



Symbolic Implementation of Arbitrary-order Perturbation Theory Using Computer Algebra: Application To Vibrational–Rotational Analysis of Diatomic Molecules

John M. Herbert* and Walter C. Ermler†‡

Mathematics and Computer Science Division and Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

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Abstract—Theoretical details necessary to calculate arbitrary-order correction terms to vibrational–rotational energies and wave functions in Rayleigh–Schrödinger perturbation theory are presented. Since manual derivation of high-order perturbation formulae is not feasible due to the lengthy algebra involved, the commercial computer algebra software *Mathematica*[®] is employed to perform the symbolic manipulations necessary to derive the requisite correction formulae in terms of universal constants, molecular constants, and quantum numbers. Correction terms through sixth order for ¹Σ diatomic molecules are derived and then evaluated for H₂, HD, N₂, CO, and HF. It is thus possible, with the aid of computer-generated algebra, to apply arbitrarily high-order perturbation theory successfully to the problem of intramolecular nuclear motion. © 1998 Published by Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

Perturbation theory has traditionally been the method of choice for describing the low-lying vibrational and rotational states of polyatomic molecules (Sprandel and Kern, 1972). Perturbation procedures furnish successively higher-order correction terms to energies and wave functions; with suitable convergence this method can, in principle, be extended to arbitrary order until the correction terms become negligibly small. In practice, however, the calculation of high-order corrections to vibrational–rotational energies and wave functions is limited by the accuracy of the molecular potential energy surface and by the inherent complexity of the perturbation formulae themselves (Dudas *et al.*,

1992). Fortunately, advances in high-speed computing over the past two decades have assuaged the former problem and made feasible the calculation of accurate *ab initio* potential energy surfaces for small molecules (see, for example, Krohn *et al.*, 1974; Harding and Ermler, 1985; Dunning, 1990).

The second problem with high-order perturbation theory, however, has yet to be satisfactorily resolved: even relatively low-order perturbation calculations involve prohibitively massive algebraic expressions. Because of this complexity, analytic perturbation theory is seldom applied to the intramolecular nuclear motion problem beyond the second order of approximation (Levine, 1975; Carney *et al.*, 1978). Instead, numerical solution of the perturbed Schrödinger equation (Sprandel and Kern, 1972) or variation-perturbation methods (Sanders and Scherr, 1969) are employed to calculate high-order correction terms. However, whereas derivation of an analytic formula for each perturbation correction requires no a priori knowledge of molecular data, and therefore provides a general expression that can be applied to any system (upon substitution of the appropriate molecular constants), numerical techniques require that molecular

*Present address: Department of Chemistry, Kansas State University, Manhattan, KS 66506, U.S.A.

†Permanent address: Department of Chemistry and Chemical Biology, Stevens Institute of Technology, Hoboken, NJ 07030, U.S.A.

‡Author for correspondence. Telephone: (201) 216-5530; Fax: (201) 216-8240; E-mail: ermler@mcs.anl.gov.

parameters be inserted into equations *before* these equations are solved. Thus, the entire numerical procedure must be repeated each time the molecular constants are changed. Furthermore, variational techniques suffer from catastrophic scaling behavior as a function of the number of atoms and are consequently limited to small (i.e. 3–5 atom) molecules (Carney *et al.*, 1978; Carter and Handy, 1982; Romanowski *et al.*, 1985; Choi and Light, 1992).

Although manual computation of explicit algebraic correction formulae to arbitrary order is not feasible, the growing availability of algebraic software capable of large-scale symbolic manipulations offers the possibility of obtaining the desired expressions via computer. To this end, high-order quantum-mechanical perturbation theory has been successfully applied to some simple systems using computer algebra; these applications, however, are limited to the electronic spectra of atoms (Vinette and Čížek, 1988; Adams, 1992; McRae and Vrscay, 1992; Fernández, 1992; Adams and Arteca, 1994). Furthermore, these authors take advantage of the Hellmann–Feynman and hypervirial theorems to circumvent explicit calculation of wave functions.

A more general computer algebra-based approach to a perturbation problem was presented in a series of papers by Bouanich (1987a) Bouanich (1987b,c) in which the author uses commercial algebra software to derive symbolic algebraic formulae for vibrational–rotational matrix elements. Because of the nature of the potential energy function employed, however, Bouanich (1987c) concludes that it is not feasible to extend these results to arbitrary order of correction. More recently, Dudas *et al.* (1992) have developed a computer program (suitable for implementation in the commercial algebraic software environment *Mathematica*[®] (Wolfram, 1996)) that can derive certain matrix elements to arbitrary order of correction.

This article presents a general perturbation-theoretical treatment applied to the analysis of vibrations and rotations in diatomic molecules. Using the general perturbation energy formula developed by Herbert, (1997a) and incorporating the *Mathematica*[®] code described above (Dudas *et al.*, 1992), one may derive explicit algebraic formulae for energy and wave function correction terms to arbitrary order in the *Mathematica*[®] environment. These expressions incorporate universal and molecular constants strictly in symbolic form, so that the solution is not specific to a particular molecule. Thus, after initial computation of these formulae, it is a simple matter to substitute appropriate constants and thereby calculate vibrational–rotational energies and wave functions to arbitrary order of correction for any molecule.

2. THE HAMILTONIAN

Within the Born–Oppenheimer approximation, the time-independent Schrödinger equation for the nuclear motion of a diatomic molecule in a body-fixed coordinate system can be written as

$$[\hat{T} + U(R)]\psi = E\psi \quad (1)$$

where E is the system's internal energy (i.e. the total energy less translational and electronic contributions) and \hat{T} is the nuclear kinetic energy operator in the body-fixed frame. The potential energy $U(R)$ is the sum of the vibrational potential U_{vib} and rotational potential U_{rot} as functions of the internuclear separation R . For completeness and internal consistency of notation, a few standard results of perturbation theory as applied to molecular vibrations and rotations are presented in Section 2.1.

2.1. The Zeroth-order Approximation

To obtain the eigenfunctions and eigenvalues of equation (1), let $U_{\text{vib}}(R)$ be expanded as a Taylor series about the equilibrium internuclear separation R_e :

$$U_{\text{vib}}(R) = \frac{U''_{\text{vib}}(R_e)(R - R_e)^2}{2!} + \frac{U'''_{\text{vib}}(R_e)(R - R_e)^3}{3!} + \frac{U^{(iv)}_{\text{vib}}(R_e)(R - R_e)^4}{4!} + \dots \quad (2)$$

where $U'(R_e) = 0$ because $U(R_e)$ is the minimum potential energy; for convenience, $U(R_e)$ has been set equal to zero. The radius of convergence of this series is approximately $2R_e$ (Dudas *et al.*, 1992). It can be shown (Levine, 1975) that the rotational potential U_{rot} has the form

$$U_{\text{rot}}(R) = \frac{J(J+1)\hbar^2}{2\mu R^2}, \quad (3)$$

where $J = 0, 1, 2, \dots$ is the rotational quantum number and μ is the system's reduced mass (including electrons). Expansion of U_{rot} as a power series in $(R - R_e)$ provides

$$U_{\text{rot}}(R) = \frac{J(J+1)\hbar^2}{2I_e} \left[1 - 2\frac{(R - R_e)}{R_e} + 3\frac{(R - R_e)^2}{R_e^2} - \dots \right], \quad (4)$$

where $I_e \equiv \mu R_e^2$ is the molecule's equilibrium moment of inertia. The equation (4) converges whenever $R < 2R_e$ (Ogilvie, 1981, 1982).

For small displacements from equilibrium, $R \approx R_e$, and all terms in equation (2) and equation (4) except the first are small (Levine, 1975). Neglecting these higher terms corresponds to the harmonic oscillator/rigid-rotator model, which provides a zeroth-order approximation to the true internal nuclear motion of a diatomic molecule. The zeroth-order vibrational–rotational wave functions are (Levine, 1975)

$$\psi_{v,J,M}^{(0)} = \frac{\Psi_v(Q)}{Q + R_e} Y_J^M(\theta, \phi), \quad (5)$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number, $M = -J, -J+1, \dots, J-1, J$ is an angular momentum quantum number, and $Q \equiv R - R_e$ is the internuclear displacement coordinate. $Y_J^M(\theta, \phi)$ in equation (5) is a spherical harmonic function (aris-

ing from rigid rotation), while $\Psi_v(Q)$ is a harmonic oscillator wave function.

For molecules whose ground electronic state is $^1\Sigma$, the vibrational–rotational eigenenergies in the harmonic oscillator/rigid-rotator approximation are (Townes and Schawlow, 1955)

$$E_{v,J}^{(0)} = (v + 1/2)\omega_e + J(J + 1)B_e, \quad (6)$$

where $\omega_e \equiv 2\pi\nu_e$, ν_e is the classical frequency of oscillation and

$$B_e \equiv \frac{\hbar^2}{2I_e}, \quad (7)$$

is the *equilibrium rotational constant*. Note that in the cgs system, ω_e , B_e , and $E_{v,J}^{(0)}$ in equation (6) are in units of ergs. Following the convention of Levine (1975), wavenumber units are obtained by using the constants $\tilde{\omega}_e$ and \tilde{B}_e in place of ω_e and B_e , where

$$\tilde{\omega}_e \equiv \frac{\omega_e}{hc}, \quad \tilde{B}_e \equiv \frac{B_e}{hc}. \quad (8)$$

2.2. Perturbation Corrections

Successively higher-order corrections for anharmonicity, centrifugal distortion, and vibration–rotation coupling effects are obtained by incorporating additional terms of the potential energy series of equation (2) and equation (4) as perturbations to the harmonic oscillator/rigid-rotator Hamiltonian. It is known (Sprandel and Kern, 1972) that the sequence of energy correction terms from perturbation theory is most likely to converge when the Hamiltonian is expanded as a power series with infinitely many separate perturbations; the vibrational and rotational potential energy equation (2) and equation (4) are ideally suited for such an expansion.

Within the radii of convergence of equation (2) and equation (4), the exact Hamiltonian operator for internal nuclear motion is obtained by incorporating all terms from these series plus the kinetic energy operator from equation (1):

$$\hat{\mathcal{H}} = \hat{T} + \frac{1}{2}k_e Q^2$$

$$+ \sum_{i=1}^{\infty} \left[\frac{(-1)^i (i+1)(J+1)JB_e}{R_e^i} Q^i + \frac{k_{i+2}}{(i+2)!} Q^{i+2} \right], \quad (9)$$

where $k_e \equiv U''(R_e)$ is the *equilibrium molecular force constant*, and the j th-order force constant k_j is defined as

$$k_j \equiv U^{(j)}(R_e) \quad (10)$$

for all $j > 2$. Some authors [e.g. Sprandel and Kern (1972)] incorporate the factorial terms from equation (9) into the force constants; however, equation (10) provides a better analogy to the harmonic oscillator potential $U_{HO} = \frac{1}{2}k_e Q^2$. Notice that the first term in equation (4) is not incorporated into \mathcal{H} because this term is constant and was

subsumed (Levine, 1975) into the harmonic oscillator/rigid-rotator eigenenergies in equation (6).

Following the formalism of Kern and Matcha (1968) and of Herbert (1997a), the Hamiltonian operator, its eigenvalues, and its eigenfunctions are rewritten in the form

$$\begin{aligned} \hat{\mathcal{H}} &= \hat{\mathcal{H}}^{(0)} + \sum_{i=1}^{\infty} \hat{\mathcal{H}}^{(i)}, \quad E_{v,J} = E_{v,J}^{(0)} + \sum_{i=1}^{\infty} E_{v,J}^{(i)}, \quad \psi_{v,J,M} \\ &= \psi_{v,J,M}^{(0)} + \sum_{i=1}^{\infty} \psi_{v,J,M}^{(i)} \end{aligned} \quad (11)$$

where the unperturbed Hamiltonian operator

$$\hat{\mathcal{H}}^{(0)} \equiv \hat{T} + \frac{1}{2}k_e Q^2 \quad (12)$$

corresponds to the harmonic oscillator/rigid-rotator system. There are numerous ways of constructing the perturbed Hamiltonian operators $\hat{\mathcal{H}}^{(i)}$ such that their sum is equal to the full Hamiltonian operator of equation (9). When perturbation theory is applied through second order, the perturbations traditionally are written (Dennison and Hecht, 1962) as follows:

$$\begin{aligned} \hat{\mathcal{H}}^{(1)} &\equiv \frac{1}{6}k_3 Q^3 - \frac{2J(J+1)B_e}{R_e} Q, \\ + \hat{\mathcal{H}}^{(2)} &\equiv \frac{1}{24}k_4 Q^4 - \frac{3J(J+1)B_e}{R_e^2} Q^2, \end{aligned} \quad (13)$$

Here the first-order perturbation $\hat{\mathcal{H}}^{(1)}$ comprises both the first-order vibrational correction (that is, the cubic anharmonicity correction or the second term in equation (2)) and the first-order rotational correction (the second term in equation (4)). Likewise, the second-order perturbation $\hat{\mathcal{H}}^{(2)}$ incorporates second-order potential energy corrections for both vibration and rotation. Extending this rationale to arbitrary order provides a convenient form for the perturbed Hamiltonian operators:

$$\hat{\mathcal{H}}^{(i)} \equiv \frac{k_{i+2}}{(i+2)!} Q^{i+2} + \frac{(-1)^i (i+1)J(J+1)B_e}{R_e^i} Q^i, \quad (14)$$

or equivalently

$$\hat{\mathcal{H}}^{(i)} = \frac{k_{i+2}}{(i+2)!} Q^{i+2} + \frac{(-1)^i (i+1) \|\mathbf{L}\|^2}{2I_e} \left(\frac{Q}{R_e} \right)^i, \quad (15)$$

since the total angular momentum \mathbf{L} of a rotating diatomic molecule has magnitude $\|\mathbf{L}\| = \hbar \text{SQRT}\{J(J+1)\}$. The form of the perturbations in equation (15) parallels that used in second- (Nielsen, 1951) and fourth-order (Goldsmith *et al.*, 1956; Amat *et al.*, 1971) perturbation treatments of polyatomic molecules, in which each perturbed Hamiltonian is the sum of an anharmonicity correction and a rotational term containing momenta divided by moments or products of inertia.

2.3. Matrix Elements

To calculate energy corrections $E_{v,j}^{(i)}$ and perturbed wave functions $\psi_{v,j,M}^{(i)}$ one must evaluate numerous integrals of the form

$$\mathcal{H}_{\xi_1, \xi_2}^{(z)} \equiv \langle \psi_{\xi_1}^{(0)} | \hat{\mathcal{H}}^{(z)} | \psi_{\xi_2}^{(0)} \rangle, \quad (16)$$

where the ordered triple $\xi_i (= (v_i, J_i, M_i))$ specifies the system's quantum state. Integrals such as equation (16) can, in general, be evaluated numerically; however, for the case of internal nuclear motion simple procedures exist whereby an analytic solution may be obtained.

The sixth-rank tensor $\mathcal{H}^{(i)}$ is known (Levine, 1975) to be diagonal in both J and M . Using this fact in conjunction with equation (14), one can easily show that

$$\begin{aligned} \mathcal{H}_{v_1, v_2}^{(i)} &= \frac{k_{i+2}}{(i+2)!} \langle Q^{i+2} \rangle_{v_1, v_2} \\ &+ \frac{(-1)^i (i+1) J (J+1) B_e}{R_e^i} \langle Q^i \rangle_{v_1, v_2}, \end{aligned} \quad (17)$$

where, for brevity,

$$\langle Q^z \rangle_{v_1, v_2} \equiv \langle \psi_{v_1, J, M}^{(0)} | Q^z | \psi_{v_2, J, M}^{(0)} \rangle, \quad (18)$$

since the Q tensor is also diagonal in J and M . Note that the matrix $\mathcal{H}_{v_1, v_2}^{(i)}$ element contains an implicit parametric dependence upon J ; thus, for each value of J there exists a separate, two-dimensional matrix $\mathcal{H}^{(i)}$.

The matrix elements $\langle Q \rangle_{v_1, v_2}$ are obtained from the harmonic oscillator wave functions either by using linear algebra techniques (Matsen, 1970) or by taking advantage of the recursive nature of the Hermite polynomials appearing in these wave functions (Levine, 1975; Niño and Muñoz-Caro, 1995). These matrix elements are found to be

$$\langle Q \rangle_{v', v} = \left[\frac{v}{2\alpha} \right]^{1/2} \delta_{v', v-1} + \left[\frac{v+1}{2\alpha} \right]^{1/2} \delta_{v', v+1} \quad (19)$$

where δ is the Kronecker delta function and

$$\alpha \equiv \frac{4\pi^2 v_e \mu}{h} \quad (20)$$

is a constant appearing in the harmonic oscillator wave functions. The elements of $Q^z (z > 1)$ are obtained from equation (19) via matrix multiplication; recursive algorithms for this procedure are provided by Dudas *et al.* (1992) and by Niño and Muñoz-Caro (1995). Explicit formulae for these matrix elements up to $\langle Q \rangle_{4v', v}$ are tabulated by Wilson Jr. *et al.* (1980).

It should be noted that the matrix Q^i has at most i nonzero codiagonals on each side of the main diagonal, so there are but a finite number of nonzero Hamiltonian matrix elements $\mathcal{H}_{v_1, v_2}^{(i)}$. As such, perturbation formulae arising from the Hamiltonian described here will not involve infinite summations, but instead will be expressible in closed (albeit lengthy) forms. Thus, these formulae are exact solutions to the Schrödinger equation at each order.

3. RAYLEIGH-SCHRÖDINGER EXPANSIONS

For vibrational-rotational analysis problems, it is convenient to use the Rayleigh-Schrödinger form of perturbation theory, in which the set of unperturbed wave functions $\{\psi_{\xi}^{(0)}\}$ is assumed to form a basis for the Hilbert space containing the true wave functions ψ_{ξ} . Each perturbed wave function $\psi_{\xi}^{(n)}$ is expressed as a linear combination of these basis functions:

$$\psi_{\xi}^{(n)} = \sum_{\xi'} c_{\xi'}^{(n)} \psi_{\xi'}^{(0)} \quad (21)$$

where $c_{\xi'}^{(n)}$ is the n th-order expansion coefficient associated with quantum state ξ' . In this application, the summation in equation (21) runs over all possible values of the three quantum numbers v , J , and M .

3.1. Preliminary Considerations

Three useful results will greatly expedite calculation of the coefficients in equation (21). First, it is known (Dalgarno, 1961; Levine, 1974) that the expansion coefficient $c_{v, J, M}^{(n)}$ does not affect the perturbation energy $E_{v, J}^{(n)}$ so one may set $c_{v, J, M}^{(n)} = 0$ in the Rayleigh-Schrödinger expansion of $\psi_{v, J}^{(n)}$. The equation (21) then simplifies to

$$\psi_{\xi}^{(n)} = \sum_{\xi' \neq \xi} c_{\xi'}^{(n)} \psi_{\xi'}^{(0)} \quad (22)$$

Second, observe that

$$\langle \psi_{\xi_1}^{(m)} | \hat{\mathcal{H}}^{(i)} | \psi_{\xi_2}^{(n)} \rangle = \sum_{\xi' \neq \xi_1} \left[c_{\xi'}^{(m)} \sum_{\xi'' \neq \xi_2} c_{\xi''}^{(n)} \hat{\mathcal{H}}_{\xi', \xi''}^{(i)} \right] \quad (23)$$

and, finally,

$$\langle \psi_{\xi_1}^{(m)} | \psi_{\xi_2}^{(n)} \rangle = \sum_{\xi' \neq \xi_1} \left[c_{\xi'}^{(m)} \sum_{\xi'' \neq \xi_2} c_{\xi''}^{(n)} \delta_{\xi', \xi''} \right]. \quad (24)$$

Equation (24) follows from the orthonormality of the zeroth-order wave functions. If either of m or n is zero in equation (23) or equation (24), then there is no need to expand one or both of the wave functions. Equation (23) and equation (24) are still valid, however, provided one defines

$$c_{\xi'}^{(0)} \equiv \delta_{\xi, \xi'}, \quad (25)$$

where ξ is the quantum state whose wave function is to be expanded and ξ' is the index variable of the Rayleigh-Schrödinger expansion of equation (22).

3.2. A General Expansion Formula

Using the results obtained above, one can derive a general formula for the Rayleigh-Schrödinger expansion coefficients from the so-called perturbation equations, which relate the series expansions in equation (11) of \mathcal{H} , E , and ψ (Kern and Matcha, 1968; Herbert, 1997a). Applying the Rayleigh-Schrödinger expansion of equation (22) to the n th-order perturbation equation provides

$$\sum_{\xi'' \neq \xi} c_{\xi''}^{(n)} (\hat{\mathcal{H}}^{(0)} - E_{v,J}^{(0)}) \psi_{\xi''}^{(0)} = \sum_{i=1}^n (E_{v,J}^{(i)} - \hat{\mathcal{H}}^{(i)}) \psi_{\xi}^{(n-i)}. \quad (26)$$

Since the coefficients for $n = 0$ are known (from equation (25)), let n be greater than zero. Multiplication of equation (26) by the complex conjugate $\psi_{\xi'}^{(0)*}$ of the zeroth-order wave function for state ξ' followed by integration yields

$$\sum_{\xi'' \neq \xi} c_{\xi''}^{(n)} (E_{v',J'}^{(0)} - E_{v,J}^{(0)}) \delta_{\xi',\xi''} = \sum_{i=1}^n E_{v,J}^{(i)} \langle \psi_{\xi'}^{(0)} | \psi_{\xi}^{(n-i)} \rangle - \sum_{i=1}^n \langle \psi_{\xi'}^{(0)} | \hat{\mathcal{H}}^{(i)} | \psi_{\xi}^{(n-i)} \rangle. \quad (27)$$

As ξ' is arbitrary, choose ξ' such that $\xi' \neq \xi$. Under this condition, the wave functions $\psi_{\xi'}^{(0)}$ and $\psi_{\xi}^{(n-i)}$ are not necessarily orthogonal (Herbert, 1997a); however, in the case where $i = n$, these two functions are orthogonal. Thus, using equation (23) and equation (24), one may reduce equation (27) to a simple recursive formula:

$$c_{\xi'}^{(n)} (E_{v',J'}^{(0)} - E_{v,J}^{(0)}) = \sum_{i=1}^{n-1} c_{\xi'}^{(n-i)} E_{v,J}^{(i)} - \sum_{i=1}^n \sum_{\xi'' \neq \xi} c_{\xi''}^{(n-i)} \mathcal{H}_{\xi',\xi''}^{(i)} \quad (28)$$

for all $n > 0$.

Equation (28) is nearly the desired general formula for the expansion coefficients; however, if ξ and ξ' are degenerate states in the zeroth-order approximation, then the left side of equation (28) is zero, and no information regarding the expansion coefficients can be obtained from this formulation. Hence, assume for the moment that $E_{v',J'}^{(0)} \neq E_{v,J}^{(0)}$. Solving equation (28) for $c_{\xi'}^{(n)}$ and substituting this expression into equation (22) affords the expansion

$$\psi_{\xi}^{(n)} = \sum_{\xi' \neq \xi} \left[\frac{1}{E_{v',J'}^{(0)} - E_{v,J}^{(0)}} \times \left(\sum_{i=1}^{n-1} c_{\xi'}^{(n-i)} E_{v,J}^{(i)} - \sum_{i=1}^n \sum_{\xi'' \neq \xi} c_{\xi''}^{(n-i)} \mathcal{H}_{\xi',\xi''}^{(i)} \right) \psi_{\xi'}^{(0)} \right]. \quad (29)$$

Observe from equation (28) with $n = 1$ that each first-order expansion coefficient $c_{\xi'}^{(1)}$ is simply a perturbed Hamiltonian matrix element divided by an energy difference. By induction on n , one may show that every set of n th-order expansion coefficients $\{c_{\xi'}^{(n)}\}$ is a sum of such terms, some of which are multiplied by an energy correction $E_{v,J}^{(i)}$. Since each perturbed Hamiltonian matrix $\mathcal{H}^{(i)}$ is diagonal in J and M , the entire right side of equation (29) must be zero whenever $J' \neq J$ or $M' \neq M$, so the summations over $\xi' \neq \xi$ and $\xi'' \neq \xi$ in equation (29) reduce to summations over $v' \neq v$ and $v'' \neq v$, respectively. Applying this simplification and making use of equation (25), one may recast equation (28)

in its simplest form:

$$c_{\xi'}^{(n)} (E_{v',J'}^{(0)} - E_{v,J}^{(0)}) = -\mathcal{H}_{v,v'}^{(n)} + \sum_{i=1}^{n-1} c_{\xi'}^{(n-i)} E_{v,J}^{(i)} - \sum_{i=1}^{n-1} \sum_{v'' \neq v} c_{\xi''}^{(n-i)} \mathcal{H}_{v',v''}^{(i)}. \quad (30)$$

Note that the outer summation in the final Rayleigh–Schrödinger expansion of equation (29) runs over only quantum numbers $v \neq v'$, and therefore excludes $J = J'$ and $M \neq M'$. Under these conditions, the difference in zeroth-order energies between states ξ and ξ' is

$$E_{v',J'}^{(0)} - E_{v,J}^{(0)} = (v' - v)\omega_e \quad (J = J') \quad (31)$$

from equation (6). Hence, $E_{v',J'}^{(0)} - E_{v,J}^{(0)} \neq 0$ if $v' \neq v$. Since equation (30) relates to the Rayleigh–Schrödinger expansion

$$\psi_{v,J,M}^{(n)} = \sum_{v' \neq v} c_{v',J,M}^{(n)} \psi_{v',J,M}^{(0)}, \quad (32)$$

this condition is met, and the assumption that $E_{v',J'}^{(0)} \neq E_{v,J}^{(0)}$ is now justified. Moreover the rotational quantum number J appears in equation (30) only as a multiplicative constant (recall equation (14)) and the quantum number M does not appear in equation (30) at all. Hence, the Rayleigh–Schrödinger expansion coefficients in equation (32) will hereafter be denoted by $c_{v'}^{(n)}$, where an implicit parametric dependence on J (analogous to that of $\mathcal{H}_{v,v'}^{(i)}$) is assumed. The final expression for the Rayleigh–Schrödinger expansion coefficients is obtained from equation (30):

$$c_{v'}^{(n)} = \frac{1}{(v' - v)\hbar\nu_e} \times \left[\mathcal{H}_{v,v'}^{(n)} - \sum_{i=1}^{n-1} c_{v'}^{(n-i)} E_{v,J}^{(i)} + \sum_{i=1}^{n-1} \sum_{v'' \neq v} c_{v''}^{(n-i)} \mathcal{H}_{v',v''}^{(i)} \right]. \quad (33)$$

Equation (33) provides an important recursive relation whereby each new set of expansion coefficients $\{c_{v'}^{(n)}\}$ ($n > 1$) is determined by all of the coefficients of order less than n , while the first-order coefficients ($n = 1$) are determined directly from the elements of $\mathcal{H}^{(1)}$. Since reference to molecular vibrations and rotations was made only in the context of obtaining a value for $E_{v',J'}^{(0)} - E_{v,J}^{(0)}$, the remainder of this derivation is valid for any Rayleigh–Schrödinger perturbation problem involving arbitrarily many separate perturbations to the Hamiltonian.

4. IMPLEMENTATION

Equation (32) and equation (33) are necessary in order to expand the perturbed wave function $\psi_{v',J,M}^{(i)}$ in terms of the known functions in the set $\{\psi_{v',J,M}^{(0)}\}$. Such perturbed wave functions appear in the equation for the n th-order energy correction

(Herbert, 1997a),

$$\begin{aligned}
 E_{v,J}^{(n)} = & \sum_{j=1}^{\kappa} \sum_{i=j}^{\kappa} [(2 - \delta_{n,2i}) \langle \psi_{\xi}^{(j-1)} | \hat{\mathcal{H}}^{(n-i-j+1)} | \psi_{\xi}^{(i)} \rangle] \\
 & + \sum_{i=0}^{\kappa-1} \langle \psi_{\xi}^{(i)} | \hat{\mathcal{H}}^{(n-2i)} | \psi_{\xi}^{(i)} \rangle \\
 & - \sum_{j=2}^{\kappa} \sum_{i=j}^{\kappa} [(2 - \delta_{n,2i}) E_{v,J}^{n-i-j+1} \langle \psi_{\xi}^{(j-1)} | \psi_{\xi}^{(i)} \rangle] \\
 & - \sum_{i=1}^{\kappa-1} E_{v,J}^{(n-2i)} \langle \psi_{\xi}^{(i)} | \psi_{\xi}^{(i)} \rangle + [\langle \psi_{\xi}^{(\kappa)} | \hat{\mathcal{H}}^{(1)} | \psi_{\xi}^{(\kappa)} \rangle \\
 & - E_{v,J}^{(1)} \langle \psi_{\xi}^{(\kappa)} | \psi_{\xi}^{(\kappa)} \rangle (1 - \delta_{n,1})] \delta_{n,2\kappa+1}, \quad (34)
 \end{aligned}$$

where the parameter κ is defined as

$$\kappa \equiv \lfloor \frac{1}{2}n \rfloor, \quad (35)$$

the greatest integer less than or equal to $\frac{1}{2}n$. Only the wave function terms $\psi_{\xi}^{(0)}, \psi_{\xi}^{(1)}, \dots, \psi_{\xi}^{(\kappa)}$ are necessary to express the n th-order energy correction $E_{v,J}^{(n)}$ (Dalgarno, 1961).

4.1. *Mathematica*[®] Programs

An existing *Mathematica*[®] code (Dudas *et al.*, 1992) can evaluate the matrices \mathbf{Q}^z for any positive integer z and return analytic functions of the vibrational quantum number analogous to equation (19); thus, one may easily obtain algebraic expressions for the perturbed Hamiltonian matrix elements in equation (34) by using this code in conjunction with equation (17), equation (23) and equation (24). In fact, all of the necessary theoretical pieces are now in place to calculate explicit formulae for the successive perturbation corrections to energies and wave functions.

Equation (23), equation (24), equation (30), and equation (34) pertain to Rayleigh–Schrödinger perturbation theory in general, and these equations (along with a few assorted rules for manipulating quantum-mechanical matrix elements) were coded together into a package of *Mathematica*[®] functions called RSPERTURB. Equation (17) and equation (31), on the other hand, apply specifically to diatomic vibrational–rotational analysis problems and were compiled into a separate *Mathematica*[®] package called DIATOMICVIBROT. Early versions of the RSPERTURB and DIATOMICVIBROT programs are published in Herbert (1997b). Together, these programs can be used to derive symbolic formulae for diatomic vibrational–rotational energies and wave functions in terms of universal constants, molecular constants, and quantum numbers. Moreover, since all application-specific equations are collected in a separate program, the package RSPERTURB can be applied to solve perturbation problems other than the one discussed here.

In deriving energy formulae using RSPERTURB and DIATOMICVIBROT, the quantum number v was not incorporated symbolically, but instead a separ-

ate energy expression was derived for each value of v . There are several reasons why this approach was taken. First and foremost, when v is known explicitly, summations over quantum numbers $v' \neq v$, etc., may be quickly evaluated, so it is enormously simpler (and much more efficient) to derive formulae in this manner. Furthermore, perturbation theory is most accurate when v is small (that is, when R is near R_e , so that relatively few values of v will ever be required).

In fact, it is of interest to derive a general algebraic energy expression in terms of both v and J only in order to factor such an expression into a polynomial in $J(J+1)$ and $(v+1/2)$ and thereby obtain *ab initio* formulae for spectroscopic constants. However, perturbation analyses do not, in general, yield energies that can be factored into powers of $J(J+1)$ and $(v+1/2)$ (Darling and Dennison, 1939), and indeed the expansion in $(v+1/2)^j [J(J+1)]^j$ is more often used simply as a numerical fitting equation. In light of this, the most efficient way to obtain theoretical values for spectroscopic constants is to calculate vibrational and rotational energy levels from first principles, then numerically to fit these values to an appropriate power series in much the same way that *ab initio* electronic energies are fitted to an analytic potential energy function.

4.2. Symbolic Results And Discussion

Using *Mathematica*[®] version 2.2 (running on a Sun SPARC 5 workstation) and the external packages RSPERTURB and DIATOMICVIBROT, *Mathematica*[®] derived analytic formulae for the energy correction terms $E^{(1)}$ through $E^{(6)}$ and for vibrational states $v=0$ through $v=10$. The odd-order perturbation energies were found to be zero, owing to the fact that perturbed Hamiltonian matrix elements $\mathcal{H}_{v_1, v_2}^{(i)}$ as defined in equation (17) have a definite parity due to the parity of $\langle Q^z \rangle_{v, v'}$, as discussed by Levine (1975).

Using intrinsic *Mathematica*[®] functions for algebraic simplification, it is possible to separate each correction formula into a linear combination of small terms; the linear combination coefficients are integers whose values depend upon the vibrational state. By taking advantage of linear combination notation and intrinsic patterns in the correction formulae, one can reduce these expressions from literally hundreds of pages of algebra into compact forms. For example, energy correction formulae through sixth order for the first eleven vibrational states can be expressed in only twelve pages of tables; these formulae have been compiled by Herbert (1997b). For demonstrative purposes, the compact expressions for $E^{(2)}$ are reproduced here as Appendix A.

The procedure used to derive $E^{(2)}, E^{(4)}$, and $E^{(6)}$ is completely general and works for arbitrarily high orders of correction; the maximum order of correction is limited only by computer constraints. Previously, researchers using *Mathematica*[®] to solve problems in quantum chemistry have reported (Jones, 1994) that this software is perhaps too slow to be of practical use. For the perturbation calcu-

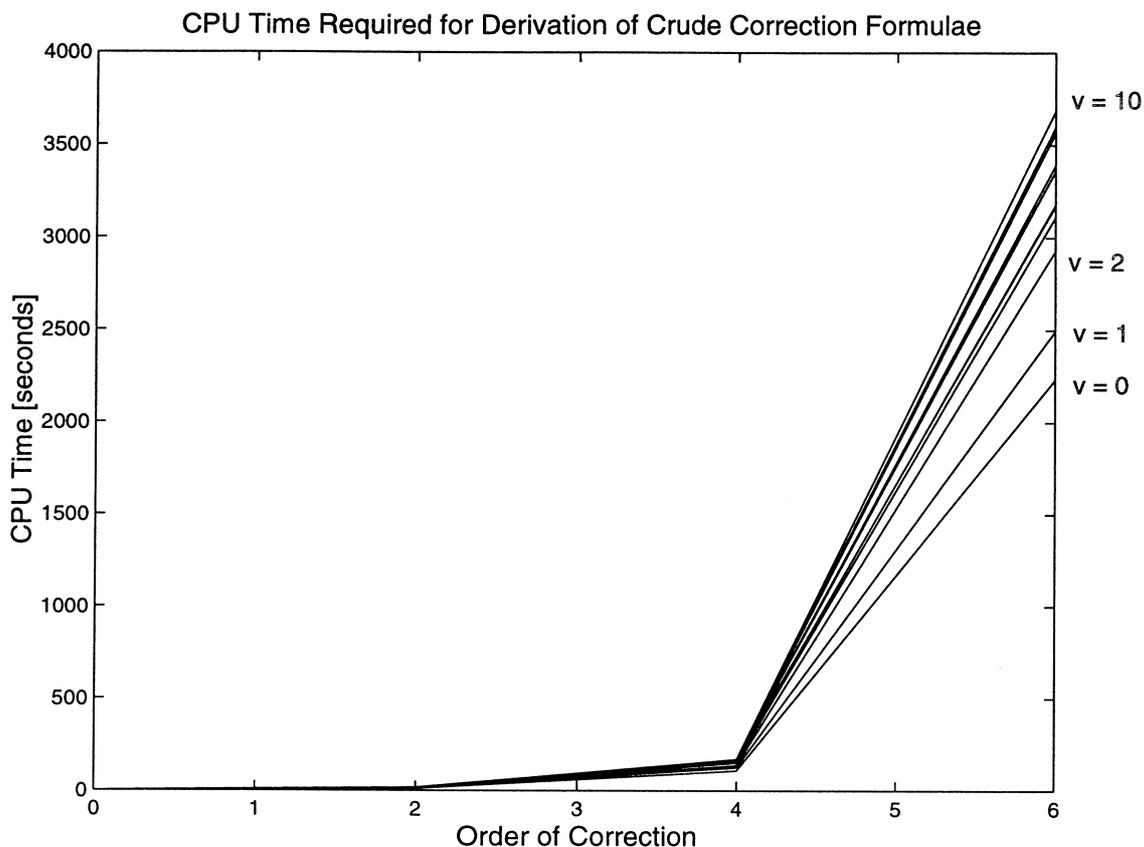


Fig. 1. CPU time required by *Mathematica*[®] to derive symbolic energy correction formulae. All computations were performed on a Sun SPARC 5 workstation using *Mathematica*[®] version 2.2 for Unix. Results are shown for the first eleven vibrational states, ranging from $v = 0$ to $v = 10$.

lations presented in this report, however, such is not the case.

Figure 1 presents the CPU time required for initial derivation of successive orders of perturbation formulae in their crudest forms, while Fig. 2 shows the time required to simplify these crude formulae into their most compact forms. Combining the timing data from Fig. 1 and Fig. 2, the amount of CPU time required to derive and simplify an n th-order correction formula is seen in all cases to be of the order of $10^{0.5n}$ seconds. Furthermore, for a given value of n , CPU time scales linearly with v .

Although Fig. 1 and Fig. 2 indicate exponential scaling with respect to the order of perturbation theory, three facts make this problem more tractable. First, algebraic simplification of crude correction formulae is not strictly necessary and is useful only if the perturbation formulae are to be elsewhere transcribed. Elimination of simplification steps reduces requisite CPU time by the amounts shown in Fig. 2.

Second, because of the v dependence of CPU time, the correction formulae for very low-lying vibrational states require significantly less time to derive and simplify than those for higher vibrational states (since negative values of v are not allowed, summations over $v' \neq v$ are considerably less involved for small v). Because Rayleigh-Schrödinger perturbation theory is applicable only

to low-lying vibrational states, the formulae that are of primary interest are also the ones that require the least time to obtain.

Finally, it is worth noting that RSPERTURB is not the most efficient possible algorithm for deriving energy correction formulae because the expansion coefficients $c_v^{(i)}$ in RSPERTURB are recalculated from the general formula *each time* they are needed. It would be enormously more efficient to first calculate as many Rayleigh-Schrödinger coefficients as are required, then store these expressions so that *Mathematica*[®] may reference them during the course of a computation.

In the case of diatomic molecules, however, the point is to demonstrate that arbitrary-order perturbation formulae *can* in fact be derived using computer algebra. In our future work with polyatomic molecules (where emphasis is placed on obtaining actual numerical values for vibrational-rotational energies), a more efficient algorithm will be employed.

5. NUMERICAL RESULTS

Numerical values for perturbation energies through sixth order for selected molecules are quickly obtained by substituting appropriate numerical parameters into the perturbation formulae derived by the RSPERTURB and DIATOMICVIBROT

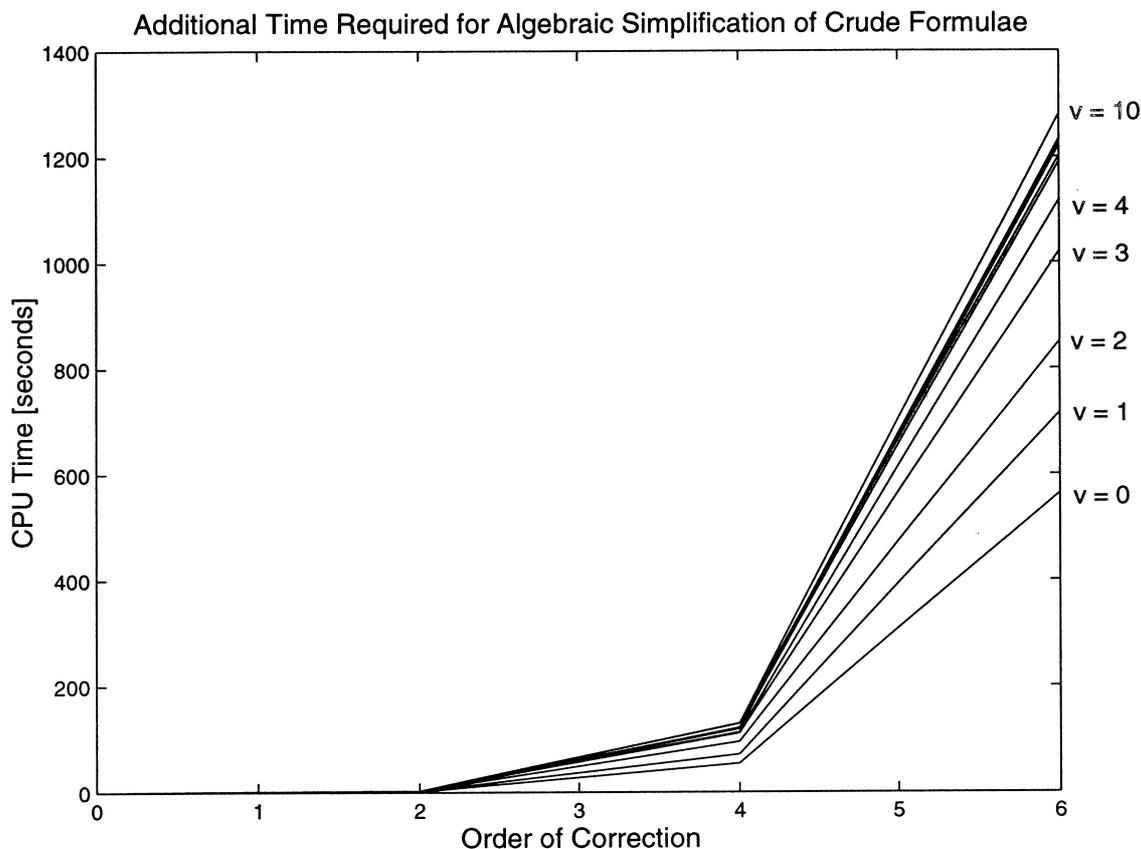


Fig. 2. CPU time required by *Mathematica*[®] to manipulate crude energy formulae into their simplest forms. Results are shown for the first eleven vibrational states.

programs. In a fully *ab initio* treatment, the force constants and equilibrium internuclear separation R_e , are determined by means of electronic energy calculations, and for $^1\text{H}_2$ this was accomplished by fitting existing *ab initio* electronic energy data (Kolos and Wolniewicz, 1964) to an eighth-degree Taylor polynomial. By using force constants obtained from this potential, vibrational-rotational energy levels for $^1\text{H}_2$ were calculated to the sixth order of Rayleigh-Schrödinger perturbation theory RSPT(6). However, because the Taylor polynomial fit is good only within some finite radius of convergence, the theoretical data obtained from this potential energy expansion are not usable beyond a certain value of v . (In this application, it was found that beyond $v = 4$ the energies actually began to decrease as v increased.) Thus, to assess the reliability of sixth-order perturbation calculations for larger values of v , we chose to employ an empirical potential energy function rather than a numerical fit of *ab initio* data.

5.1. Potential Energy Functions

Two of the most common empirical potential energy functions for diatomic molecules are the Morse function (Morse, 1929) and the Hulburt-Hirschfelder function (Hulburt and Hirschfelder, 1941; Hulburt and Hirschfelder, 1961). Molecular force constants (equation (2)) may be obtained from either of these functions by means of analytic

differentiation. For the Morse potential, these force constants may be written (Sprandel and Kern, 1972) in a convenient closed form. For the Hulburt-Hirschfelder potential function, no such closed-form expression exists; however, *Mathematica*[®] can easily perform the requisite symbolic differentiation.

For comparative purposes, RSPT(6) vibrational-rotational energies for $^1\text{H}_2$ were calculated by using first Morse and then Hulburt-Hirschfelder force constants. In Fig. 3 and Fig. 4, RSPT(6) energies for each vibrational state $v = 0$ through $v = 10$ are plotted as functions of the rotational state J and compared with experimental values (Stoicheff, 1957; Herzberg and Howe, 1959; Herzberg and Monfils, 1960). For the lowest vibrational levels (i.e. $v \leq 4$), theoretical energies obtained from Hulburt-Hirschfelder force constants are essentially indistinguishable from experimental values. As v increases, so does the discrepancy between theory and experiment; this rift also increases (to a lesser extent) with increasing J .

Although force constants from the Morse potential appear to provide a better fit for $v = 7$ through $v = 10$, the decision was made to use the Hulburt-Hirschfelder potential function for all calculations because Rayleigh-Schrödinger perturbation theory is most applicable to the lowest vibrational levels. This last point cannot be overemphasized and, in performing such theoretical calculations, it is im-

RSPT(6) Versus Experiment for Molecular Hydrogen (Morse Potential Function)

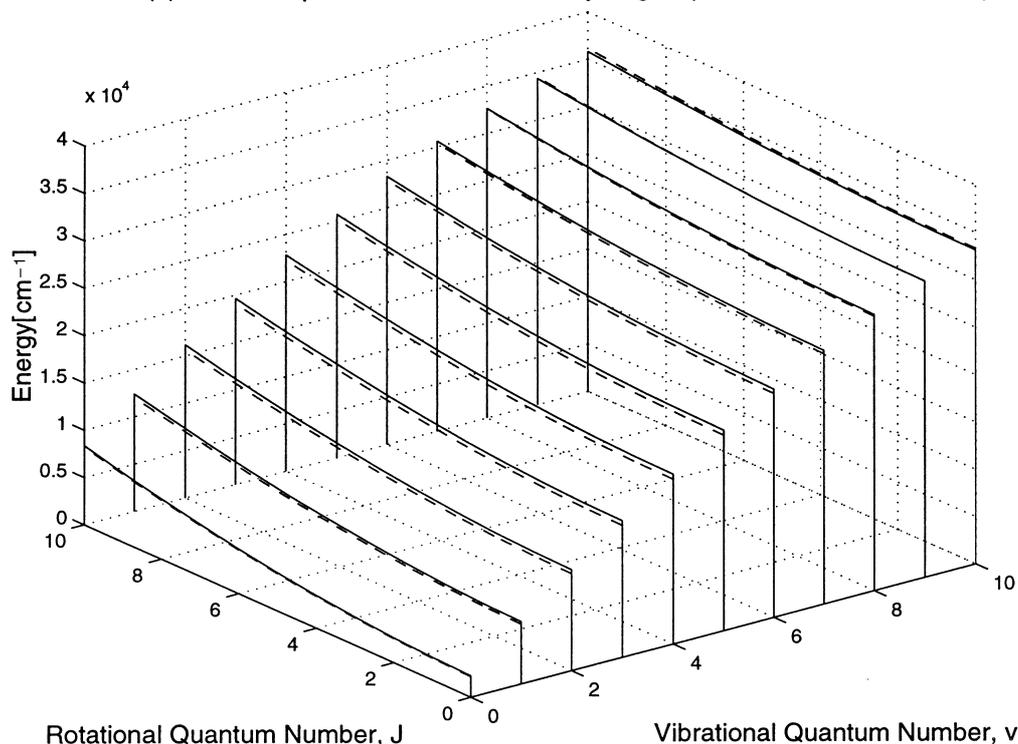


Fig. 3. Energy calculations through sixth order for $X^1\Sigma_g^+ \text{H}_2$, using force constants obtained from the Morse potential. Each solid line shows the theoretical energy for a particular vibrational state as a function of the rotational quantum number, and dashed lines represent experimental values. Morse parameters were obtained from Sprandel and Kern (1972). The experimental zero-point energy was obtained from Herzberg and Monfils (1960), while the remaining experimental energies were calculated using the vibrational quanta and mean rotational constants obtained experimentally by Stoicheff (1957) and by Herzberg and Howe (1959).

perative that one understand precisely how many vibrational and rotational energy levels can accurately be described by using the given theory and all its intrinsic approximations and assumptions.

5.2. Accuracy Of Perturbation Calculations

The maximum vibrational–rotational energy that can be calculated to a given level of accuracy depends upon the potential energy surface, the order of perturbation theory, and the molecule itself. In this section a paradigmatic analysis of the applicability of RSPT(6) calculations to H_2 is provided, beginning with a look at the sequence of energy corrections for this molecule.

Table 1 lists the individual correction terms for several different vibrational–rotational states of H_2 . Several important trends in the perturbation

energy corrections, which are true for nearly all diatomic molecules, are exemplified by this data. First, note that corrections to the zeroth-order energy are significantly smaller for $v = 0$ than for $v = 1$. This difference in the relative magnitudes of correction terms is even more pronounced at larger values of v and illustrates a general trend: the perturbation correction at each order becomes larger (in an absolute sense) as v increases. This is not surprising, given that the harmonic oscillator model becomes increasingly less accurate at higher and higher vibrational energy levels; for highly excited vibrational states, significant correction to this idealized model is required.

Table 1 also demonstrates, however, that perturbation corrections at each order increase relatively slowly with J . Although this phenomenon is illus-

Table 1. Energy correction terms for six vibrational–rotational states of $X^1\Sigma_g^+ \text{H}_2$

Correction term	Vibrational–rotational energy contributions, $\tilde{E}_{v,J}^{(i)}$ (waves cm^{-1})*			Vibrational–rotational energy contributions $\tilde{E}_{v,J}^{(i)}$ (cm^{-1})		
	$v = 0, J = 0$	$v = 0, J = 1$	$v = 0, J = 2$	$v = 1, J = 0$	$v = 2, J = 0$	$v = 3, J = 0$
$E^{(0)}$	2202.42	2324.14	2567.58	6607.27	11 012.12	15 416.97
$E^{(2)}$	-23.34	-26.59	-34.21	-274.04	-775.45	-1527.56
$E^{(4)}$	-0.52	-0.49	-0.42	1.99	45.91	101.48
$E^{(6)}$	0.02	0.02	0.02	-0.51	-5.05	-20.57

*The tilde is used over the energy correction in this and subsequent tables to indicate units of waves per centimeter.

RSPT(6) Versus Experiment for Molecular Hydrogen (Hulburt–Hirschfelder Potential)

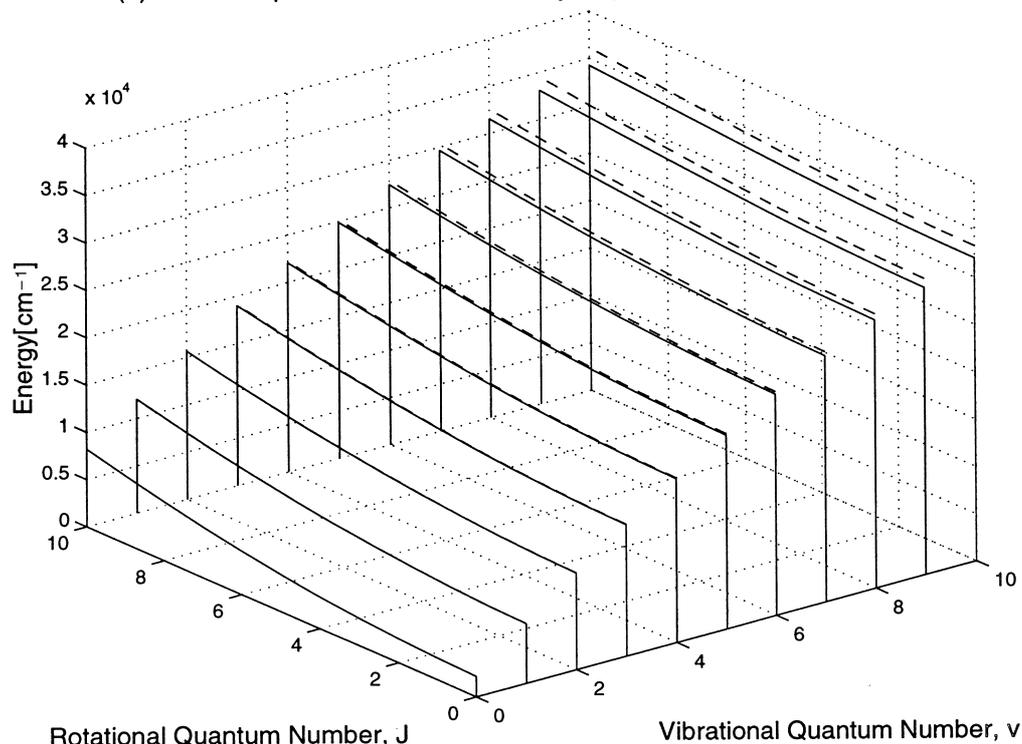


Fig. 4. Energy calculations through sixth order for $X^1\Sigma_g^+ \text{H}_2$, using force constants obtained from the Hulburt–Hirschfelder potential. Each solid line shows the theoretical energy of a particular vibrational state as a function of the rotational quantum number, and dashed lines represent experimental values. Hulburt–Hirschfelder parameters were obtained from Hulburt and Hirschfelder (1941). The experimental zero-point energy was obtained from Herzberg and Monfils (1960), while the remaining experimental energies were calculated using the vibrational quanta and mean rotational constants obtained experimentally by Stoicheff (1957) and by Herzberg and Howe (1959).

trated in Table 1 only for the ground vibrational state, it is in fact a general trend for low-lying vibrational and rotational states: within a given vi-

brational state, energy corrections increase slowly with J , but within a given rotational state, the correction terms increase quite rapidly with v . This

Table 2. RSPT(6) vibrational–rotational energies (cm^{-1}) for the lowest vibrational–rotational states of $X^1\Sigma_g^+ \text{H}_2^*$

	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$	$J = 5$	$J = 6$	$J = 7$	$J = 8$	$J = 9$	$J = 10$
$v = 0$	2178.59	2297.08	2532.96	2884.09	3347.34	3918.67	4593.28	5365.67	6229.81	7179.21	8206.94
	2179.27	2297.76	2533.66	2884.81	3348.07	3919.46	4594.24	5367.17	6232.69	7185.19	8219.31
$v = 1$	6334.71	6447.26	6671.22	7004.58	7444.28	7986.38	8626.23	9358.52	10177.4	11076.6	12049.5
	6340.41	6452.97	6677.04	7010.54	7450.30	7992.13	8630.80	9360.00	10172.4	11059.6	12012.2
$v = 2$	10246.7	10353.4	10565.6	10881.3	11297.6	11810.7	12415.9	13108.2	13881.8	14730.6	15648.2
	10266.4	10373.2	10585.7	10901.9	11318.8	11832.2	12436.9	13126.9	13894.9	14732.7	15631.2
$v = 3$	13914.8	14015.4	14215.8	14513.8	14906.4	15390.1	15960.3	16611.9	17339.2	18136.6	18997.4
	13961.6	14062.7	14263.9	14563.3	14958.0	15444.5	16018.4	16674.8	17408.3	18213.4	19084.6
$v = 4$	17335.4	17430.0	17618.2	17897.9	18266.4	18719.8	19253.8	19863.2	20542.7	21286.4	22087.9
	17429.7	17525.1	17715.0	17997.6	18370.0	18828.9	19369.8	19988.1	20678.5	21435.6	22253.9
$v = 5$	20501.9	20590.1	20765.6	21026.3	21369.4	21791.2	22287.2	22852.5	23481.5	24168.4	24907.0
	20671.2	20761.0	20939.6	21205.2	21555.2	21986.2	22494.0	23074.0	23721.2	24430.2	25195.8
$v = 6$	23403.8	23485.3	23647.4	23888.0	24204.3	24592.5	25048.2	25566.3	26141.4	26767.7	27438.7
	23684.9	23769.0	23936.2	24184.7	24512.0	24914.7	25388.8	25929.6	26532.4	27191.8	27902.6
$v = 7$	26027.3	26101.7	26249.4	26468.5	26756.0	27108.2	27520.5	27988.0	28505.0	29065.5	29663.3
	26467.1	26545.2	26700.7	26931.6	27235.6	27609.2	28048.8	28549.6	29107.1	29716.0	30371.4
$v = 8$	28355.2	28421.9	28554.1	28749.9	29006.3	29319.5	29684.8	30097.2	30551.0	31040.0	31557.7
	29010.3	29082.3	29225.5	29438.1	29717.6	30060.9	30463.9	30922.2	31431.2	31985.6	32580.5
$v = 9$	30366.7	30424.9	30540.3	30710.8	30933.3	31204.0	31518.1	31870.4	32254.9	32665.5	33095.4
	31303.2	31368.7	31498.9	31692.0	31945.6	32256.3	32620.3	33033.2	33490.1	33986.0	34515.8
$v = 10$	32037.5	32086.5	32183.5	32326.3	32511.8	32735.9	32993.8	33280.1	33588.7	33913.1	34246.3
	33329.5	33387.9	33504.0	33676.0	33901.2	34176.5	34497.8	34860.5	35259.5	35689.2	36144.1

*The lower entry in each cell is an experimental value. The experimental zero-point energy was obtained from Herzberg and Monfils, (1960), while the remaining experimental energies were calculated using the vibrational quanta and mean rotational constants obtained experimentally by Stoicheff, (1957) and by Herzberg and Howe, (1959). Theoretical calculations used Hulburt–Hirschfelder force constants with parameters obtained from Hulburt and Hirschfelder, (1941).

Table 3. Relative percentage differences between theoretical RSPT(6) and experimental energies for the lowest vibrational–rotational states of $X^1\Sigma_g^+ \text{H}_2$

	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$	$J = 5$	$J = 6$	$J = 7$	$J = 8$	$J = 9$	$J = 10$
$v = 0$	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02	-0.03	-0.05	-0.08	-0.15
$v = 1$	-0.09	-0.09	-0.09	-0.09	-0.08	-0.07	0.05	-0.02	0.05	0.15	0.31
$v = 2$	-0.19	-0.19	-0.19	-0.19	-0.19	-0.18	-0.17	-0.14	-0.09	-0.01	0.11
$v = 3$	-0.34	-0.34	-0.34	-0.34	-0.35	-0.35	-0.36	-0.38	-0.40	-0.42	-0.46
$v = 4$	-0.54	-0.54	-0.55	-0.55	-0.56	-0.58	-0.60	-0.63	-0.66	-0.70	-0.75
$v = 5$	-0.82	-0.82	-0.83	-0.84	-0.86	-0.89	-0.92	-0.96	-1.01	-1.07	-1.15
$v = 6$	-1.19	-1.19	-1.21	-1.23	-1.26	-1.29	-1.34	-1.40	-1.47	-1.56	-1.66
$v = 7$	-1.66	-1.67	-1.69	-1.72	-1.76	-1.81	-1.88	-1.97	-2.07	-2.19	-2.33
$v = 8$	-2.26	-2.27	-2.30	-2.34	-2.39	-2.47	-2.56	-2.67	-2.80	-2.96	-3.14
$v = 9$	-2.99	-3.01	-3.04	-3.10	-3.17	-3.26	-3.38	-3.52	-3.69	-3.89	-4.12
$v = 10$	-3.88	-3.90	-3.94	-4.01	-4.10	-4.22	-4.36	-4.53	-4.74	-4.98	-5.25

behavior arises because the vibrational potential energy series of equation (2), is term-by-term much larger than the rotational potential energy series of equation (4) (Dennison and Hecht, 1962).

The results of RSPT(6) energy calculations for the lowest 121 vibrational–rotational states of H_2 are listed in Table 2, along with the corresponding experimental energies (Stoicheff, 1957; Herzberg and Howe, 1959; Herzberg and Monfils, 1960); for convenience, the relative differences between theoretical and experimental energies are tabulated in Table 3. The data in Table 3 indicate excellent agreement between theory and experiment for low-lying vibrational states (for instance, when $v \leq 4$, the difference between theoretical and experimental energies is less than 1 per cent for all eleven ro-

tational levels considered); moreover, the relative differences in Table 3 are not altogether large even for higher vibrational states. However, it should be noted that when $v > 4$, the absolute difference between theoretical and experimental energies is on the order of hundreds of wavenumbers for all eleven rotational levels in Table 2. Thus, it appears that for $v > 4$ one might wish to include eighth- or higher-order perturbation corrections.

The small relative differences in Table 3 can be somewhat misleading, for equation (2) and equation (4) may not converge for all values of v and J listed in this table. An estimate of the maximum values of v and J for which convergence is guaranteed can be obtained by examining the radii of convergence of these series. Figure 5 depicts a

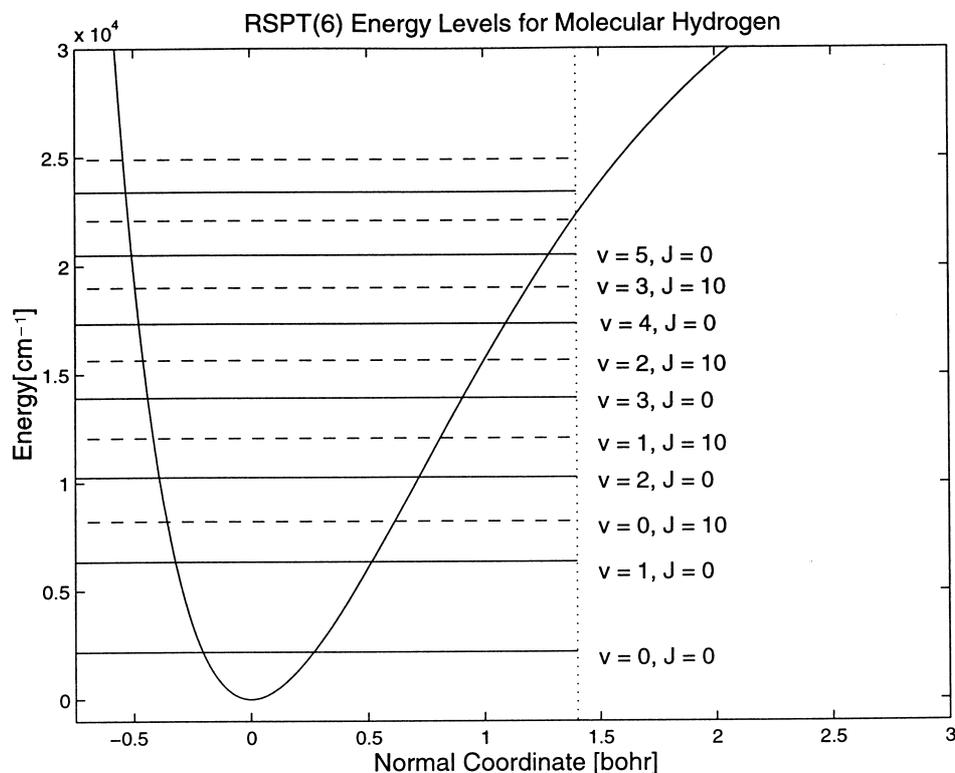


Fig. 5. Hulbert–Hirschfelder potential energy curve and vibrational–rotational energy levels for the ground rotational state (solid lines) and the $J = 10$ rotational state (dashed lines) of $X^1\Sigma_g^+ \text{H}_2$. These energies were obtained from RSPT(6) calculations by using Hulbert–Hirschfelder force constants, with Hulbert–Hirschfelder parameters taken from Hulbert and Hirschfelder (1941). The dotted vertical line is located at $Q = R_e$.

Table 4. Experimental and RSPT(6) vibrational–rotational energies for $X^1\Sigma_g^+ {}^{14}\text{N}_2$ (cm^{-1})*

$\tilde{E}_{v,J}$	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	RSPT(6)	Exp.								
${}^{14}\text{N}_2$										
$v = 0$	1176.69	1175.70	1180.69	1179.68	1188.68	1187.64	1200.68	1199.58	1216.67	1215.49
$v = 1$	3507.55	3505.62	3511.51	3509.56	3519.43	3517.45	3531.32	3529.28	3547.16	3545.06
$v = 2$	5808.20	5806.89	5812.12	5810.77	5819.97	5818.58	5831.74	5830.31	5847.43	5845.95
$v = 3$	8077.78	8079.39	8081.65	8083.27	8089.42	8091.02	8101.08	8102.64	8116.62	8118.14
$v = 4$	10315.4	10323.2	10319.2	10327.0	10326.9	10334.7	10338.5	10334.7	10353.8	10361.6

*Theoretical calculations used the Hulburt–Hirschfelder potential model with parameters obtained from Hulburt and Hirschfelder (1941), while experimental energies were obtained (Huber and Herzberg, 1979) from a polynomial fit of experimental data.

Table 5. Experimental and RSPT(6) vibrational–rotational energies for $X^1\Sigma^+ {}^{12}\text{C}^{16}\text{O}$ (cm^{-1})*

$\tilde{E}_{v,J}$	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	RSPT(6)	Exp.								
${}^{12}\text{C}^{16}\text{O}$										
$v = 0$	1081.07	1081.59	1084.92	1085.31	1092.60	1093.12	1104.14	1104.66	1119.51	1120.03
$v = 1$	3223.08	3224.86	3226.89	3228.67	3234.51	3236.29	3245.94	3247.72	3261.17	3262.96
$v = 2$	5338.70	5341.65	5342.47	5345.42	5350.02	5352.97	5361.34	5364.30	5376.44	5379.40
$v = 3$	7427.71	7432.03	7431.44	7435.77	7438.92	7443.25	7450.14	7454.46	7465.09	7469.42
$v = 4$	9489.88	9496.06	9493.59	9499.76	9500.99	9507.17	9512.10	9518.28	9526.91	9533.10

*Theoretical calculations used the Hulburt–Hirschfelder potential model with parameters obtained from Hulburt and Hirschfelder (1941), while experimental energies were obtained (Huber and Herzberg, 1979) from a polynomial fit of experimental data.

plot of the Hulburt–Hirschfelder potential energy curve for ${}^1\text{H}_2$; overlaid onto this plot are the RSPT(6) vibrational energy levels for the ground rotational state and the $J = 10$ rotational state. The vertical line in Fig. 5 is located at $Q = R_e$, which represents the best estimate (Dudas *et al.*, 1992) of the radii of convergence of equation (2) and equation (4). Although the quantum-mechanical harmonic oscillator may tunnel out of the potential well of Fig. 5, the wave function falls off very rapidly for values of Q outside this well. Hence, to a good approximation one may restrict Q to values within the potential energy well.

Note that for vibrational levels above $v = 5$ (in the ground rotational state) and above $v = 3$ (in the $J = 10$ rotational state), Q may drift beyond R ,

yet still be within the potential well. For these energy levels, the perturbation equation (11) cannot be assumed to converge for all values of Q , so the perturbation treatment presented here is not applicable. Since $J = 10$ and $J = 0$ are, respectively, the highest and lowest rotational levels examined for ${}^1\text{H}_2$, Fig. 5 establishes boundary conditions for convergence of the perturbation series for this molecule. For all rotational levels in the interval $0 \leq J \leq 10$, one anticipates convergent perturbation series up to *at least* the $v = 3$ vibrational level but *no higher* than the $v = 5$ vibrational level.

One last comment concerning the accuracy of molecular hydrogen calculations is in order. This molecule (and, in particular, the diprotium isotope examined here) represents a worst-case scenario for

Table 6. Experimental and RSPT(6) vibrational–rotational energies for $X^1\Sigma^+ {}^1\text{H}^{19}\text{F}$ (cm^{-1})*

$\tilde{E}_{v,J}$	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	RSPT(6)	Exp.								
${}^1\text{H}^{19}\text{F}$										
$v = 0$	2054.70	2046.80	2095.73	2087.94	2177.79	2170.34	2300.75	2294.2	2464.47	2460.02
$v = 1$	6018.60	6008.23	6057.99	6048.05	6136.73	6129.21	6254.72	6254.73	6411.81	6429.14
$v = 2$	9813.65	9797.62	9851.46	9836.40	9927.04	9918.26	10040.3	10051.8	10191.1	10249.9
$v = 3$	13445.2	1341.97	13481.5	13457.7	13554.0	13542.2	13662.7	13690.1	13807.5	13926.8
$v = 4$	16916.0	16878.6	16950.8	16916.1	17020.3	17005.2	17124.6	17173.8	17263.4	17464.2

*Theoretical calculations used the Hulburt–Hirschfelder potential model with parameters obtained from Hulburt and Hirschfelder (1941), while experimental energies were obtained (Huber and Herzberg, 1979) from a polynomial fit of experimental data.

Table 7. Experimental and RSPT(6) vibrational–rotational energies for $X^1\Sigma_g^+ {}^1\text{H}_2\text{H}$ (cm^{-1})*

$\tilde{E}_{v,J}$	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	RSPT(6)	Exp.								
${}^1\text{H}_2\text{H}$										
$v = 0$	1890.33	1883.75	1979.58	1972.96	2157.47	2150.74	2422.78	2415.85	2773.71	2766.42
$v = 1$	5519.06	5515.90	5604.42	5601.02	5774.54	5770.64	6028.23	6023.50	6363.74	6357.73
$v = 2$	8962.80	8971.00	9044.32	9051.95	9206.76	9213.23	9448.96	9453.58	9769.20	9771.13
$v = 3$	12222.6	12253.2	12300.2	12329.9	12455.0	12482.7	12685.7	12710.4	12990.6	13011.0
$v = 4$	15297.5	15366.7	15371.2	15439.2	15518.2	15583.5	15737.2	15798.4	16026.7	16081.9

*Theoretical calculations used the Hulburt–Hirschfelder potential model with parameters obtained from Hulburt and Hirschfelder (1941), while experimental energies were obtained (Huber and Herzberg, 1979) from a polynomial fit of experimental data.

Table 8. Relative percentage differences between theoretical RSPT(6) and experimental energies for the heavy molecules $^{14}\text{N}_2$ and $^{12}\text{C}^{16}\text{O}$

	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	N_2	CO								
$v = 0$	0.08	-0.05	0.09	-0.04	0.09	-0.05	0.09	-0.05	0.10	-0.05
$v = 1$	0.06	-0.06	0.06	-0.06	0.06	-0.06	0.06	-0.05	0.06	-0.05
$v = 2$	0.02	-0.06	0.02	-0.06	0.02	-0.06	0.02	-0.06	0.03	-0.06
$v = 3$	-0.02	-0.06	-0.02	-0.06	-0.02	-0.061	-0.02	-0.06	-0.02	-0.06
$v = 4$	-0.08	-0.07	-0.08	-0.06	-0.08	-0.071	0.04	-0.06	-0.08	-0.06

Table 9. Relative percentage differences between theoretical RSPT(6) and experimental energies for the light molecules $^1\text{H}^{19}\text{F}$ and $^1\text{H}^2\text{H}$

	$J = 0$		$J = 1$		$J = 2$		$J = 3$		$J = 4$	
	HF	HD								
$v = 0$	0.39	0.35	0.37	0.34	0.34	0.31	0.29	0.29	0.18	0.26
$v = 1$	0.17	0.06	0.16	0.06	0.12	0.07	0.00	0.08	-0.27	0.09
$v = 2$	0.16	-0.09	0.15	-0.08	0.09	-0.07	-0.11	-0.05	-0.57	-0.02
$v = 3$	0.19	-0.25	0.18	-0.24	0.09	-0.22	-0.20	-0.19	-0.86	-0.16
$v = 4$	0.22	-0.45	0.21	-0.44	0.09	-0.42	-0.29	-0.39	-1.15	-0.34

vibrational-rotational energy calculations. Because it is the lightest molecule, high-order energy corrections for H_2 should be the most significant of any diatomic molecule (Dunham, 1932). Furthermore, the breakdown of the Born-Oppenheimer approximation is known (Bunker, 1972) to be more significant for isotopomers of H_2 than for other diatomic molecules. Thus, H_2 represents something of a lower limit to the accuracy of perturbation calculations.

5.3. Additional Results

Table 4, Table 5, Table 6 and Table 7 present experimental and RSPT(6) energies for several other representative diatomic molecules, while Table 8 and Table 9 list the relative differences between theory and experiment for each set of calculations. Notice that these differences are typically much smaller for heavier molecules ($^{14}\text{N}_2$ and $^{12}\text{C}^{16}\text{O}$) than for lighter ones ($^1\text{H}^{19}\text{F}$ and $^1\text{H}^2\text{H}$), which affirms Dunham's result (Dunham, 1932) for dinuclear vibrational-rotational energies: the accuracy of low-order perturbation calculations increases with the molecular reduced mass.

The RSPT(6) calculations in Tables 4-6 and Table 7 are all based upon Hulburt-Hirschfelder force constants, where the parameters in the Hulburt-Hirschfelder potential function were taken from those explicitly tabulated by Hulburt and Hirschfelder (1941). These parameters [which are related (Hulburt and Hirschfelder, 1941, 1961) to experimentally measured spectroscopic constants] were also calculated by using more recent experimental data (Huber and Herzberg, 1979). When force constants obtained in this manner were used in RSPT(6) calculations, the theoretical energies obtained for $^1\text{H}^{19}\text{F}$ and $^1\text{H}^2\text{H}$ fell several wavenumbers closer to experimental values, thus demonstrating the importance of possessing an accurate potential energy function.

One final numerical result is presented. Theoretical values for spectroscopic constants of $^1\text{H}_2$, were obtained by fitting RSPT(6) energy data for $^1\text{H}_2$ to a polynomial in $(v + 1/2)$ and $(J + 1)$.

Mathematica[®]'s intrinsic function `NonlinearRegress` was used to perform the numerical fitting procedure, and the $^1\text{H}_2$ energy data from Table 2 for $0 \leq v \leq 3$ and $0 \leq J \leq 10$ were used as input [since the energy series of equation (11) converges for each of these vibrational-rotational states]. The theoretical spectroscopic constants obtained in this manner are listed in Table 10 alongside their experimental counterparts (Huber and Herzberg, 1979), which are valid for $0 \leq v \leq 3$. The numerical fit of the theoretical data has an estimated standard deviation of 1.24 waves per centimeter.

6. CONCLUSIONS

Equation (29) provides a general expression for the Rayleigh-Schrödinger expansion of perturbed wave functions when a molecular Hamiltonian containing arbitrarily many separate perturbations is employed. This formula is valid for any application of Rayleigh-Schrödinger perturbation theory — for instance, the polyatomic vibrational-rotational analysis problem — and complements the general perturbation energy formula obtained by Herbert (1997a). These two formulae are included in the *Mathematica*[®] package `RSPERTURB`, which contains all of the equations necessary to implement arbitrary-order Rayleigh-Schrödinger perturbation the-

Table 10. Theoretical and experimental spectroscopic constants for $X^1\Sigma_g^+ ^1\text{H}_2$

Spectroscopic constant	Theoretical value (cm ⁻¹)*	Experimental value (cm ⁻¹)†
$\tilde{\omega}_e$	4400.33	4401.213
$\tilde{\omega}_e x_e$	-122.135	-121.336
B_e	60.616	60.8530
$\tilde{\alpha}_e$	3.0655	-3.0622
\tilde{D}_e	-0.0399509	-0.0471
\tilde{Y}_{00}	10.2031	8.93

*Theoretical values were obtained from a numerical fit of RSPT(6) vibrational-rotational energy data for $0 \leq v \leq 3$ and $0 \leq J \leq 10$ and were calculated by *Mathematica*[®] to six significant digits.

†Experimental constants were obtained from Huber and Herzberg (1979) and are valid for $0 \leq v \leq 3$.

Table 11. Linear combination coefficients for $E^{(2)}$

v	$a_2^{(v)}$	$b_2^{(v)}$	$a_2^{(v-r)}$	$b_2^{(v-r)}$
0	11	1	3	1
1	71	5	9	3
2	191	13	15	5
3	371	25	21	7
4	611	41	27	9
5	911	61	33	11
6	1271	85	39	13
7	1691	113	45	15
8	2171	145	51	17
9	2711	181	57	19
10	3311	221	63	21

Table 12. Symbolic term factors [equation (38)] for $E^{(2)}$

	ℓ_1	ℓ_2	ℓ_3	ℓ_4	ℓ_5	ℓ_6	ℓ_7	ℓ_8	Ω
$A_2^{(v)}$	0	0	0	2	0	3	0	1	-288
$B_2^{(v)}$	0	0	0	0	1	2	0	0	32
$A_2^{(v-r)}$	1	1	1	0	0	1	2	0	2
$B_2^{(v-r)}$	1	1	1	1	0	2	1	1	2

ory. This program can be used not only to calculate energies but also to obtain wave functions to arbitrary order of correction. This is a major advantage of Rayleigh–Schrödinger perturbation theory, for explicit knowledge of the quantum-mechanical wave function enables one to calculate directly spectral line intensities and expectation values for molecular properties such as the molecular dipole moment (Ermler and Hsieh, 1990; Niño and Muñoz-Caro, 1995).

In this article, RSPERTURB was used in conjunction with another *Mathematica*[®] package, DIATOMICVIBROT, to apply arbitrary-order Rayleigh–Schrödinger perturbation theory to diatomic vibrational–rotational analysis problems. Symbolic perturbation energy formulae were derived and then evaluated numerically for several molecules, and a procedure was given whereby the applicability of such theoretical calculations may be estimated. However, the numerical results are not the focus of what is reported here; rather, the RSPERTURB and DIATOMICVIBROT programs are the principal results, for they allow one to implement perturbation theory to arbitrary order of correction (RSPERTURB). In particular, the diatomic vibrational–rotational analysis problem may now be easily solved to arbitrary order by using DIATOMICVIBROT.

Although derivation of symbolic high-order perturbation formulae requires a significant amount of computation time due to the nature of the *Mathematica*[®] software package, appreciable improvements in algorithm efficiency (as discussed in Section 4.2) will be made when this analysis is applied to polyatomic molecules. Even so, the methods presented here are more efficient than numerical procedures, for the calculations performed by *Mathematica*[®] result in symbolic formulae that express perturbation corrections in terms of user-supplied universal and molecular constants.

Admittedly, perturbation theory is not the preferred method for calculating the vibrational and rotational energies of diatomic molecules (Sprandel and Kern, 1972); however, this work demonstrates

that perturbation corrections can be calculated accurately, efficiently, and systematically for any order of correction. These results furnish important insight into the general quantum-mechanical vibrational–rotational problem and provide a framework for studies of the vibration and rotation of large polyatomic molecules, where perturbation theory is the most tractable and accurate method of analysis. Efforts are under way to develop a polyatomic analogue of the DIATOMICVIBROT program that will enable efficient calculation of arbitrary-order correction terms to polyatomic vibrational–rotational energies, wave functions, line intensities, and property expectation values.

6.1. Program Availability

The latest versions of RSPERTURB and DIATOMICVIBROT, along with a text file describing their use in detail, are available by anonymous FTP at <ftp://info.mcs.anl.gov/pub/perturb>.

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REFERENCES

- Adams, B. G. (1992) *Physical Review, Series A* **46**, 4060.
- Adams, B. G. and Artega, G. A. (1994) *Computers in Physics* **8**, 343.
- Amat, G., Nielsen, H. H. and Tarrago, G. (1971) *Rotation–Vibration of Polyatomic Molecules*. Marcel Dekker, New York.
- Bouanich, J. P. (1987a) *Computer Physics Communications* **47**, 259.
- Bouanich, J. P. (1987b) *Journal of Quantitative Spectroscopy and Radiative Transfer* **37**, 17.

- Bouanich, J. P. (1987c) *Journal of Quantitative Spectroscopy and Radiative Transfer* **38**, 89.
- Bunker, P. R. (1972) *Journal of Molecular Spectroscopy* **5**, 478.
- Carney, G. D. Sprandel, L. L. and Kem, C. W. (1978) In *Advances in Chemical Physics*, eds I. Prigogine and S. A. Rice, Vol. 37, pp. 305-379. John Wiley, New York.
- Carter, S. and Handy, N. C. (1982) *Molecular Physics* **47**, 1445.
- Choi, S. E. and Light, J. C. (1992) *Journal of Chemical Physics* **97**, 7031.
- Dalgamo, A. (1961) In *Quantum Theory, Elements*, ed. D. R. Bates, Vol. I, pp. 171-209. Academic Press, New York.
- Darling, B. T. and Dennison, D. M. (1939) *Physical Review* **57**, 128.
- Dennison, D. M. and Hecht, K. T. (1962) In *Quantum Theory, Aggregates of Particles*, ed. D. R. Bates, Vol. II, pp. 247-322. Academic Press, New York.
- Dudas, M. M., Hsieh, H. C. and Ermler, W. C. (1992) *Mathematica Journal* **2**, 66.
- Dunham, J. L. (1932) *Physical Review* **41**, 721.
- Dunning Jr. T. H. ed. (1990) In *Advances in Molecular Electronic Structure Theory Calculation and Characterization of Molecular Potential Energy Surfaces*, Vol. I. JAI Press, Greenwich.
- Ermler, W. C. and Hsieh, H. C. (1990) In *Advances in Molecular Electronic Structure Theory*. Calculation and Characterization of Molecular Potential Energy Surfaces, ed. T. H. Dunning, Vol. I, pp. 1-44. JAI Press, Greenwich.
- Fernández, F. M. (1992) *Journal of Physics, Series A* **25**, 495.
- Goldsmith, M., Arnat, G. and Nielsen, H. H. (1956) *Journal of Chemical Physics* **24**, 1178.
- Harding, L. B. and Ermler, W. C. (1985) *Journal of Computational Chemistry* **6**, 13.
- Herbert, J. M. (1997a) *Technical Memorandum No. 222*, Argonne National Laboratory, Division of Mathematics and Computer Science. (Available by anonymous FTP at ftp://info.mcs.anl.gov/pub/tech_reports/reports/TM222.ps.Z).
- Herbert, J. M. (1997b) *Argonne National Laboratory Report No. 97111*, 1997. (Available by anonymous FFP at ftp://info.mcs.anl.gov/pub/tech_reports/reports/ANL9711.ps.Z).
- Herzberg, G. and Howe, L. L. (1959) *Canadian Journal of Physics* **37**, 636.
- Herzberg, G. and Monfils, A. (1960) *Journal of Molecular Spectroscopy* **5**, 482.
- Huber, K. P. and Herzberg, G. (1979) *Molecular Spectra and Molecular Structure*, Vol. IV. Constants of Diatomic Molecules. Van Nostrand Reinhold, New York.
- Hulburt, H. M. and Hirschfelder, J. O. (1941) *Journal of Chemical Physics* **9**, 61.
- Hulburt, H. M. and Hirschfelder, J. O. (1961) *Journal of Chemical Physics* **35**, 1901.
- Jones, H. W. (1994) *International Journal of Quantum Chemistry* **51**, 417.
- Kern, C. W. and Matcha, R. L. (1968) *Journal of Chemical Physics* **49**, 2081.
- Kolos, W. and Wolniewicz, L. (1964) *Journal of Chemical Physics* **41**, 3663.
- Krohn, B. J., Ermler, W. C. and Kern, C. W. (1974) *Journal of Chemical Physics* **60**, 22.
- Levine, I. N. (1974) *Quantum Chemistry*, 2nd ed. Allyn and Bacon, Boston.
- Levine, I. N. (1975) *Molecular Spectroscopy*. John Wiley, New York.
- Matsen, F. A. (1970) *Vector Spaces and Algebras for Chemistry and Physics*. Holt, Rinehart, and Winston, New York.
- McRae, S. M. and Vrscaj, E. R. (1992) *Journal of Mathematical Physics* **33**, 3004.
- Morse, P. M. (1929) *Physical Review* **34**, 57.
- Nielsen, H. H. (1951) *Reviews of Modern Physics* **23**, 90.
- Niño, A. and Muñoz-Caro, C. (1995) *Computers and Chemistry* **19**, 371.
- Ogilvie, J. F. (1981) *Proceeding of the Royal Society of London, Series A* **378**, 287.
- Ogilvie, J. F. (1982) *Proceeding of the Royal Society of London, Series A* **381**, 479.
- Romanowski, H., Bowman, J. M. and Harding, L. B. (1985) *Journal of Chemical Physics* **82**, 4155.
- Sanders, F. C. and Scherr, C. W. (1969) *Physical Review* **181**, 84.
- Sprandel, L. L. and Kern, C. W. (1972) *Molecular Physics* **24**, 1383.
- Stoicheff, B. P. (1957) *Canadian Journal of Physics* **35**, 730.
- Townes, C. H. and Schawlow, A. L. (1955) *Microwave Spectroscopy*. McGraw-Hill, New York.
- Vinette, E. and Čížek, J. (1988) *Computer Physics Communications* **52**, 35.
- Wilson Jr., E. B., Decius, J. C. and Cross, P. C. (1980) *Molecular Vibrations*. Dover, New York.
- Wolfram, S. (1996) *The Mathematica Book*, 3rd ed. Wolfram Media, Champaigne; and Cambridge University Press, Cambridge.

APPENDIX A

6.1.0.1. Second-order correction formulae.

For each vibrational state, $E^{(2)}$ is a linear combination of the purely vibrational terms, purely rotational terms, and vibrational-rotational coupling terms listed below.

$$\text{VIBRATIONAL TERMS: } A_2^{(v)}, B_2^{(v)}$$

$$\text{ROTATIONAL TERMS: } A_2^{(r)}, B_2^{(r)}$$

$$\text{COUPLING TERMS: } A_2^{(v-r)}, B_2^{(v-r)}$$

Using lower-case letters to represent the integer coefficients of a linear combination, the complete second-order energy correction can be written as

$$\begin{aligned} E_{v,J}^{(2)} = & a_2^{(v)} A_2^{(v)} + b_2^{(v)} B_2^{(v)} + a_2^{(v-r)} A_2^{(v-r)} + b_2^{(v-r)} B_2^{(v-r)} \\ & + a_2^{(r)} A_2^{(r)} + b_2^{(r)} B_2^{(r)} = a_2^{(v)} A_2^{(v)} + b_2^{(v)} B_2^{(v)} \\ & + a_2^{(v-r)} A_2^{(v-r)} + b_2^{(v-r)} B_2^{(v-r)} + \geq \leq 2 \end{aligned} \quad (36)$$

where the coefficients depend upon the vibrational state v . The coefficients of the two rotational terms are independent of the vibrational state, so these terms have been grouped together into the *second-order constant of pure rotation* R_2 , whose value is

$$R_2 = \frac{-2J^2(J+1)^2 B_e^2}{\alpha R_e^2 h \nu_e} \quad (37)$$

Values of the linear combination coefficients from equation (36) are listed in Table 11 for the first eleven vibrational states.

Capital letters in the energy formula equation (36) represent collections of universal and molecular constants having the form

$$\frac{J^{\ell_1}(J+1)^{\ell_2}B_e^{\ell_3}k_3^{\ell_4}k_4^{\ell_5}}{\Omega\alpha^{\ell_6}R_e^{\ell_7}(h\nu_e)^{\ell_8}} \quad (38)$$

where Ω , ℓ_1 , ℓ_2 , ..., ℓ_8 are integers whose values are listed in Table 12 for all vibrational and coupling terms.

The correction formulae for $E^{(4)}$ and $E^{(6)}$ can be represented in analogous fashion. The linear combination representing $E^{(4)}$ consists of 20 vibrationally dependent terms plus R_4 , the fourth-order constant of pure rotation, while the linear combination representing $E^{(6)}$ contains 75 vibrationally dependent terms, plus R_6 . Finally, recall that

Darling and Dennison (1939) predicted that high-order perturbation formulae would not be factorable into integer powers of $J(J+1)$ and $(v+1/2)$. In fact, R_4 is found to be

$$R_4 = \frac{12J^3(J+1)^3B_e^3}{\alpha^2R_e^4(h\nu_e)^2} + \frac{4J^3(J+1)B_e^3k_3}{\alpha^3R_e^3(h\nu_e)^3}(3J^2 - 2J + 3), \quad (39)$$

which indeed cannot be factored exactly into powers of $J(J+1)$.