf{NA}}(\mathbf{R})$  are of the same absolute order with respect to  $\kappa^4$ , namely  $(\mathbf{m}_e/\mu)^2$ ; however the latter function  $V^{NA}(R)$  contains intrinsically all this dependence. The other two functions which represent the rotational and vibrational inertia of the electrons in relation to the motions of the nuclei are intrinsically of order only  $\mathbf{m}_{e}/\mu$  because the other like factor appears externally in equation 12. Therefore, relative to their addends unity (as they appear as  $1 + \alpha(R)$ ) and  $1 + \beta(\mathbf{R})$  respectively), they are intrinsically of order only  $\mathbf{m}_{e}/\mu$ ;  $\mathbf{V}^{NA}(\mathbf{R})$  is of order  $(\mathbf{m}_{e}/\mu)^{2}$ relative to  $V^{BO}(R)$ , and  $V^{AD}(R)$  is correspondingly of order  $m_e/\mu$  relative to  $V^{BO}(R)$ . Our subsequent treatment according to perturbation theory, which is hence approximate, is valid for only the terms that are relatively of first order in  $m_e/\mu$  or  $\kappa^4$ ; for this reason of consistency we henceforth neglect the existence of  $V^{NA}(R)$ . Our treatment in section III is analogous to that previously described by Watson,<sup>12</sup> but we have maintained a common notation with section II. Furthermore, because the form of Watson's function  $\tilde{R}^{(n)}(R)$  is in general unknown, one cannot be certain that any particular choice of  $R_0$  makes  $\tilde{R}^{(n)}(R_0)$  vanish; therefore our criterion is more general than that of Watson.<sup>12</sup>

Hence we express the radial Schrodinger equation in the form

$$\left\{\frac{d}{dx}\left(1+\frac{m_{e}}{\mu_{c}}\sum_{j=0}\Xi_{j}x^{j}\right)\frac{d}{dx}+\frac{1}{B_{e}}\left[E_{vJ}/(hc)-a_{0}x^{2}\left(1+\sum_{j=1}a_{j}x^{j}\right)-\frac{m_{e}}{\mu_{c}}\sum_{j=0}\eta_{j}x^{j}\right]-J(J+1)\left(1+\frac{m_{e}}{\mu_{c}}\sum_{j=0}\zeta_{j}x^{j}\right)/(1+x)^{2}\right\}\psi_{vJ}=0.$$
(34)

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TABLE I. Adiabatic and nonadiabatic contributions to the vibration-rotational terms in some expressions  $\mathbf{Z}_{\textbf{kl}}.$ 

$$Z_{0,0} = \eta_0 + B_e[\Xi_0(7a_1^2/32 - 3a_2/8) - \Xi_1a_1/16 - 9\Xi_2/8] + \gamma^2[\eta_1(-21a_1^3/32 + 23a_1a_2/16 - 15a_3/16) + \eta_2(7a_1^2/16 - 3a_2/8) - 7\eta_3a_1/16 + 3\eta_4/8] + \gamma^3[\Xi_j \cdots] + \gamma^4[\eta_j \cdots] + \dots$$

$$Z_{0,1} = B_e \zeta_0 + \gamma^2 \eta_1 + B_e \gamma^2 [(\zeta_0 - \Xi_0)(21a_1^3/16 - 23a_1a_2/8 + 15a_3/8 + 21a_1^2/16 - 9a_2/8 + 7a_1/4 + 15/8) + \zeta_1(-21a_1^3/32 + 23a_1a_2/16 - 15a_3/16 - 7a_1^2/8 + 3a_2/4 - 21a_1/16 - 3/2) + \zeta_2(7a_1^2/16 - 3a_2/8 + 7a_1/8 + 9/8) - \zeta_3(7a_1/16 + 3/4) + 3\zeta_4/8 + \Xi_1(13a_1^2/32 - 5a_2/8 + 3a_1/16 + 1/4) - \Xi_2a_1/8 - 27\Xi_3/8] + \gamma^4 [\eta_j \cdots] + \cdots$$

$$Z_{0,2} = B_e \gamma^2 [-2\zeta_0 + \zeta_1] + \gamma^4 [-3\eta_1(a_1/2 + 1) + \eta_2] + \gamma^4 [\zeta_j, \Xi_j \cdots] + \cdots$$
  
$$Z_{0,3} = B_e \gamma^4 [3\zeta_0(a_1 + 3) - \zeta_1(3a_1/2 + 5) + \zeta_2] + \gamma^6 [\eta_1(9a_1^2/2 - 2a_2 + 27a_1/2)]$$

$$+15) - 3\eta_2(a_1+2) + \eta_3] + \gamma^6[\zeta_j, \Xi_j \dots] + \dots$$

$$Z_{0,4} = B_e \gamma^6 [\zeta_0 (-9a_1^2 + 4a_2 - 36a_1 - 52) + \zeta_1 (9a_1^2/2 - 2a_2 + 39a_1/2 + 30) -\zeta_2 (3a_1 + 8) + \zeta_3] + \gamma^8 [\eta_1 (-135a_1^3/8 + 15a_1a_2 - 5a_3/2 - 135a_1^2/2 +24a_2 - 117a_1 - 91) + \eta_2 (45a_1^2/4 - 4a_2 + 36a_1 + 39) -9\eta_3 (a_1/2 + 1) + \eta_4] + \gamma^8 [\zeta_j, \Xi_j \cdots] + \cdots$$

$$\begin{split} Z_{1,0} &= -B_e \Xi_0 / \gamma + \gamma (-3a_1\eta_1/2 + \eta_2) + B_e \gamma [\Xi_0 (3465a_1^4/1024 - 1377a_1^2a_2/128 \\ &+ 201a_2^2/64 + 285a_1a_3/32 - 75a_4/16) + \Xi_1 (-111a_1^3/128 + 61a_1a_2/32 \\ &- 15a_3/16) + \Xi_2 (37a_1^2/64 - 11a_2/16) + 77\Xi_3a_1/16 - 53\Xi_4/8] \\ &+ \gamma^3 [\eta_1 (-31185a_1^5/2048 + 14259a_1^3a_2/256 - 5145a_1^2a_3/128 \\ &- 4677a_1a_2^2/128 + 795a_1a_4/32 + 715a_2a_3/32 - 175a_5/16) \\ &+ \eta_2 (10395a_1^4/1024 - 3213a_1^2a_2/128 + 335a_2^2/64 + 475a_1a_3/32 \\ &- 75a_4/16) + \eta_3 (-1155a_1^3/128 + 459a_1a_2/32 - 95a_3/16) \\ &+ \eta_4 (459a_1^2/64 - 67a_2/16) - 95a_1\eta_5/16 + 25\eta_6/8] + \gamma^3 [\Xi_j \cdots] + \cdots \end{split}$$

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$$Z_{1,1} = B_{\epsilon} \gamma [3(\zeta_0 - \Xi_0/2)(a_1 + 1) - \zeta_1 (3a_1/2 + 2) + \zeta_2 - \Xi_1] + \gamma^3 [3\eta_1 (9a_1^2/4 - 2a_2 + 9a_1/4 + 2) - 3\eta_2 (3a_1/2 + 1/2) + 3\eta_3] + B_{\epsilon} \gamma^3 [\zeta_j, \Xi_j \cdots] + \gamma^5 [\eta_j \cdots] + \cdots$$

$$Z_{1,2} = B_{\epsilon}\gamma^{3}[3(\zeta_{0} - \Xi_{0}/4)(-9a_{1}^{2}/2 + 3a_{2} - 9a_{1} - 19/2) + 3\zeta_{1}(9a_{1}^{2}/4 - 2a_{2} + 21a_{1}/4 + 6) - 3\zeta_{2}(3a_{1}/2 + 5/2) + 3\zeta_{3} + 3\Xi_{1}/2 - \Xi_{2}]$$
  
+ $\gamma^{5}[3\eta_{1}(-189a_{1}^{3}/16 + 33a_{1}a_{2}/2 - 5a_{3} - 189a_{1}^{2}/8 + 15a_{2} - 423a_{1}/16 - 19) + 3\eta_{2}(63a_{1}^{2}/8 - 5a_{2} + 45a_{1}/4 + 57/8)$   
 $-27\eta_{3}(a_{1} + 1)/2 + 6\eta_{4}] + \gamma^{5}[\zeta_{j}, \Xi_{j} \cdots] + \gamma^{7}[\eta_{j} \cdots] + \cdots$ 

$$Z_{2,0} = B_e[3\Xi_0(5a_1^2/8 - a_2/2) + 3\Xi_1a_1/4 - \Xi_2/2] + \gamma^2[3\eta_1(-15a_1^3/8 + 13a_1a_2/4 - 5a_3/4) + 3\eta_2(5a_1^2/4 - a_2/2) - 15\eta_3a_1/4 + 3\eta_4/2] + \gamma^2[\Xi_j \cdots] + \cdots$$

$$Z_{2,1} = B_e \gamma^2 [3(\zeta_0 - \Xi_0)(15a_1^3/4 - 13a_1a_2/2 + 5a_3/2 + 15a_1^2/4 - 3a_2/2 + 5a_1 + 5/2) + 3\zeta_1(-15a_1^3/8 + 13a_1a_2/4 - 5a_3/4 - 5a_1^2/2 + a_2 - 15a_1/4 - 2) + 3\zeta_2(5a_1^2/4 - a_2/2 + 5a_1/2 + 3/2) - 3\zeta_3(5a_1/4 + 1) + 3\zeta_4/2 + 3\Xi_1(-a_1^2/8 + a_2/2 - 3a_1/4 - 1) + 3\Xi_2a_1/2 - 3\Xi_3/2] + \gamma^4 [3\eta_1(45a_1^4/2 - 207a_1^2a_2/4 + 13a_2^2 + 95a_1a_3/4 - 15a_4/2 + 45a_1^3/2 - 117a_1a_2/4 + 15a_3/2 + 45a_1^2/2 - 13a_2 + 65a_1/4 + 15/2) + 3\eta_2(-15a_1^3 + 397a_1a_2/2 - 5a_3 - 45a_1^2/4 + 3a_2 - 10a_1 - 5/2) + 3\eta_3(45a_1^2/4 - 13a_2/2 + 15a_1/2 + 5) - 3\eta_4(13a_1/2 + 3/2) + 15\eta_5/2] + \gamma^4 [\zeta_j, \Xi_j \cdots] + \gamma^6 [\eta_j \cdots] + \cdots$$

This equation applies specifically to a homonuclear diatomic molecule (i.e. both atomic nuclei have the same atomic number or number of protons, but not necessarily the same number of neutrons); this simplification permits us to replace the separate contributions of each atomic type, for instance  $a_i(R)$  and  $\alpha_b(R)$  according to equation 15, by a common function a(R) for purposes of illustration of the relative contributions to the eigenvalues. Moreover we have also included explicitly the mass dependence of the adiabatic and nonadiabatic functions; by this means the coefficients  $\zeta_j, \Xi_j$  and  $\eta_j$ , pertaining to the rotational nonadiabatic, vibrational non-

adiabatic and adiabatic effects respectively, are supposed to become formally independent of mass. Although the vibrational nonadiabatic function appears explicitly in equation 34 as a polynomial in x, in practice we carried the function through all the calculations in the symbolic form  $\beta(\mathbf{R})$  until the **final** stage so as to avoid the problems with the asymptotic behaviour of the polynomial form described above. This equation includes all effects up to first order in the ratio  $\mathbf{m_e}/\mu$ , which suffice at present to reproduce the most accurate and precise measurements of the frequencies and wavenumbers of pure rotational and vibration-rotational transitions, within the experimental uncertainties of those measurements. The corresponding eigenvalues or energy terms are expressed

$$E_{vJ} = hc \sum_{k=0} \sum_{l=0} \left( Y_{kl} + \frac{m_e}{\mu_e} (Z_{kl}^v + Z_{kl}^r) \right) (v + \frac{1}{2})^k [J(J+1)]^l$$
(35)

in which we have suppressed the explicit isotopic dependence of  $\mathbf{E}_{vJ}$ ,  $\mathbf{Y}_{kl}$ ,  $\mathbf{Z}_{kl}^{v}$  and  $\mathbf{Z}_{kl}^{r}$ . Of the term coefficients in the latter three sets,  $\mathbf{Y}_{kl}$  are supposed to take into account only the mechanical effects (those effects that depend on only the internuclear potential energy V(x) or, equivalently, the coefficients  $\mathbf{a}_{j}$ ); the term coefficients  $\mathbf{Z}_{kl}^{v}$  encompass the additional adiabatic and nonadiabatic effects that would result from purely the rotationless effective potential energy with the associated centrifugal term, whereas the coefficients  $\mathbf{Z}_{kl}^{r}$  incorporate all effects that result from the additional centrifugal contributions to the energy terms. According to equation 31 the adiabatic effects through the coefficients  $\mathbf{\Xi}_{j}$  naturally contribute to  $\mathbf{Z}_{kl}^{v}$ , whereas both the rotational and the vibrational nonadiabatic effects through the coefficients  $\mathbf{\Xi}_{j}$  naturally contribute to  $\mathbf{Z}_{kl}^{v}$ , whereas both the rotational and the vibrational nonadiabatic effects through the greece of the factor  $\mathbf{J}_{\mathbf{B}} = \mathbf{B}_{\mathbf{C}} \mathbf{J}(\mathbf{J} + \mathbf{1})/\omega_{\mathbf{c}}$  in both equations 30 and 32. According to equation 34 we expect the magnitudes of the coefficients  $\eta_{j}$  to be comparable with that of  $\mathbf{a}_{0}$ , hence of order  $\mathbf{B}_{\mathbf{c}}/\gamma^{2}$ ; both  $\mathbf{a}_{0}$  and all  $\eta_{j}$  have dimensions, specifically of the quantity wavenumber according to this equation. In contrast we expect the magnitudes of all the dimensionless coefficients, specifically  $\mathbf{a}_{j}$  with j > 0,  $\zeta_{j}$  and  $\Xi_{j}$ , to be of order unity.

The topic of particular interest is what quantities can be determined individually from experiment, explicitly from the frequencies and wavenumbers of pure rotational and vibration-rotational transitions of isotopic variants of a particular homonuclear diatomic molecular species (neutral molecule or ion) in a  ${}^{1}\Sigma$  electronic state to which equations 34 and 35 specifically pertain. (The generalisation of these equations to heteronuclear diatomic molecules in a  ${}^{1}\Sigma$  state presents no additional problems.) To proceed, we recall that for all known stable diatomic molecules in their electronic ground states  $\gamma^{2}$  is of the same order of magnitude as  $\kappa^{4,17}$ . If we have data of two or more isotopic variants then we can distinguish the effects of the potential-energy coefficients  $a_{j}$  from other effects because, in the process of fitting simultaneously the term differences  $E_{v'j'}$   $\cdot E_{vJ}$  of the experimental data to both the quantum numbers v and J and the reduced mass  $\mu_{c}$ , we can separate the contributions of  $Y_{kl}^{(0)}$  from those of  $Z_{kl}^{v}$  and  $Z_{kl}^{r}$ ;

the quantities  $Y_{kl}^{(0)}$  determine the coefficients  $a_i$  (according to the relations derived by Dunham') which in turn enable the calculation of the related coefficients  $Y_{kl}^{(p)}$  of higher order, p > 0, as many as are required. The additional dependence of the coefficients  $\mathbf{Z_{kl}}^{r}$  on J(J + 1)relative to  $\mathbf{Z_{kl}}^{v}$  permits the independent determination of both these sets of coefficients. To decide which coefficients of the fundamental radial functions the determination of the quantities  $\mathbf{Z_{kl}}^{r}$  and  $\mathbf{Z_{kl}}^{v}$  might yield we examine the expressions in table I. The coefficient  $\eta_0$  appears in only the expression for  $Z_{0,0}$ ; as the latter is essentially a contribution to the zero-point energy neither it nor correspondingly its leading term  $\eta_0$  can be directly determined according to experimental fits of frequency data. Within the expression for  $Z_{0,1}$  the first two terms are  $B_e \zeta_1$ and  $\gamma^2 \eta_1$  which are actually of the same order of magnitude according to the preceding argument. Consistent with our neglect of effects that are second order in  $m_e/\mu_c$  (or  $\kappa^4$ ) relative to the appropriate leading contributions in the hamiltonian, we must neglect in any applications to spectral analysis all further sets of terms in the expression for  $Z_{0,1}$  and correspondingly in other expressions; some sets of terms of higher order are presented explicitly in the expressions for  $Z_{0,0}, Z_{0,1}$  and  $Z_{1,0}$ , and formally in other expressions, only to illustrate the relative orders of magnitudes of the sundry contributions in terms of  $\gamma$  to diverse powers. Because the contribution  $\gamma^2 \eta_1$  in  $Z_{0,1}$  belongs to  $Z_{0,1}^{v}$  whereas  $B_e \zeta_0$  belongs to  $Z_{0,1}^{r}$ , we can separate them and hence determine independently  $\zeta_0$  and  $\eta_1$ . Although from the corresponding contributions of  $Z_{0,1}$ <sup>r</sup> with l > 1 it appears that we can determine separately the values of further coefficients  $\zeta_{i}$ , j > 11, in fact when we separate these term coefficients into the components  $Z_{0,1}^{r}$  and  $Z_{0,1}^{v}$ , we find that there arise additional terms involving the coefficients  $\Xi_j$  which cancel exactly when  $Z_{0,1}$ <sup>r</sup> and  $Z_{0,1}^{v}$  are combined to form the expressions shown for  $Z_{0,1}$  in the table. To illustrate this phenomenon we show the cases  $Z_{0,2}^{r} = B_e \gamma^2 (\Xi_0 - 2\xi_0 + \xi_1)$  and  $Z_{0,2}^{v} = -B_e \gamma^2 \Xi_0 + \gamma^4 [-3\eta_1(a_1/2)]$  $(+1) + \eta_2$ ], indicating only the leading contributions. Thereby the numbers of the coefficients  $\zeta_i \equiv_i$  and  $\eta_i$  of the three radial functions increase too rapidly with 1 in  $\mathbb{Z}_{0,1}$  for one to solve for them separately. Although other coefficients  $Z_{kl}$  with k > 0 provide further relations involving the same sets of variables, the same linear combinations of the coefficients appear. For instance in  $Z_{1,0}^{v} = -\gamma^{-1}B_{e}\Xi_{0} + \gamma(-3a_{1}\eta_{1}/2 + \eta_{2})$  there exists a linear combination of the coefficients  $\Xi_{0}$ and  $\eta_2$  equivalent to that which appears in  $Z_{0,2}^{v}$ . Because examination of the related sets of term coefficients  $Z_{kl}$  proves this condition to be general, then except  $\zeta_0$  and  $\eta_1$  only linear combinations of the coefficients either  $\Xi_i$  and  $\zeta_i$  or  $\Xi_i$  and  $\eta_i$  may be determined as a result of fitting the frequency and wavenumber data of spectral transitions. Consistent with their relationship to purely centrifugal effects, according to equation 30, the coefficients  $\zeta_i$  appear in no expressions for  $Z_{k,0}$ ; in fact all the latter expressions belong purely to the class  $Z_{kl}^{v}$ .

This discovery that one can in principle determine individually, by means of only experimental measurements of transition frequencies in the absence of external electric magnetic fields, the coefficients  $\eta_1$  and  $\zeta_0$  is contrary to the conclusion drawn by Watson following his less detailed analysis,<sup>6</sup> \* although his conclusion about the general inseparability of these coefficients,

apart from these two exceptions, remains valid. Actual application of these results in the analysis of the spectra of **diatomic** molecules will be discussed in forthcoming publications.

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### APPENDIX A

Here we develop a general formula for the rate of change of the eigenvalues of a general Sturm-Liouville operator with respect to a parameter. The Sturm-Liouville equation is of the form

$$L\psi(x) = [DP(x)D + Q(x) + EW(x)]\psi(x) = 0, D = d/dx,$$
(A1)

in which  $\mathbf{E}$  is an eigenvalue of the problem and P(x) satisfies appropriate boundary conditions so that L is self-adjoint. We seek to obtain an expression for the rate of change of E with respect to an arbitrary parameter  $\boldsymbol{\xi}$  in P(x). Hence we differentiate the expectation value of L,

$$\langle \mathbf{L} \rangle = \langle \psi | L | \psi \rangle, \langle \psi | \psi \rangle = 1,$$
(A2)

with respect to  $\boldsymbol{\xi}$  and obtain a version of the well known Hellmann-Feynman theorem:

$$\partial < \mathbf{L} > /\partial \xi = <\partial L / \partial \xi > = < D(\partial P / \partial \xi) D > + (\partial E / \partial \xi) < \mathbf{W} > = \mathbf{0}.$$
(A3)

In order to obtain a more convenient expression for  $\partial E/\partial \xi$  which lacks the differential operator D, we consider the commutator [L,F(x)D + G(x)] in which

$$F(x) = P(x)^{1/2} \int_{x_0}^x [\partial P(t)^{-1/2} / \partial \xi] dt + F(x_0),$$
(A4)

and

$$G(x) = F'(z) - \int_{x_0}^{x} F(t) P''(t) / P(t) dt - F'(x_0) + G(x_0).$$
(A5)

In the latter equation the prime denotes a derivative with respect to the argument of the corresponding function. With this choice the commutator reads

$$[\mathbf{L}, \mathbf{FD} + \mathbf{G}] = -D(\partial P/\partial \xi)D - \mathbf{FQ}' - \mathbf{EFW}' + (\mathbf{F}'' P - FP''/2)'.$$
(A6)

Because  $\langle [L, FD + G] \rangle = 0$  we rewrite Eq. (A3) as

$$\frac{\partial E}{\partial \xi} < W > = < FQ' > +E < FW' > + < (\frac{1}{2}FP'' - F''P)' > .$$
(A7)

This expression proves useful to introduce nonadiabatic effects by means of parameters into the effective hamiltonian for the vibration-rotational energies of **diatomic** molecules. We consider also the case in which both P(x) and Q(x) depend on  $\xi$ . According to the reasoning above we find

$$\frac{\partial E}{\partial \xi} < W > = - < \frac{\partial Q}{\partial \xi} > + < FQ' > SE < FW' > + < (\frac{1}{2}FP'' - F''P)' > .$$
(A8)

#### APPENDIX B

Here we derive the main equations necessary for the application of perturbation theory without wavefunction. They are customarily obtained from the hypervirial theorems but in what follows we use a different argument.

We write the dimensionless eigenvalue equation in the form

$$\Psi''(x) = 2[U(x) - E]\Psi(x),$$
(B1)

*in* which E is the energy, U(x) is an effective potential-energy function and each prime denotes differentiation with respect to x. It follows from this equation that the square of the wavefunction  $\rho(\mathbf{x}) = \Psi(\mathbf{x})^2$  satisfies the third-order differential equation

$$\rho''' + 8(E - U)\rho' - 4U'\rho = 0.$$
(B2)

We multiply it by a differentiable function f(x) and integrate by parts. Because in the present case  $\Psi(x)$  vanishes at  $\pm \infty$  no additional condition is required. If the physical problem imposes finite boundary conditions one may choose f(x) to satisfy them. Assuming  $\Psi$  normalized to unity we find the result

$$< f''' > +8E < f' > -8 < f'U > -4 < fU' > = 0,$$
 (B3)

in which  $c \dots >$  denotes the quantum-mechanical expectation value.

For the application of Eq. (B2) to perturbation theory one selects the function f(x) in accordance with the form of U(x). When this function is a polynomial or can be expanded in series of x to non-negative powers, the natural choice is  $f(x) = x^N$ ; thus Eq. (B3) becomes

$$N(N - 1)(N - 2) < x^{N-3} > +8NE < x^{N-1} > -8N < x^{N-1}U > -4 < x^{N}U' > = 0.$$
(B4)

In the latter two cases this equation provides a useful recurrence relation for the expectation

values of the coordinate to various non-negative powers; these values are commonly described as moments of the density function.

If, as in the present case, the perturbation parameter  $\lambda$  appears explicitly in U(x), the Hellmann-Feynman theorem

$$\frac{\partial E}{\partial \lambda} = \langle \frac{\mathbf{a}\mathbf{u}}{\partial \lambda} \rangle, \tag{B5}$$

provides an additional relation between the energy and the moments. Equations B4 and **B5** suffice for a convenient and systematic application of perturbation theory.

### REFERENCES

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- 1. J. L. Dunham, Phys. Rev. 41, 721 (1932).
- 2. A. G. Maki, W. B. Olson, and G. Thompson, J. Mol. Spectrosc. 144,257 (1990) and references therein.
- 3. R. G. Woolley, Adv. Phys. 25, 27 (1976).
- 4. M. Born and J. R. Oppenheimer, Ann. Phys. Leipzig, 84,457 (1927).
- 5. J. H. Van Vleck, J. Chem. Phys. 4,327 (1936).
- 6. B. Rosenblum, A. H. Nethercot, and C. H. Townes, Phys. Rev. 109,400 (1958).
- 7. R. M. Herman and A. Asgharian, J. Mol. Spectrosc. 19,305 (1966).
- 8. P. R. Bunker, J. Mol. Spectrosc. 28,422 (1968).
- 9. P. R. Bunker, J. Mol. Spectrosc. 35,306 (1970).
- 10. P. R. Bunker, J. Mol. Spectrosc. 68,367 (1977).
- 11. P. R. Bunker and R. E. Moss, Mol. Phys. 33,417 (1977); R. E. Moss, private communication, 1990.
- 12. J.K.G. Watson, J. Mol. Spectrosc. 80, 411 (1980) and references therein.
- **13.** J. F. **Ogilvie**, Spectrochim. **Acta**, **A46**, **43** (1990).
- 14. J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. 12, 3(1967).
- 15. A.H.M. Ross, R. S. Eng, and H. Kildal, Opt. Commun. 12,433 (1974).
- 16. F. M. Fernández and J. F. Ogilvie, Phys. Rev. A 42, 4001 (1990).
- 17. J. F. Ogilvie, J. Mol. Spectrosc. 148,243 (1991) and to be published.