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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 \( \Sigma \) diatomic molecules are derived and then evaluated for \( \text{H}_2 \), \( \text{HD} \), \( \text{N}_2 \), \( \text{CO} \), and \( \text{HF} \). 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.

Key words: perturbation theory, computer algebra, molecular spectroscopy, vibration and rotation, diatomic molecules

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 \textit{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...
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 Ciček, 1988; Adams, 1992; McRae and Vrseay, 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

\[ \hat{T} + U(R)\psi = E\psi \] (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 \( U(\ell) \) is the sum of the vibrational potential \( U_{\text{vib}} \) and rotational potential \( U_{\text{rot}} \) 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 \( U_{\text{vib}}(\ell) \) be expanded as a Taylor series about the equilibrium internuclear separation \( R_0 \):

\[ U_{\text{vib}}(R) = U_{\text{vib}}^{(0)}(R_0)(R - R_0)^2 + \frac{U_{\text{vib}}^{(2)}}{2!}(R - R_0)^4 + \ldots \] (2)

where \( U(R_0) = 0 \) because \( U(R) \) is the minimum potential energy; for convenience, \( U(R_0) \) has been set equal to zero. The radius of convergence of this series is approximately \( 2R_0 \) (Dudas et al., 1992). It can be shown (Levine, 1975) that the rotational potential \( U_{\text{rot}} \) has the form

\[ U_{\text{rot}}(R) = \frac{J(J + 1)R^2}{2\mu R^2}, \] (3)

where \( J = 0, 1, 2,... \) is the rotational quantum number and \( \mu \) is the system’s reduced mass (including electrons). Expansion of \( U_{\text{rot}} \) as a power series in \( (R - R_0) \) provides

\[ U_{\text{rot}}(R) = \frac{J(J + 1)R^2}{2\mu R^2} \left[ 1 - \frac{1}{2} \left( \frac{R - R_0}{R_0} \right)^2 + \frac{3}{4} \left( \frac{R - R_0}{R_0} \right)^4 - \ldots \right], \] (4)

where \( \mu R_0^2 \) is the molecule’s equilibrium moment of inertia. The equation (4) converges whenever \( R < 2R_0 \) (Ogilvie, 1981, 1982).

For small displacements from equilibrium, \( R \approx R_0 \) 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)

\[ \psi_{J,M}^{(0)} = \frac{\Psi(Q)}{Q + R_0} \, Y^M_J(\theta,\phi). \] (5)

where \( v = 0, 1, 2,... \) is the vibrational quantum number, \( M = -J, -J + 1,..., J - 1, J \) is an angular momentum quantum number, and \( Q \equiv R - R_0 \) is the internuclear displacement coordinate. \( Y^M_J(\theta,\phi) \) in equation (5) is a spherical harmonic function (aris-
ing from rigid rotation), while \( \Psi_0(\mathbf{Q}) \) 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)

\[
E^{(0)} = (v + 1/2) \omega_v + J(J + 1)B_v,
\]

where \( \omega_v = 2 \pi v \), \( v \) is the classical frequency of oscillation and

\[
B_v = \frac{\hbar^2}{\omega_v},
\]

is the equilibrium rotational constant. Note that in the egs system, \( \omega_v \), \( B_v \), and \( E_v^{(0)} \) in equation (6) are in units of ergs. Following the convention of Levine (1975), wavenumber units are obtained by using the constants \( \omega_v \) and \( B_v \) in place of \( \omega_v \) and \( B_v \), where

\[
\omega_v \equiv \frac{\omega_v}{\hbar}, \quad B_v \equiv \frac{B_v}{\hbar^2}.
\]

### 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 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):

\[
\hat{H} = \hat{T} + \frac{1}{2} k_\ell \hat{Q}^2 + \sum_{i=1}^{\infty} \left[ \frac{(-1)^i (i + 1)(J + 1)J B_v}{R^i} \hat{Q}^i + \frac{k_{ij+2}}{(i + 2)!} \hat{Q}^{i+2} \right],
\]

where \( k_\ell \equiv U'(R_\ell) \) is the equilibrium molecular force constant, and the \( j \)th-order force constant \( k_j \) is defined as

\[
k_j \equiv U^{(i)}(R_\ell)
\]

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 \( U_{\text{HO}} = \frac{1}{2} k_v \hat{Q}^2 \). Notice that the first term in equation (4) is not incorporated into \( \hat{H} \) 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

\[
\hat{H} = \hat{H}^{(0)} + \sum_{i=1}^{\infty} \hat{H}^{(i)}(i) \quad E_i J = E_i^{(0)} + \sum_{i=1}^{\infty} E_i^{(i)} \psi_{i,j,M} \]

where the unperturbed Hamiltonian operator

\[
\hat{H}^{(0)} \equiv \hat{T} + \frac{1}{2} k_\ell \hat{Q}^2
\]

corresponds to the harmonic oscillator/rigid-rotator system. There are numerous ways of constructing the perturbed Hamiltonian operators \( \hat{H}^{(i)} \) 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:

\[
\hat{H}^{(1)} = \frac{1}{6} k_\ell \hat{Q}^3 - \frac{2J(J + 1)B_v}{R_\ell} \hat{Q},
\]

\[
+ \hat{H}^{(2)} = \frac{1}{24} k_\ell Q^4 - \frac{3J(J + 1)B_v}{R_\ell^2} Q^2,
\]

Here the first-order perturbation \( \hat{H}^{(1)} \) 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 \( \hat{H}^{(2)} \) 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:

\[
\hat{H}^{(i)} = \frac{k_{ij+2}}{(i + 2)!} \hat{Q}^{i+2} + \frac{(-1)^i(i + 1)(J + 1)B_v}{R_\ell} \hat{Q},
\]

or equivalently

\[
\hat{H}^{(i)} = \frac{k_{ij+2}}{(i + 2)!} \hat{Q}^{i+2} + \frac{(-1)^i(i + 1)J(J + 1)}{2I_\ell} \left( \frac{Q}{R_\ell} \right)^i.
\]

since the total angular momentum \( L \) of a rotating diatomic molecule has magnitude \( ||L|| = \hbar \) 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 $E^{(i)}_{ij}$ and perturbed wave functions $\psi_{(i)M}$ one must evaluate numerous integrals of the form

$$\mathcal{H}^{(i)}_{ij} = \langle \psi^{(i)}_{M} | \mathcal{H}^{(i)} | \psi^{(0)}_{M} \rangle,$$

(16)

where the ordered triple $\{i,j,M\}$ 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

$$\mathcal{H}^{(i)}_{ij} = \frac{k_{i+2}}{(i+2)!} (Q^{i+2})_{ij},$$

(17)

where, for brevity,

$$\langle Q^{i} \rangle_{ij} = \langle \psi^{(0)}_{ij} | \langle Q \rangle | \psi^{(0)}_{ij} \rangle,$$

(18)

since the $Q$ tensor is also diagonal in $J$ and $M$. Note that the matrix $\mathcal{H}^{(i)}_{ij}$ 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 $\langle Q \rangle_{ij}$ 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

$$\langle Q \rangle_{ij} = \left[ \frac{\alpha}{2} \right]^{1/2} \delta_{i,j-1} + \left[ \frac{\alpha + 1}{2} \right]^{1/2} \delta_{i,j+1},$$

(19)

where $\delta$ is the Kronecker delta function and

$$\alpha \equiv \frac{4\pi^{2}v_{i}\mu}{\hbar}$$

(20)

is a constant appearing in the harmonic oscillator wave functions. The elements of $Q^{i} (i > 1)$ 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 formulæ for these matrix elements up to $\langle Q \rangle_{i}^{5}$ 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 $\mathcal{H}^{(i)}_{ij}$. As such, perturbation formulæ arising from the Hamiltonian described here will not involve infinite summations, but instead will be expressible in closed (albeit lengthy) forms. Thus, these formulæ 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 $\{|\psi^{(0)}_{i}\rangle\}$ is assumed to form a basis for the Hilbert space containing the true wave functions $\psi_{i}$. Each perturbed wave function $\psi^{(n)}_{i}$ is expressed as a linear combination of these basis functions:

$$\psi^{(n)}_{i} = \sum_{\zeta} c^{(n)}_{\zeta i} \psi^{(0)}_{\zeta},$$

(21)

where $c^{(n)}_{\zeta i}$ is the $n$th-order expansion coefficient associated with quantum state $\zeta$. In this application, the summation in equation (21) runs over all possible values of the three quantum numbers $n$, $J$, 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 $c^{(n)}_{\zeta M}$ does not affect the perturbation energy $E_{ij}^{(n)}$ so one may set $c^{(n)}_{\zeta M} = 0$ in the Rayleigh–Schrödinger expansion of $\psi^{(n)}_{i}$. The equation (21) then simplifies to

$$\psi^{(n)}_{i} = \sum_{\zeta} c^{(n)}_{\zeta i} \psi^{(0)}_{\zeta},$$

(22)

Second, observe that

$$\langle \psi^{(n)}_{\zeta} | \mathcal{H}^{(i)} | \psi^{(0)}_{\zeta'} \rangle = \sum_{\zeta''} c^{(n)}_{\zeta \zeta'} \langle \psi^{(0)}_{\zeta'} | \mathcal{H}^{(i)} | \psi^{(0)}_{\zeta''} \rangle,$$

(23)

and, finally,

$$\langle \psi^{(n)}_{\zeta} | \psi^{(n)}_{\zeta'} \rangle = \sum_{\zeta''} c^{(n)}_{\zeta \zeta'} \langle \psi^{(n)}_{\zeta'} | \psi^{(n)}_{\zeta''} \rangle,$$

(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

$$c^{(0)}_{\zeta i} = \langle \psi^{(0)}_{\zeta} | \psi^{(0)}_{i} \rangle,$$

(25)

where $\zeta$ is the quantum state whose wave function is to be expanded and $\zeta'$ 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 $\psi$ (Kern and Matcha, 1968; Herbert, 1997a). Applying the Rayleigh–Schrödinger expansion of equation (22) to the $n$th-order perturbation equation provides
\[
\sum_{\xi \neq \xi'} c^{(n)}_{\xi} (\hat{H}^{(0)} - E^{(0)}_{\nu,\xi}) \psi^{(0)}_{\xi} = \sum_{i=1}^{n} (E^{(i)}_{\nu,\xi} - \hat{H}^{(i)}_{\nu,\xi}) \psi^{(n-1)}_{\xi}. 
\]

(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 \( \psi^{(0)*}_{\xi'} \) of the zeroth-order wave function for state \( \xi' \) followed by integration yields

\[
\sum_{\xi \neq \xi'} c^{(n)}_{\xi} (E^{(0)}_{\nu,\xi'} - E^{(0)}_{\nu,\xi}) \delta_{\xi,\xi'} = \sum_{i=1}^{n} E^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi} - \sum_{i=1}^{n} \sum_{\xi \neq \xi'} c^{(n-1)}_{\xi} \hat{H}^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi}. 
\]

(27)

As \( \xi' \) is arbitrary, choose \( \xi' \) such that \( \xi' \neq \xi \). Under this condition, the wave functions \( \psi^{(0)}_{\xi} \) and \( \psi^{(n-1)}_{\xi} \) 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:

\[
c^{(n)}_{\xi} (E^{(0)}_{\nu,\xi'} - E^{(0)}_{\nu,\xi}) = \sum_{i=1}^{n-1} E^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi} - \sum_{i=1}^{n} \sum_{\xi \neq \xi'} c^{(n-1)}_{\xi} \hat{H}^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi} 
\]

(28)

for all \( n > 0 \).

Equation (28) is nearly the desired general formula for the expansion coefficients; however, if \( \xi \) and \( \xi' \) 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 \( E^{(0)}_{\nu,\xi'} \neq E^{(0)}_{\nu,\xi} \).

Solving equation (28) for \( c^{(n)}_{\xi} \) and substituting this expression into equation (22) affords the expansion

\[
\psi^{(n)}_{\xi} = \sum_{\xi \neq \xi'} \left[ \frac{1}{E^{(0)}_{\nu,\xi'} - E^{(0)}_{\nu,\xi}} \left( \sum_{i=1}^{n} E^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi} - \sum_{i=1}^{n} \sum_{\xi \neq \xi'} c^{(n-1)}_{\xi} \hat{H}^{(i)}_{\nu,\xi} \psi^{(n-1)}_{\xi} \right) \right] \psi^{(0)}_{\xi'}. 
\]

(29)

Observe from equation (28) with \( n = 1 \) that each first-order expansion coefficient \( c^{(1)}_{\xi} \) 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 \( c^{(n)}_{\xi} \) is a sum of such terms, some of which are multiplied by an energy correction \( E^{(i)}_{\nu,\xi} \). Since each perturbed Hamiltonian matrix \( \hat{H}^{(i)}_{\nu,\xi} \) 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 \( \nu \neq \nu' \) and \( \nu' \neq \nu \), respectively. Applying this simplification and making use of equation (25), one may recast equation (28) in its simplest form:

\[
c^{(n)}_{\xi} (E^{(0)}_{\nu,\xi'} - E^{(0)}_{\nu,\xi}) = -\mathcal{H}^{(n)}_{\nu,\xi} + \sum_{i=1}^{n} c^{(n-1)}_{\xi} E^{(i)}_{\nu,\xi} 
\]

(30)

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

\[
E^{(0)}_{\nu,\xi'} - E^{(0)}_{\nu,\xi} = (\nu' - \nu) \omega \quad (J = J') 
\]

(31)

from equation (6). Hence, \( E^{(0)}_{\nu,J} \neq E^{(0)}_{\nu,J'} \) if \( \nu' \neq \nu \). Since equation (30) relates to the Rayleigh–Schrödinger expansion

\[
\psi^{(n)}_{\nu,M} = \sum_{\nu' \neq \nu} c^{(n)}_{\nu,\nu'} \psi^{(0)}_{\nu',M} .
\]

(32)

this condition is met, and the assumption that \( E^{(0)}_{\nu,J} \neq E^{(0)}_{\nu,J'} \) 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 \( c^{(n)}_{\nu,J} \), where an implicit parametric dependence on \( J \) (analogous to that of \( \mathcal{H}^{(n)}_{\nu,J} \)) is assumed. The final expression for the Rayleigh–Schrödinger expansion coefficients is obtained from equation (30):

\[
c^{(n)}_{\nu,J} = \frac{1}{(\nu - \nu') \hbar \omega} \times \left[ \mathcal{H}^{(n)}_{\nu,J} - \sum_{i=1}^{n} c^{(n-1)}_{\nu,J} E^{(i)}_{\nu,J} + \sum_{i=1}^{n} \sum_{\nu' \neq \nu} c^{(n-1)}_{\nu',\nu} \mathcal{H}^{(i)}_{\nu',J} \right] .
\]

(33)

Equation (33) provides an important recursive relation whereby each new set of expansion coefficients \( c^{(n)}_{\nu,J} \) is determined by all of the coefficients of order less than \( n \), while the first-order coefficients \( c^{(1)}_{\nu,J} \) 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 \( E^{(0)}_{\nu,J} - E^{(0)}_{\nu,J'} \), 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 \( \psi^{(n)}_{\nu,M} \) in terms of the known functions in the set \( \{\psi^{(0)}_{\nu,M}\} \). Such perturbed wave functions appear in the equation for the \( n \)th-order energy correction.
Where the parameter $\kappa$ is defined as

$$\kappa = \frac{1}{2} n,$$  \hspace{1cm} (35)

the greatest integer less than or equal to $\frac{1}{2} n$. Only the wave function terms $\psi_{\kappa}^{(0)} \psi_{\kappa}^{(1)} \psi_{\kappa}^{(2)}, \ldots, \psi_{\kappa}^{(4)}$ are necessary to express the nth-order energy correction $E_{n,j}^{(k)}$ (Dalgarno, 1961).

### 4.4. Mathematica Programs

An existing Mathematica code (Dudas et al., 1992) can evaluate the matrices $Q^n$ for any positive integer $n$ 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 formulas 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 RSPTURB. 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 RSPTURB 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 RSPTURB can be applied to solve perturbation problems other than the one discussed here.

In deriving energy formulae using RSPTURB and DIATOMICVIBROT, the quantum number $v$ was not incorporated symbolically, but instead a separate 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 this 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 $R_c$, 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 Demison, 1939), and indeed the expansion in $(v + 1/2)[J(J + 1)]$ 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 RSPTURB and DIATOMICVIBROT, Mathematica derived analytic formulae for the energy correction terms $E^v(3)$ through $E^v(6)$ 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 $\mathbf{H}_{v',v}^{(2j)}$ as defined in equation (17) have a definite parity due to the parity of $Q_{v',v'}$, 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 calcula-
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 nth-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 $c_{nu}^{(k)}$ 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...
programs. In a fully \textit{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 \textit{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 conver-
gence, the theoretical data obtained from this po-
tential 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 re-
liability 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 \textit{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, \textit{Mathematica}®
can easily perform the requisite sym-
bolic 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 indistin-
guishable from experimental values. As $v$ increases,
so does the discrepancy between theory and exper-
iment; this rift also increases (to a lesser extent)
with increasing $J$.

Although force constants from the Morse poten-
tial 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-

![Graph: Additional Time Required for Algebraic Simplification of Crude Formulae](image)
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 $^1$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 $^1$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 $^1$H$_2$**

<table>
<thead>
<tr>
<th>Correction term</th>
<th>Vibrational–rotational energy contributions, $\tilde{E}_{\nu,J}(i)$ (waves cm$^{-1}$)</th>
<th>Vibrational–rotational energy contributions $\tilde{E}_{\nu,J}(i)$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^{(0)}$</td>
<td>$\nu = 0, J = 0$</td>
<td>2202.42</td>
</tr>
<tr>
<td>$E^{(1)}$</td>
<td>$\nu = 0, J = 1$</td>
<td>2324.14</td>
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<tr>
<td>$E^{(2)}$</td>
<td>$\nu = 0, J = 2$</td>
<td>2567.58</td>
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<tr>
<td>$E^{(3)}$</td>
<td>$\nu = 1, J = 0$</td>
<td>6607.27</td>
</tr>
<tr>
<td>$E^{(4)}$</td>
<td>$\nu = 2, J = 0$</td>
<td>11,012.12</td>
</tr>
<tr>
<td>$E^{(5)}$</td>
<td>$\nu = 3, J = 0$</td>
<td>15,416.97</td>
</tr>
</tbody>
</table>

*The tilde is used over the energy correction in this and subsequent tables to indicate units of waves per centimeter.*
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 vibrational state, energy corrections increase slowly with $J$, but within a given rotational state, the correction terms increase quite rapidly with $u$. This energy dependence is clearly illustrated in Fig. 4. The calculations shown there are for the $X^1\Sigma_g^+\ H_2$ state 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).

Table 2. RSPT(6) vibrational–rotational energies (cm$^{-1}$) for the lowest vibrational–rotational states of $X^1\Sigma_g^+\ H_2$.

<table>
<thead>
<tr>
<th>$u$</th>
<th>$J$ = 0</th>
<th>$J$ = 1</th>
<th>$J$ = 2</th>
<th>$J$ = 3</th>
<th>$J$ = 4</th>
<th>$J$ = 5</th>
<th>$J$ = 6</th>
<th>$J$ = 7</th>
<th>$J$ = 8</th>
<th>$J$ = 9</th>
<th>$J$ = 10</th>
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</thead>
<tbody>
<tr>
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<td>2178.59</td>
<td>2297.08</td>
<td>2352.96</td>
<td>2384.09</td>
<td>3347.34</td>
<td>3918.67</td>
<td>4593.28</td>
<td>5365.67</td>
<td>6229.81</td>
<td>7179.21</td>
<td>8206.94</td>
</tr>
<tr>
<td>1</td>
<td>6344.71</td>
<td>6447.26</td>
<td>6671.22</td>
<td>7004.58</td>
<td>7446.28</td>
<td>7992.13</td>
<td>8630.80</td>
<td>9360.00</td>
<td>10174.7</td>
<td>11076.6</td>
<td>12049.5</td>
</tr>
<tr>
<td>2</td>
<td>10246.7</td>
<td>10353.4</td>
<td>10565.6</td>
<td>10881.3</td>
<td>11297.6</td>
<td>11810.7</td>
<td>12415.9</td>
<td>13088.1</td>
<td>13730.6</td>
<td>14568.2</td>
<td>15484.6</td>
</tr>
<tr>
<td>3</td>
<td>13914.8</td>
<td>14015.4</td>
<td>14215.8</td>
<td>14513.8</td>
<td>14906.4</td>
<td>15390.1</td>
<td>15960.3</td>
<td>16619.9</td>
<td>17339.2</td>
<td>18136.6</td>
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</tr>
<tr>
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<td>13961.6</td>
<td>14062.7</td>
<td>14263.9</td>
<td>14563.3</td>
<td>14958.0</td>
<td>15444.5</td>
<td>16018.4</td>
<td>16674.8</td>
<td>17408.3</td>
<td>18213.4</td>
<td>19084.6</td>
</tr>
<tr>
<td>5</td>
<td>17335.4</td>
<td>17430.0</td>
<td>17618.2</td>
<td>17897.9</td>
<td>18264.6</td>
<td>18719.8</td>
<td>19253.8</td>
<td>19863.2</td>
<td>20542.7</td>
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<td>17715.0</td>
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<td>18828.9</td>
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<td>19988.1</td>
<td>20768.5</td>
<td>21453.6</td>
<td>22253.9</td>
</tr>
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<td>20765.6</td>
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<td>21364.9</td>
<td>21791.2</td>
<td>22287.2</td>
<td>22852.5</td>
<td>23431.5</td>
<td>24070.0</td>
<td>24707.0</td>
</tr>
<tr>
<td>8</td>
<td>20671.2</td>
<td>20761.0</td>
<td>20939.6</td>
<td>21205.2</td>
<td>21555.2</td>
<td>21986.2</td>
<td>22494.0</td>
<td>23074.0</td>
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<td>24230.2</td>
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</tr>
<tr>
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<td>23485.3</td>
<td>23647.4</td>
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<td>24204.3</td>
<td>24925.2</td>
<td>25482.2</td>
<td>26122.1</td>
<td>26852.3</td>
<td>27652.0</td>
<td>28505.0</td>
</tr>
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<td>10</td>
<td>26273.7</td>
<td>26340.1</td>
<td>26488.5</td>
<td>26750.0</td>
<td>27108.2</td>
<td>27525.0</td>
<td>27985.0</td>
<td>28505.0</td>
<td>29065.5</td>
<td>29663.3</td>
<td>30340.0</td>
</tr>
<tr>
<td>11</td>
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<td>26545.2</td>
<td>26700.7</td>
<td>26931.6</td>
<td>27235.6</td>
<td>27509.2</td>
<td>27889.8</td>
<td>28356.2</td>
<td>28849.2</td>
<td>29367.5</td>
<td>30001.3</td>
</tr>
<tr>
<td>12</td>
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<td>28421.9</td>
<td>28554.1</td>
<td>28749.9</td>
<td>29006.3</td>
<td>29319.5</td>
<td>29684.8</td>
<td>30097.2</td>
<td>30551.0</td>
<td>31000.0</td>
<td>31557.7</td>
</tr>
<tr>
<td>13</td>
<td>29101.3</td>
<td>29082.3</td>
<td>29225.5</td>
<td>29438.1</td>
<td>29717.6</td>
<td>30060.9</td>
<td>30463.9</td>
<td>30922.2</td>
<td>31431.2</td>
<td>31955.6</td>
<td>32580.5</td>
</tr>
<tr>
<td>14</td>
<td>30366.7</td>
<td>30424.9</td>
<td>30540.3</td>
<td>30718.0</td>
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<td>32256.3</td>
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<td>34515.8</td>
</tr>
<tr>
<td>16</td>
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<td>32086.5</td>
<td>32183.5</td>
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<td>32735.9</td>
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<td>33487.0</td>
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<td>33676.0</td>
<td>33901.2</td>
<td>34176.5</td>
<td>34497.8</td>
<td>34860.5</td>
<td>35259.5</td>
<td>35689.2</td>
<td>36144.1</td>
</tr>
</tbody>
</table>

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).
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 $^1\text{H}_2$ are listed in Table 2, along with the corresponding experimental energies (Stoicheff, 1957; Herzberg and Monfils, 1960); for convenience, the relative differences between theoretical and experimental energies (Stoicheff, 1957; 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 rotational levels in Table 2. Thus, it appears that for $v > 4$, the difference between theoretical and experimental energies is less than 1 per cent for all eleven rotational 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

<table>
<thead>
<tr>
<th>$J = 0$</th>
<th>$J = 1$</th>
<th>$J = 2$</th>
<th>$J = 3$</th>
<th>$J = 4$</th>
<th>$J = 5$</th>
<th>$J = 6$</th>
<th>$J = 7$</th>
<th>$J = 8$</th>
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<tbody>
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<td>$v = 0$</td>
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<td>$-0.03$</td>
<td>$-0.03$</td>
<td>$-0.03$</td>
<td>$-0.02$</td>
<td>$-0.02$</td>
<td>$-0.02$</td>
<td>$-0.03$</td>
<td>$-0.05$</td>
<td>$-0.05$</td>
</tr>
<tr>
<td>$v = 1$</td>
<td>$-0.09$</td>
<td>$-0.09$</td>
<td>$-0.09$</td>
<td>$-0.09$</td>
<td>$-0.08$</td>
<td>$-0.07$</td>
<td>$0.05$</td>
<td>$0.02$</td>
<td>$0.05$</td>
<td>$0.15$</td>
</tr>
<tr>
<td>$v = 2$</td>
<td>$-0.19$</td>
<td>$-0.19$</td>
<td>$-0.19$</td>
<td>$-0.19$</td>
<td>$-0.19$</td>
<td>$-0.18$</td>
<td>$-0.17$</td>
<td>$-0.14$</td>
<td>$-0.09$</td>
<td>$-0.01$</td>
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<td>$-0.34$</td>
<td>$-0.34$</td>
<td>$-0.34$</td>
<td>$-0.35$</td>
<td>$-0.35$</td>
<td>$-0.36$</td>
<td>$-0.38$</td>
<td>$-0.40$</td>
<td>$-0.42$</td>
</tr>
<tr>
<td>$v = 4$</td>
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<td>$-0.55$</td>
<td>$-0.55$</td>
<td>$-0.56$</td>
<td>$-0.58$</td>
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<td>$-0.63$</td>
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<td>$v = 5$</td>
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<td>$-0.82$</td>
<td>$-0.83$</td>
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<td>$-0.86$</td>
<td>$-0.89$</td>
<td>$-0.92$</td>
<td>$-0.96$</td>
<td>$-1.01$</td>
<td>$-1.07$</td>
</tr>
<tr>
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<td>$-1.34$</td>
<td>$-1.40$</td>
<td>$-1.47$</td>
<td>$-1.56$</td>
</tr>
<tr>
<td>$v = 7$</td>
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<td>$-1.67$</td>
<td>$-1.69$</td>
<td>$-1.72$</td>
<td>$-1.76$</td>
<td>$-1.81$</td>
<td>$-1.88$</td>
<td>$-1.97$</td>
<td>$-2.07$</td>
<td>$-2.19$</td>
</tr>
<tr>
<td>$v = 10$</td>
<td>$-3.88$</td>
<td>$-3.90$</td>
<td>$-3.94$</td>
<td>$-4.01$</td>
<td>$-4.10$</td>
<td>$-4.22$</td>
<td>$-4.36$</td>
<td>$-4.53$</td>
<td>$-4.74$</td>
<td>$-4.98$</td>
</tr>
</tbody>
</table>

Fig. 5. Hulburt–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 $^1\Sigma_u^+ \text{H}_2$. These energies were obtained from RSPT(6) calculations by using Hulburt–Hirschfelder force constants, with Hulburt–Hirschfelder parameters taken from Hulburt and Hirschfelder (1941). The dotted vertical line is located at $Q = R_e$. 

Table 3. Relative percentage differences between theoretical RSPT(6) and experimental energies for the lowest vibrational–rotational states of $^1\Sigma_u^+ \text{H}_2$.
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 4. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - 14\text{N}_2$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
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<td>1175.70</td>
<td>1180.69</td>
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<td>1188.68</td>
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</tr>
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<td>10319.20</td>
<td>10327.00</td>
<td>10326.90</td>
</tr>
</tbody>
</table>

Table 5. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - ^{12}\text{C}^{16}\text{O}$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 0$</td>
<td>1081.07</td>
<td>1081.59</td>
<td>1084.92</td>
<td>1085.31</td>
<td>1092.60</td>
</tr>
<tr>
<td>$J = 1$</td>
<td>3223.08</td>
<td>3224.86</td>
<td>3226.89</td>
<td>3228.67</td>
<td>3234.51</td>
</tr>
<tr>
<td>$J = 2$</td>
<td>5338.70</td>
<td>5341.65</td>
<td>5342.47</td>
<td>5345.42</td>
<td>5350.02</td>
</tr>
<tr>
<td>$J = 3$</td>
<td>7427.71</td>
<td>7432.03</td>
<td>7434.74</td>
<td>7437.77</td>
<td>7448.96</td>
</tr>
<tr>
<td>$J = 4$</td>
<td>9489.88</td>
<td>9496.06</td>
<td>9493.59</td>
<td>9499.76</td>
<td>9500.99</td>
</tr>
</tbody>
</table>

Table 6. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - ^1\text{H}^1\text{F}$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 0$</td>
<td>2054.71</td>
<td>2046.80</td>
<td>2095.73</td>
<td>2087.94</td>
<td>2177.79</td>
</tr>
<tr>
<td>$J = 1$</td>
<td>6018.60</td>
<td>6008.23</td>
<td>6057.99</td>
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<td>6136.73</td>
</tr>
<tr>
<td>$J = 2$</td>
<td>9813.65</td>
<td>9797.62</td>
<td>9851.46</td>
<td>9836.40</td>
<td>9927.04</td>
</tr>
<tr>
<td>$J = 3$</td>
<td>13445.2</td>
<td>13419.7</td>
<td>13481.5</td>
<td>13457.7</td>
<td>13554.0</td>
</tr>
<tr>
<td>$J = 4$</td>
<td>16916.0</td>
<td>16878.6</td>
<td>16950.8</td>
<td>16916.1</td>
<td>17020.3</td>
</tr>
</tbody>
</table>

Table 7. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - ^1\text{H}^2\text{H}$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 0$</td>
<td>1890.33</td>
<td>1883.75</td>
<td>1979.58</td>
<td>1972.96</td>
<td>2157.47</td>
</tr>
<tr>
<td>$J = 1$</td>
<td>5519.06</td>
<td>5515.90</td>
<td>5604.42</td>
<td>5601.02</td>
<td>5774.54</td>
</tr>
<tr>
<td>$J = 2$</td>
<td>8962.80</td>
<td>8971.00</td>
<td>9044.32</td>
<td>9051.95</td>
<td>9206.76</td>
</tr>
<tr>
<td>$J = 3$</td>
<td>12222.6</td>
<td>12235.2</td>
<td>12300.2</td>
<td>12329.9</td>
<td>12455.0</td>
</tr>
<tr>
<td>$J = 4$</td>
<td>15297.5</td>
<td>15366.7</td>
<td>15371.2</td>
<td>15439.2</td>
<td>15518.2</td>
</tr>
</tbody>
</table>

Table 8. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - ^3\text{H}^2\text{H}$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 0$</td>
<td>1080.17</td>
<td>1081.59</td>
<td>1084.92</td>
<td>1085.31</td>
<td>1092.60</td>
</tr>
<tr>
<td>$J = 1$</td>
<td>3223.08</td>
<td>3224.86</td>
<td>3226.89</td>
<td>3228.67</td>
<td>3234.51</td>
</tr>
<tr>
<td>$J = 2$</td>
<td>5338.70</td>
<td>5341.65</td>
<td>5342.47</td>
<td>5345.42</td>
<td>5350.02</td>
</tr>
<tr>
<td>$J = 3$</td>
<td>7427.71</td>
<td>7432.03</td>
<td>7434.74</td>
<td>7437.77</td>
<td>7448.96</td>
</tr>
<tr>
<td>$J = 4$</td>
<td>9489.88</td>
<td>9496.06</td>
<td>9493.59</td>
<td>9499.76</td>
<td>9500.99</td>
</tr>
</tbody>
</table>

Table 9. Experimental and RSPT(6) vibrational–rotational energies for $X^3\Sigma^+ - ^1\text{H}^3\text{H}$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
<th>$\nu = 2$</th>
<th>$\nu = 3$</th>
<th>$\nu = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 0$</td>
<td>1890.33</td>
<td>1883.75</td>
<td>1979.58</td>
<td>1972.96</td>
<td>2157.47</td>
</tr>
<tr>
<td>$J = 1$</td>
<td>5519.06</td>
<td>5515.90</td>
<td>5604.42</td>
<td>5601.02</td>
<td>5774.54</td>
</tr>
<tr>
<td>$J = 2$</td>
<td>8962.80</td>
<td>8971.00</td>
<td>9044.32</td>
<td>9051.95</td>
<td>9206.76</td>
</tr>
<tr>
<td>$J = 3$</td>
<td>12222.6</td>
<td>12235.2</td>
<td>12300.2</td>
<td>12329.9</td>
<td>12455.0</td>
</tr>
<tr>
<td>$J = 4$</td>
<td>15297.5</td>
<td>15366.7</td>
<td>15371.2</td>
<td>15439.2</td>
<td>15518.2</td>
</tr>
</tbody>
</table>

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 $Q = R_c$, 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 $\nu = 5$ (in the ground rotational state) and above $\nu = 3$ (in the $J = 10$ rotational state), $Q$ may drift beyond $R_c$, 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 $\nu = 3$ vibrational level but no higher than the $\nu = 5$ 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
vibrational–rotational energy calculations. Because it is the lightest molecule, high-order energy corrections for \( \text{H}_2 \) 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 \( \text{H}_2 \) than for other diatomic molecules. Thus, \( \text{H}_2 \) 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 (\( \text{N}_2 \) and \( \text{CO} \)) than for lighter ones (\( \text{HF} \) and \( \text{H}_2 \)), which affirms Dunham’s result (Dunham, 1932) for diatomic molecules. Thus, \( \text{H}_2 \) represents something of a lower limit to the accuracy of perturbation calculations.

#### 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 RSPERTUR[8], which contains all of the equations necessary to implement arbitrary-order Rayleigh–Schrödinger perturbation theory.
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; Nin˜o and Mun˜oz-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.

**Acknowledgements**—This work was supported in part by the Mathematical, Information, and Computational Sciences Division subprogram Office of Computational and Technology Research, and by the Office of Basic Energy Sciences, Division of Chemical Sciences, United States Department of Energy, under Contract W-31-109-Eng-38. John M. Herbert is a participant in the Research Semester program of the Department of Energy, Science and Engineering.

### REFERENCES

Symbolic Implementation of Arbitrary-order Perturbation Theory

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.

**Vibrational Terms:** $A_1^{(v)}, B_1^{(v)}$

**Rotational Terms:** $A_2^{(r)}, B_2^{(r)}$

**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

$$E^{(2)}_{ij} = a_v^{(i)} A_1^{(v)} + b_v^{(i)} B_1^{(v)} + a_r^{(r)} A_2^{(r)} + b_r^{(r)} B_2^{(r)} + a_{v-r}^{(v-r)} A_2^{(v-r)} + b_{v-r}^{(v-r)} B_2^{(v-r)}$$

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

$$R_2 = -\frac{2J(J+1)B_2}{2R_v^2}$$

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...
where $\Omega$, $\ell_1$, $\ell_2$, ..., $\ell_8$ 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 $(\nu + 1/2)$. In fact, $R_4$ is found to be

$$R_4 = \frac{12J^3(J + 1)^3}{x^2 R^2_v(h\nu)^2} + \frac{4J^3(J + 1)B^2_3}{x^2 R^2_v(h\nu)^2}(3J^2 - 2J + 3),$$

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

$$\frac{J(J + 1)^2 B^4_3 k_3 k_3'}{\Omega^2 R^2_v(h\nu)^2}$$

(38)

(39)