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Theoretical studies of vibrationally excited polyatomic molecules using canonical Van Vleck perturbation theory

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The highly excited vibrational states of polyatomic molecules are investigated using canonical Van Vleck perturbation theory, implemented in a superoperator framework. This approach is used to transform a vibrational Hamiltonian to a new representation which has a form ideally suited to the study of the dynamics of interest. The key advantage is that the solution to the full problem is obtained in the new representation using significantly smaller basis sets than are needed to obtain the solutions in the original representation. The transformations are applied to the Hamiltonian operator itself, not the Hamiltonian matrix; this superoperator approach obviates the need for large basis sets. The tedious and complex algebra, that is required to perform these transformations, is readily implemented with FORTRAN codes. Combining these two features has enabled the investigations of vibrational dynamics in energy regimes and densities of states, unattainable by standard methods. These methods are applied to two model problems and to the study of the highly excited overtones of CHD_3 with up to five quanta of excitation in the CH bond.

I. INTRODUCTION

It is well recognized that the character, rate, and mechanism of intramolecular flow of energy play a fundamental role in several areas of chemical dynamics.¹⁻³ The important areas of the RRKM theory of kinetics,⁴ of multiphoton excitation,⁵ overtone induced reactions,⁶ and of mode selective processes⁷⁻⁹ all require the elucidation of internal energy flow phenomena. Central to these goals is the proper quantum mechanical description of the nature of highly excited vibrational states.¹⁻³ This endeavor has received intense theoretical and experimental scrutiny; the study of highly vibrationally excited molecules is a subject of ongoing interest to both spectroscopists and dynamacists alike. A great deal of this interest is directed towards developing new methods of obtaining vibrational eigenvalues and eigenfunctions.¹⁰⁻²⁸ In this paper we focus on one such method (canonical Van Vleck perturbation theory) and successfully apply it to several vibrational problems. Before discussing these ideas, we briefly review other state-of-the-art methods used in this field.

For low energies, variational approaches have been quite successful.¹⁰ Here research has focused on determining the best choice of coordinate system and basis functions to be used. Recent efforts have implemented ideas developed in the context of *ab initio* calculations. Several workers have optimized their product wave functions by introducing a self-consistent field (SCF) step in their variational calculations to obtain the energetically best vibrational product functions. These SCF modes are then coupled in a configuration-interaction-like coupling scheme.¹¹⁻¹⁴ Davis and Heller¹⁵ have used basis set expansions based on complex Gaussian wave functions with centers distributed throughout the space of interest. These methods have been improved upon by using the underlying classical dynamics as a guide in the construction of the appropriate Gaussian basis func-

tions.^{16,17} Light and co-workers¹⁸ have demonstrated the utility of multicentered expansions using distributed real Gaussian wave functions. These methods are well suited to molecules undergoing large amplitude motions, particularly if there exists more than one minimum on the potential energy surface.

Wyatt and co-workers¹⁹ have developed a recursive method, based on the Lanczos method,²⁰ of obtaining tridiagonal matrices. In particular, these workers have employed the Davidson algorithm²¹ and the recursive residue generation method (RRGM)¹⁹ to obtain molecular state-to-state transition probabilities induced by external fields. For sparse matrices as many as 10^6 basis functions have been used to represent the molecule's Hamiltonian and its perturbation. This method offers extremely exciting prospects for certain systems. Our preliminary investigations have indicated that the Lanczos method is not well suited to the study of overtone line shapes; very large tridiagonal matrices are required to resolve closely spaced eigenvalues which might be observed in an overtone excitation.

An alternative approach, which has been the subject of considerable attention over the past ten years, is based on a semiclassical description of molecular vibrations.²² Most of this activity has been directed towards developing new methods for determining semiclassical eigenvalues as well as providing a better understanding of vibrational dynamics. Only a few of these methods, however, have been extended to examine the realistic dynamics of triatomic systems. Two of the more successful methods are the methods of spectral quantization^{23,24} and adiabatic switching.²⁵⁻²⁷ At low energies these ideas work surprisingly well. At higher energies, where the classical dynamics is characteristically dominated by chaotic behavior, difficulties arise. Although some considerable successes have been realized,^{2(e),27,28} no clear cut methods yet exist for obtaining semiclassical eigenvalues in chaotic regimes of phase space for polyatomic molecules.

The method we use is based on canonical Van Vleck perturbation theory.²⁹⁻³¹ This theory is playing an increasing role in the treatment of electronic degrees of freedom.³²⁻³⁶ For an excellent discussion see Ref. 33. These ideas have also been applied to the analysis of molecular vibrations.³⁷⁻⁴² *The goal of the perturbation theory is to canonically transform the Hamiltonian to a new representation, where the solutions can be obtained using a significantly smaller basis set than is needed to obtain the solutions in the original representation.* The information content of the Hamiltonian is the same. This approach allows for great flexibility in choosing the form of the transformed Hamiltonian to best suit the particular characteristics of the system being studied. Several possibilities are discussed. Almost degenerate perturbation theory, whose essential feature is the transformation to an effective block diagonal Hamiltonian, is used to develop block diagonal "resonance" Hamiltonians.⁴³ We also discuss transformations which allow us to develop an effective Hamiltonian whose wave functions are SCF-like wave functions.

All these transformations are carried out in a superoperator framework.^{33,34} Although the algebraic manipulations are very cumbersome, the algebra is carried out very efficiently using FORTRAN codes. The algebraic manipulations are very similar to previous classical and semiclassical perturbative treatments which have applied perturbation theory to very high order using FORTRAN,⁴³ and C.⁴⁴ In earlier work, both Swimm *et al.*^{45(a)} and Reinhardt and co-workers^{45(b)} successfully used the algebraic manipulation routine MACSYMA to carry out related classical transformations. The canonical Van Vleck perturbation theory is suited for computational manipulation even though it leads to more cumbersome expressions than other perturbative approaches.^{33,35,36} This operator approach has the significant advantage of avoiding storage problems associated with matrix based techniques. Combining this powerful theory with modern day computing capabilities has exciting prospects for a systematic inquiry into the nature of highly excited molecular vibrations for polyatomic molecules consisting of more than three atoms.

In this paper we examine three problems. The first two are model problems consisting of two-dimensional coupled oscillators. The first of these consists of cubically coupled harmonic oscillators; the second consists of quadratically coupled Morse oscillators. The study of the Morse system clearly shows that although this work is based on using harmonic oscillators as the zero order Hamiltonian, this in no way precludes the study of significantly anharmonic systems. For large amplitude floppy molecules, these methods are, however, inappropriate and other methods should be employed. The third problem which is considered in more detail is the highly excited CH stretching vibrations of CHD₃. The overtone spectra have been studied both experimentally and theoretically in an effort to better understand the observed CH overtone spectra and, more specifically, the role of the potential coupling between the CH stretch and the degenerate bend. This coupling has been shown to play a key role in the intramolecular dynamics of several systems and it is therefore important to study simple systems in an effort to

better characterize and understand the effects of these couplings. The operator based approach is ideally suited to the study of this problem; we have been able to calculate a nine degree of freedom problem to fourth order.

The outline of the paper is as follows. The general theory is presented in Sec. II. We also discuss the various possible forms the effective Hamiltonian can take. These ideas are tested on two model problems in Sec. III and then applied to overtone excitation of CHD₃ in Sec. IV. We conclude with suggestions for further work in Sec. V.

II. GENERAL THEORY

Perturbative treatments of molecular vibrations have been used extensively to understand and analyze molecular spectra. In this section we review the basic elements of the Lie algebraic approach as we have applied it to the study of molecular vibrations. We take as our starting point the pure ($J = 0$) vibrational Hamiltonian

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots, \quad (2.1)$$

where λ is the perturbation parameter. The zero order part of the Hamiltonian describes N harmonic oscillators:

$$H^{(0)} = \frac{1}{2} \sum_{i=1}^N P_i^2 + \omega_i^2 x_i^2. \quad (2.2)$$

In a departure from standard approaches [cf. Nielson³⁷], these oscillators need not all correspond to normal modes, but instead some may describe bond modes of the system. This may be an advantage when describing local mode-type molecules. In the work of Nielson,³⁷ $H^{(1)}$ contains cubic terms, $H^{(2)}$ contains quartic terms, and so forth. We follow this prescription with the key exception that when some of the oscillators in $H^{(0)}$ describe bond modes, $H^{(1)}$ will contain both quadratic and cubic terms. Other choices of the perturbation parameter may be preferable in certain instances. The present treatment does not preclude other choices.

In order to implement the canonical Van Vleck transformations, the Hamiltonian H is reexpressed in terms of the harmonic oscillator raising and lowering operators to give

$$H(\mathbf{a}^\dagger, \mathbf{a}) = \sum_{i=1}^N \hbar \omega_i \left(a_i^\dagger a_i + \frac{1}{2} \right) + V(\mathbf{a}^\dagger, \mathbf{a}). \quad (2.3)$$

Our goal is to transform H to a new representation, K , in which the coupling terms only couple nearly degenerate states. The off-resonant anharmonic terms of the original Hamiltonian, which can lead to considerable energy shifts, are diagonal in the new representation. The key advantage of this representation is that a much smaller basis set is needed to solve for the eigenvalues and eigenvectors of K , and hence H , than if one were to use the original basis of $H^{(0)}$. Van Vleck perturbation theory if used to effect these transformations. This is accomplished using ideas related to the superoperator formalism of Primas.

A. Generating the effective Hamiltonian K

Primas³⁴ developed a canonical form of Van Vleck perturbation theory in an operator form which takes advantage of the fact that such a theory can be completely formulated in the domain of a Lie algebra. We now review the elements

of that method which we have applied to our study of molecular vibrations. A related approach is that of Ali⁴⁶ who has developed a quantum analog of the classical Birkhoff-Gustavson normal form.

The essential goal of Van Vleck perturbation theory is to transform the Hamiltonian H , to an effective Hamiltonian K , via a series of unitary transformations:

$$\exp\{i\lambda^n[S^{(n)}, \cdot]\} \cdots \exp\{i\lambda^2[S^{(2)}, \cdot]\} \times \exp\{i\lambda[S^{(1)}, \cdot]\}H = K, \quad (2.4)$$

where $S^{(i)}$ is Hermitian. Rather than calculate the transformed Hamiltonian K order by order using the expressions derived by Shavitt and Redmon,³³ we have found that it is computationally easier to implement the transformations

$$\exp\{i\lambda[S^{(1)}, \cdot]\}H = K_1, \quad (2.5a)$$

$$\exp\{i\lambda^2[S^{(2)}, \cdot]\}K_1 = K_2, \quad (2.5b)$$

⋮

$$\exp\{i\lambda^n[S^{(n)}, \cdot]\}K_{n-1} = K_n \equiv K. \quad (2.5c)$$

Here one first calculates K_1 , then K_2 , and so forth. K_1 is determined by expanding the exponential in Eq. (2.5a) using the well known Campbell-Hausdorff formula

$$\exp\{i\lambda[S^{(1)}, \cdot]\}H = H + i\lambda[S^{(1)}, H] - \frac{\lambda^2}{2!}[S^{(1)}, [S^{(1)}, H]] + \cdots, \quad (2.6)$$

then expanding H and K_1 in powers of λ and equating powers of λ to obtain

$$K_1^{(0)} = H^{(0)}, \quad (2.7)$$

$$K_1^{(1)} = H^{(1)} + i[S^{(1)}, H^{(0)}],$$

$$K_1^{(2)} = H^{(2)} + i[S^{(1)}, H^{(1)}] - \frac{1}{2}[S^{(1)}, [S^{(1)}, H^{(0)}]],$$

and so forth. In order to solve for K_1 , one must first determine $S^{(1)}$, the solution of which depends on the choice of $K_1^{(1)}$. For the general case of $H^{(1)}$ expressed in the normal form

$$H^{(1)} = \sum_{\mathbf{m}} \sum_{\mathbf{n}} c_{\mathbf{m}, \mathbf{n}} \prod_{j=1}^N (a_j^\dagger)^{m_j} (a_j)^{n_j}, \quad (2.8a)$$

a choice of

$$S^{(1)} = \sum_{\mathbf{m}}' \sum_{\mathbf{n}}' \frac{c_{\mathbf{m}, \mathbf{n}}}{i} \frac{\prod_{j=1}^N (a_j^\dagger)^{m_j} (a_j)^{n_j}}{\sum_{j=1}^N (m_j - n_j) \hbar \omega_j} \quad (2.8b)$$

leads to

$$K_1^{(1)} = \sum_{\mathbf{m}}' \sum_{\mathbf{n}}' c_{\mathbf{m}, \mathbf{n}} \prod_{j=1}^N (a_j^\dagger)^{m_j} (a_j)^{n_j}. \quad (2.8c)$$

Here N is the number of degrees of freedom. The primes and

double primes refer to restricted summations, $\Sigma_{\mathbf{m}} = \Sigma_{\mathbf{m}}' + \Sigma_{\mathbf{m}}''$. Equivalently, the terms $K_1^{(1)}$ will include a subset of the terms in $H^{(1)}$. Of key importance is the choice of terms to include in $S^{(1)}$. This choice is very flexible, however, a usual choice is that if there are no near degeneracies in $H^{(0)}$, then $S^{(1)}$ includes all the terms in $H^{(1)}$, and $K_1^{(1)}$ is zero. If there are degenerate or nearly degenerate sets of states, $K_1^{(1)}$ will include the coupling between these states. We will return to the choice of terms to include in $S^{(1)}$ after completing the discussion of the higher order transformations.

Given a choice for $S^{(1)}$, $K_1^{(i)}$ is directly determined from Eq. (2.7) to the n th order in perturbation theory. The Hamiltonian, however, only has the desired form through $K_1^{(1)}$.

The transformation process is continued by solving for K_2 using Eq. (2.5b). As before, this is accomplished by expanding K_1 and K_2 in powers of λ to obtain

$$\begin{aligned} K_2^{(0)} &= K_1^{(0)}, \\ K_2^{(1)} &= K_1^{(1)}, \\ K_2^{(2)} &= K_1^{(2)} + i[S^{(2)}, K_1^{(0)}], \\ K_2^{(3)} &= K_1^{(3)} + i[S^{(2)}, K_1^{(1)}], \end{aligned} \quad (2.9)$$

and so forth. The choice of terms to include in $S^{(2)}$ follows the same considerations as those for $S^{(1)}$, with the key exception that $K_2^{(2)}$ contains diagonal terms, i.e., terms of the form $c_{\mathbf{m}, \mathbf{m}} \prod_{j=1}^N (a_j^\dagger)^{m_j} (a_j)^{m_j}$ as well as terms that couple degenerate states. The corresponding terms cannot be included in $S^{(2)}$ and must be included in $K_2^{(2)}$. For example, if the oscillators of Eq. (2.1) correspond to the normal modes and there are no degeneracies or near degeneracies, then $K_2^{(2)}$ is zero and $K_2^{(2)}$ takes the standard form

$$K_2^{(2)} = \sum_i \sum_j \chi_{i,j} \left(\hat{N}_i + \frac{1}{2} \right) \left(\hat{N}_j + \frac{1}{2} \right), \quad (2.10)$$

where $\hat{N}_i = a_i^\dagger a_i$ is the number operator, and $\hat{N}|\mathbf{n}\rangle = \mathbf{N}|\mathbf{n}\rangle$.

The higher order transformations, required to determine K_i , are carried out in the same manner as the above transformations where K_i has the desired form through $K_i^{(i)}$. The final form of K is determined order by order.

A crucial feature of the computational procedure is that all the operators are expressed in a single form; we have chosen the normal form. This leads to easy evaluation of the commutators $[S^{(i)}, H^{(j)}]$, $[S^{(i)}, [S^{(i)}, H^{(j)}]]$, and so forth. Given that $H^{(j)}$ and $S^{(i)}$ are written in the normal form of Eq. (2.8), the algebraic manipulations leading to the transformed Hamiltonian have the form $(a^\dagger)^k (a)^l (a^\dagger)^m (a)^n$. We have omitted the subscripts here as a convenience, as terms with different subscripts commute. Evaluation of the commutator is equivalent to reexpressing these terms in the normal form. This is readily accomplished using

$$\begin{aligned} (a^\dagger)^k (a)^l (a^\dagger)^m (a)^n &= (a^\dagger)^{k+m} (a)^{l+n} + (l)(m)(a^\dagger)^{k+m-1} (a)^{l+n-1} + \frac{(l)(l-1)(m)(m-1)}{2!} (a^\dagger)^{k+m-2} (a)^{l+n-2} + \cdots \\ &+ \frac{(l)(l-1) \cdots (l-r+1)(m)(m-1) \cdots (m-r+1)}{r!} (a^\dagger)^{k+m-r} (a)^{l+n-r}, \end{aligned} \quad (2.11)$$

where r is the lesser of l and m . A central advantage of the operator approach relative to a matrix based approach is the smaller amount of space required to store the transformed Hamiltonian. Two arrays are used for this purpose. One array contains the coefficients $c_{m,n}$; another array contains the corresponding m_i and n_i information of Eq. (2.8). A more complete description of the program is given elsewhere.⁴⁷

The algebraic manipulations are simplified by dividing $S^{(i)}$ into two contributions:

$$S^{(i)} = S_a^{(i)} + S_b^{(i)},$$

where $S_b^{(i)}$ is the Hermitian conjugate of $S_a^{(i)}$. Note, $S^{(i)}$ contains no term which is the Hermitian conjugate of itself. Evaluation of the commutator $[S^{(i)}, H]$, where H is Hermitian, is now reduced twofold to calculating $[S_a^{(i)}, H]$ since

$$\begin{aligned} [S^{(i)}, H] &= [S_a^{(i)}, H] + [S_b^{(i)}, H] \\ &= [S_a^{(i)}, H] - [S_a^{(i)}, H]^\dagger. \end{aligned} \quad (2.12)$$

Once the commutator $[S_a^{(i)}, H]$ is determined and expressed as a sum of operators in normal form using Eq. (2.11), the quantity $[S_a^{(i)}, H]^\dagger$ is trivially obtained from $[S_a^{(i)}, H]$, since the complex conjugate of $(a^\dagger)^l (a)^m$ is just $(a^\dagger)^m (a)^l$.

Before proceeding to a discussion of some of the possible forms the effective Hamiltonian can take depending on the choices of $S^{(i)}$, we pause to note the extremely close similarity between the implementation of the quantal transformations and the implementation of the classical Dragt-Finn transformations^{48,49} which are based on Lie transformations,⁴⁹ and which we have recently successfully applied to generate effective classical resonance Hamiltonians.⁴³ The Dragt-Finn transformations are obtained by replacing the commutators in Eq. (2.4) with the corresponding Poisson bracket. These ideas have been extended by Fried and Ezra⁴⁴ to consider the semiclassical procedure of converting the transformed classical Hamiltonian K into a quantum mechanical operator, thereby obtaining semiclassical eigenvalues.

B. The form of the effective Hamiltonian

The choice of $S^{(i)}$ allows considerable flexibility in constructing the effective Hamiltonian. To elucidate this idea we consider several examples. We begin with a simple well known one-dimensional problem.

1. Morse oscillator basis

Previous work on local mode molecules has clearly revealed the utility of Morse oscillator basis sets. Such a basis can be perturbatively constructed using the present scheme. This is done as follows.

The Morse oscillator Hamiltonian

$$H = \frac{1}{2m} P^2 + D(1 - e^{-\alpha x})^2, \quad (2.13)$$

in which D is the dissociation energy and α the scaling parameter is written as

$$H = H^{(0)} + H^{(1)} + H^{(2)} + \dots, \quad (2.14)$$

where

$$\begin{aligned} H^{(0)} &= \frac{1}{2m} P^2 + \alpha^2 D x^2, \\ H^{(1)} &= -\alpha^3 D x^3, \\ H^{(2)} &= \frac{1}{2} \alpha^4 D x^4, \end{aligned} \quad (2.15)$$

and so forth. Application of these methods yields an effective Hamiltonian:

$$K = \hbar\omega \left(\hat{N} + \frac{1}{2} \right) - \frac{\hbar^2 \omega^2}{4D} \left(\hat{N} + \frac{1}{2} \right)^2 \quad (2.16)$$

whose solution, as is well known, is identical to the exact result. All the higher order corrections to the energy are zero. It is worth noting that the various matrix elements of the perturbative treatment of the Morse problem are also easily obtained and approximate the Morse matrix elements extremely well for $E \leq D/2$. This feature is essential to the application of these methods to the study of highly excited CH and OH overtones. For example, using the natural perturbation parameter $\beta = (\hbar\omega/4D)^{1/2}$, where the maximum number of bound levels is approximately given by $1/2\beta^2$, we find that the momentum $i(a^\dagger - a)/\sqrt{2}$ in dimensionless coordinates transforms in the Morse representation to

$$\begin{aligned} &\frac{i}{\sqrt{2}} \left[a^\dagger - \beta a^\dagger a^\dagger + \beta^2 \left(a^\dagger a^\dagger a^\dagger - \frac{3}{2} a^\dagger a a^\dagger \right) \right. \\ &\quad \left. - \beta^3 \left(a^\dagger a^\dagger a^\dagger a^\dagger - a^\dagger a^\dagger a^\dagger a - \frac{3}{2} a^\dagger a^\dagger \right) \right] \\ &\quad \dots + \text{complex conjugate}, \end{aligned} \quad (2.17)$$

where a^\dagger and a are the "raising and lowering operators" for the Morse oscillator. This provides an alternative description from that of Kellman.⁵⁰ These ideas will be further illustrated in Secs. III and IV where we consider two coupled Morse oscillator problems.

2. Self-consistent basis

Recent work on molecular vibrations has demonstrated the advantages of working with a self-consistent basis.¹¹⁻¹⁴ The transformations to obtain an effective Hamiltonian matrix, which is constructed in a basis which includes the average effects of the other degrees of freedom on a given zero order mode of the system, are provided by including only those terms in

$$S^{(i)} \doteq \sum_j S_j^{(i)}$$

for which $m_i = n_i$ for all i except one. Explicitly these terms have the form

$$S_j^{(i)} \propto \frac{(a_j^\dagger)^{m_j} (a_j)^{n_j} \prod_{i \neq j}^N (a_i^\dagger)^{m_i} (a_i)^{n_i}}{(m_j - n_j) \hbar \omega_j}. \quad (2.18)$$

As a consequence, the final transformed Hamiltonian does *not* contain the terms corresponding to Eq. (2.18). It has the form

$$K = K^0(\hat{N}) + V(\mathbf{a}^\dagger, \mathbf{a}), \quad (2.19)$$

where $V(\mathbf{a}^\dagger, \mathbf{a})$ has the same form as Eq. (2.8a), but where $m_j \neq n_j$ for at least *two* of the degrees of freedom for every

term in the summation. The eigenfunctions $|n\rangle$, where

$$K^0(\hat{N})|n\rangle = K^0(N)|n\rangle \quad (2.20)$$

have the same properties as the self-consistent wave functions for the effective Hamiltonian K . The reason for this is apparent if we note that

$$\langle n'|V(a^\dagger, a)|n\rangle = 0, \quad (2.21)$$

where $|n\rangle = |n_i\rangle|n'\rangle$ and $|n_i\rangle$ corresponds to a single arbitrary degree of freedom. The similarity between the present representation and the SCF basis lies in the neglect of precisely the same interactions. In this representation the effects of the $V(a^\dagger, a)$ are included as configuration interaction.

3. Almost degenerate perturbation theory

It was mentioned above that $S^{(i)}$ can also be constructed to lead to a block diagonal Hamiltonian matrix. As we shall see in Sec. IV, where the CH overtone spectra of CHD_3 is analyzed, the Hamiltonian can be divided into the high frequency modes which include the CH and CD stretches and the low frequency modes which include the remaining degrees of freedom. Furthermore, the high frequency modes have about twice the frequency of the low frequency modes. To take advantage of this fact, $S^{(i)}$ in Eq. (2.8) is constructed so that it includes all the terms of $H^{(i)}$ except those which satisfy

$$\sum_i' (m_i - n_i) = 2 \sum_j'' (n_j - m_j), \quad (2.22)$$

where the first summation is over the high frequency modes and the second is over the low frequency modes.

The above transformations have been applied so that the effective Hamiltonian can be diagonalized in a relatively small basis set with respect to the initial form of the Hamiltonian. The eigenvalues of both Hamiltonians are the same. The wave functions of the two Hamiltonians can be related by means of the transformations of Eq. (2.4).

Before considering several examples to further clarify these concepts, we note that many vibrational systems will not have Hamiltonians which are amenable to transformation to a block diagonal representation. In this instance a compromise can be made between the "SCF" representation and the block diagonal representation. For example, one might choose to only include the terms in $S^{(i)}$ whose coefficients are smaller than some specified number. There is usually a tradeoff between the ease of solution of the effective Hamiltonian vs the convergence of the perturbation expansion, between which one must choose.

III. APPLICATION OF VAN VLECK PERTURBATION THEORY

To illustrate the ideas of the preceding section we will consider two model Hamiltonian systems. Both systems have two degrees of freedom. The first system consists of anharmonically coupled harmonic oscillators, the second consists of quadratically coupled Morse oscillators. Having done this, we will then proceed to an examination of the highly excited vibrational dynamics of CHD_3 using the methods of the previous section.

A. Anharmonically coupled harmonic oscillators

We begin by considering the coupled harmonic oscillators the Hamiltonian of which is

$$H = \frac{1}{2}[P_1^2 + P_2^2 + (1.818\ 181\ 8)q_1^2 + q_2^2] + 0.1q_1q_2^2. \quad (3.1)$$

This system, which has a significant 2:1 resonance interaction, has been studied by Heller *et al.*⁵¹ in an effort to more clearly understand the signatures of Fermi resonance interactions such as "preresonance attraction" and "postresonance broadening" in terms of their classical analogs. Our goal here is simply to show that this Hamiltonian can be perturbatively transformed to an approximate effective one-dimensional Hamiltonian using the methods discussed in the previous section. More specifically, we will construct an effective block diagonal Hamiltonian where the blocks correspond to different values of $N_i = 2N_1 + N_2$. As in the previous section, \hat{N}_i are the number operators for the effective Hamiltonian. The final Hamiltonian has the form

$$K = K^0 + V, \quad (3.2)$$

where

$$K^0 = \sum_{l_1, l_2} C_l (a_1^\dagger)^{l_1} (a_1)^{l_1} (a_2^\dagger)^{l_2} (a_2)^{l_2} \quad (3.3)$$

and

$$V = \sum_{l_1, l_2, m_1, m_2} C_{l, m} (a_1^\dagger)^{l_1} (a_1)^{m_1} (a_2^\dagger)^{l_2} (a_2)^{m_2}. \quad (3.4)$$

The summation in Eq. (3.4) has the constraint that $2(l_1 - m_1) + (l_2 - m_2) = 0$, i.e., N_i is a constant of the motion for the effective Hamiltonian. Selected eigenvalues obtained from this Hamiltonian are compared to those obtained from a fully converged variational calculation in Table I. The agreement is quite good even for energies corresponding to $N_i = 16$.

These methods can also be used to obtain wave functions. In Figs. 1 and 2, we compare spectra obtained from a Franck-Condon transition (also studied by Heller *et al.*)⁵¹

TABLE I. Selected eigenvalues E and Franck-Condon factors f_i for Eqs. (3.1) and (3.10).

N_i	E^a	E^b	f_i^a	f_i^b
8	8.6341	8.6341	0.114	0.114
	8.7419	8.7419	5.77×10^{-2}	5.78×10^{-2}
	8.9340	8.9337		
	9.1784	9.1780		
	9.4649	9.4650		
16	15.664	15.664		
	15.840	15.839	2.50×10^{-3}	2.45×10^{-3}
	15.951	15.950	6.77×10^{-3}	6.78×10^{-3}
	16.118	16.116	1.87×10^{-3}	1.90×10^{-3}
	16.347	16.344		
	16.618	16.615		
	16.926	16.923		
	17.267	17.266		
	17.640	17.640		

^a Fourth order perturbative results from diagonalization of K .

^b Converged variational calculation.

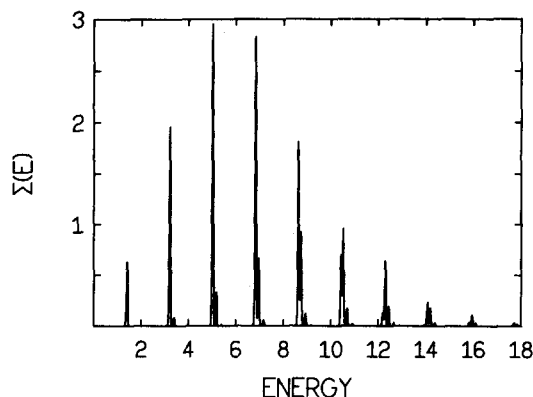


FIG. 1. A comparison of Franck-Condon spectra resulting from exciting to an upper electronic surface with $V(q_1, q_2) = \frac{1}{2}(1.818\ 181)^2 q_1^2 + \frac{1}{2} q_2^2$ from the $v = 0$ ground electronic surface whose potential is given by the harmonic part of $V(q_1, q_2)$. The upper surface is displaced by $q_0 = 2.52$ relative to the lower. The full quantum mechanical results (—) are indistinguishable from the perturbative results (---) discussed in the text. The widths of the spectral lines are due to an arbitrary broadening with a Gaussian envelope.

from an harmonic ground electronic surface (with the same harmonic frequencies as the upper surface) to an upper surface given by Eq. (3.1). The upper surface is displaced $q_0 = -2.52$ in the q_1 coordinate relative to the lower surface. The agreement between the spectra obtained using the effective Hamiltonian and the full quantum mechanical calculation is excellent.

The spectra were obtained as follows. The displaced $v = 0$ Gaussian wave function can be written as a linear combination of the upper surface normal mode wave functions as

$$|\phi\rangle = e^{-q_0^2/4} \sum_{j=0}^{\infty} \frac{q_0^j}{(2^j j!)^{1/2}} |j, 0\rangle. \quad (3.5)$$

The Gaussian wave function is then reexpressed in the block diagonal representation, to second order, using

$$|\Psi\rangle = \exp[i\lambda^2 S^{(2)}] \exp[i\lambda S^{(1)}] |\phi\rangle \\ = [1 + i\lambda S^{(1)} + \lambda^2 (iS^{(2)} - \frac{1}{2} S^{(1)} S^{(1)})] |\phi\rangle. \quad (3.6)$$

Since the $S^{(i)}$ are expressed as raising and lowering opera-

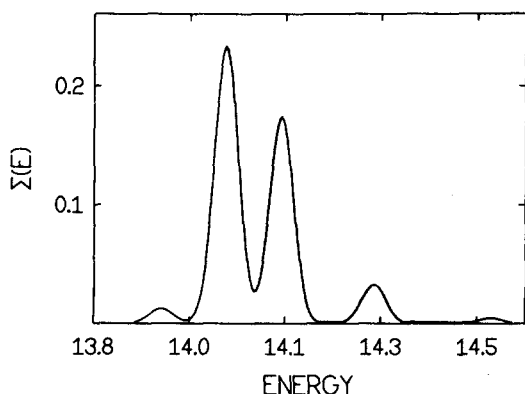


FIG. 2. A comparison of Franck-Condon spectra (cf. Fig. 1) at higher resolution. The full quantum mechanical results (—) are indistinguishable from the perturbative results (---).

tors, substitution of Eq. (3.5) into Eq. (3.6) leads directly to

$$|\psi\rangle = \sum_{n_1} \sum_{n_2} |n_1, n_2\rangle \langle n_1, n_2 | \psi \rangle. \quad (3.7)$$

The wave functions $|n_1, n_2\rangle$, which satisfy $K^0 |n_1, n_2\rangle = E^0 |n_1, n_2\rangle$, form a block diagonal representation. Each block can be diagonalized separately to obtain

$$K |\chi_{N_i}\rangle = E_n |\chi_{N_i}\rangle \quad (3.8)$$

and

$$|\chi_{N_i}\rangle = \sum_{n_1=0}^{N_i} \sum_{n_2=N_i-2n_1}^0 |n_1, n_2\rangle \langle n_1, n_2 | \chi_{N_i} \rangle. \quad (3.9)$$

In summary the initial Gaussian is: (1) written as a superposition of the upper surface normal mode basis functions using Eq. (3.5); (2) these normal mode functions are reexpressed, via Eq. (3.6), as a linear combination of the effective Hamiltonian basis functions $|n_1, n_2\rangle$; (3) these are written as a linear combination of the eigenfunctions $|\chi_{N_i}\rangle$, where the coefficients $\langle n_1, n_2 | \chi_{N_i} \rangle$ are obtained from diagonalizing each block of K . Combining Eqs. (3.7) and (3.9) gives the Franck-Condon factors f_n . The resulting spectrum $\Sigma(E)$, using the notation of Heller *et al.*, is

$$\Sigma(E) = \sum_n f_n \frac{T}{\sqrt{2\pi}} \exp[-(T^2/2)(E - E_n)^2]. \quad (3.10)$$

Here the lines have been artificially broadened with a Gaussian line shape. In Fig. 1 both the full quantum mechanical results and the above discussed perturbative results are displayed. The results are indistinguishable. In Fig. 2 higher resolution results are shown for the set of states with $N_T = 14$; again, the agreement is excellent.

B. Harmonically coupled Morse oscillators

We now turn to an examination of a two-dimensional Hamiltonian describing a system consisting of two kinetically coupled Morse oscillators

$$H(\mathbf{x}, \mathbf{P}) = \sum_i \left[\frac{1}{2} G_{ii} P_i^2 + U(x_i) \right] + G_{12}(\theta) P_1 P_2. \quad (3.11)$$

This Hamiltonian, which has received considerable past attention, is used here as a model for the OH stretching dynamics of water.

This Hamiltonian is expressed in terms of bond-angle coordinates. These are the OH bond extensions x_i , with corresponding momenta P_i , and the bending angle θ . Here θ is taken to be its equilibrium value θ_e (Table II); the bending motion is thus ignored. The potential energy is separable in the bond coordinates (nonbonded-atom interaction is ignored); each OH bond is described by an identical anharmonic Morse potential in which D is the OH bond dissociation energy and a the Morse parameter (Table II). The kinetic energy is expressed in terms of Wilson's G -matrix elements.⁵² In particular, the effective inverse masses for the bonds are

$$G_{11} = G_{22} = (M_H + M_O)/M_H M_O, \quad (3.12)$$

and the magnitude of the dynamic, or kinetic, coupling

TABLE II. Properties of the H₂O model.

$a(\text{cm}^{-1})$	$D(\text{erg})$	$\theta(\text{deg})$	$\Omega(\text{s}^{-1})$
2.175×10^8	8.84×10^{-12}	104.5	7.2916×10^{14}

between the bonds is

$$G_{12} = (\cos \theta_e)/M_O < 0. \quad (3.13)$$

This problem will be examined from both local and normal mode perspectives. First the local mode perspective is considered. Following the procedure in Sec. II B, a block diagonal Hamiltonian is derived which has $N_t = N_1 + N_2$ as a constant of the motion. An important exception is that the quadratic coupling term is included with the cubic terms in $H^{(1)}$.

In order to examine the convergence of the matrix ele-

TABLE III. Comparison of exact eigenvalues E_q with eigenvalues $E^{(n)}$ obtained from diagonalization of the n th order block diagonal Hamiltonian, in cm^{-1} .

$n_1 n_2^{\pm a}$	$E_L^{(2)} - E_q^b$	$E_L^{(4)} - E_q^b$	$E_N^{(2)} - E_q^c$	$E_N^{(4)} - E_q^c$	E_q
0,5 ⁺	-2.33	-0.03	0.35	-0.09	16 825.18
0,5 ⁻	-2.35	-0.04	-0.35	-0.09	16 825.21
1,4 ⁺	-4.62	-0.12	0.11	-0.01	17 488.79
1,4 ⁻	-4.24	-0.05	0.15	-0.10	17 497.60
2,3 ⁺	-9.25	0.52	0.87	0.12	17 786.63
2,3 ⁻	-22.77	-0.60	-0.43	0.01	17 917.76

^a Due to symmetry, the eigenvalues take the form $1/\sqrt{2} [|n_1, n_2\rangle \pm |n_2, n_1\rangle] \equiv n_1, n_2^{\pm}$.

^b Difference between local mode results and exact.

^c Difference between normal local mode results and exact.

ments, the $N_t = 5$ block of the Hamiltonian matrix is shown for second, third, and fourth order perturbation theory:

second:

	$ 5,0\rangle$	$ 4,1\rangle$	$ 3,2\rangle$	$ 2,3\rangle$	$ 1,4\rangle$	$ 0,5\rangle$
$ 5,0\rangle$	16 828.98					
$ 4,1\rangle$	-64.23	17 502.43				
$ 3,2\rangle$		-81.25	17 839.16			
$ 2,3\rangle$			-86.17	17 839.16		
$ 1,4\rangle$				-81.25	17 502.43	
$ 0,5\rangle$					-64.23	16 828.98

third:

	$ 5,0\rangle$	$ 4,1\rangle$	$ 3,2\rangle$	$ 2,3\rangle$	$ 1,4\rangle$	$ 0,5\rangle$
$ 5,0\rangle$	16 828.98					
$ 4,1\rangle$	-51.66	17 502.43				
$ 3,2\rangle$	-3.95	-65.35	17 839.16			
$ 2,3\rangle$		-5.30	-69.31	17 839.16		
$ 1,4\rangle$			-5.30	-65.35	17 502.43	
$ 0,5\rangle$				-3.95	-51.66	16 828.98

fourth:

	$ 5,0\rangle$	$ 4,1\rangle$	$ 3,2\rangle$	$ 2,3\rangle$	$ 1,4\rangle$	$ 0,5\rangle$
$ 5,0\rangle$	16 829.18					
$ 4,1\rangle$	-51.70	17 502.39				
$ 3,2\rangle$	-3.85	-65.40	17 839.00			
$ 2,3\rangle$		-3.95	-69.37	17 839.00		
$ 1,4\rangle$			-5.16	-65.40	17 502.39	
$ 0,5\rangle$				-3.85	-51.70	16 829.18

In light of the discussion on Morse oscillators in the preceding section and the fact that no other low order resonances are present at these energies, the convergence of these results is not surprising. The eigenvalues E_L obtained from the above matrices are shown in Table III. Also shown there are the results of a calculation where the Hamiltonian [Eq. (3.11)] is expressed in the normal coordinates $s = (x_1 + x_2)/\sqrt{2}$ and $a = (x_1 - x_2)/\sqrt{2}$ and then treated perturbatively as before. Comparison of these perspectives have been made previously through second order in pertur-

bation theory.⁵³⁻⁵⁵ It is important to note that, in the absence of the kinetic coupling, *both* perspectives give the exact answer for the eigenvalues. They provide equally good zero order pictures. In the presence of coupling, the eigenvalues E_N obtained in the normal mode perspective generally converge faster. This is a result of our treating the quadratic coupling term as a first order correction in the local mode perspective.

Having seen the utility of these perturbative methods in studying simple model problems, we now examine a more

realistic system, the highly excited CH stretching dynamics in CHD_3 .

IV. THE CH OVERTONE DYNAMICS OF CHD_3

The CH overtone excitation of CHX_3 ($X = \text{H, D, F, Cl,}$ and CF_3) species has been the subject of intense experimental and theoretical scrutiny.⁵⁶⁻⁶² These systems have many degrees of freedom, yet they are simple enough to begin asking detailed questions as to both the nature of highly excited dynamics and the accuracy of the *ab initio* potential energy surfaces. Previous workers have noted that an important feature of the CH overtone spectrum in these systems is a 2:1 Fermi resonance between the CH stretch and the CH bend.⁵⁶⁻⁶² For $X = \text{Cl, F,}$ or CF_3 this interaction is predominant, as the remaining degrees of freedom are sufficiently low in frequency as to eliminate the possibility of low order resonance interactions. For CHD_3 the situation is apparently more complicated, and we believe this molecule deserves further attention. The overtone spectra of CHD_3 provide a challenging test problem for application of methods presented in Sec. II. In this paper, our predominant interest is in applying the theory to a given force field as a means of testing the perturbation theory. Our effort to match our results to experiments is only preliminary.

A. Hamiltonian

Recent work has shown the utility of a curvilinear representation for these systems.⁵⁷⁻⁵⁹ In this representation, which we use, the coordinates r_i are the bond angles and lengths themselves rather than their projections onto an equilibrium configuration. The conjugate momenta are denoted as p_i .

In this representation the ($J = 0$) vibrational Hamiltonian is

$$H = \frac{1}{2} g^{1/4} \sum_{i,j} p_i g^{-1/2} G_{ij}(\mathbf{r}) p_j g^{1/4} + V(\mathbf{r}), \quad (4.1)$$

where $G_{ij}(\mathbf{r})$ are the Wilson G -matrix elements⁵² and $g = \det[G_{ij}]$. To a good approximation this Hamiltonian⁶³ can be simplified to

$$H = \frac{1}{2} \sum_i \sum_j p_i G_{ij}(\mathbf{r}) p_j + V(\mathbf{r}). \quad (4.2)$$

The omitted terms are small⁶⁴; the main contribution being one of a constant energy shift to all the levels.

Following the earlier work of Gray and Robiette,⁶⁵ we use the internal coordinates defined in Table IV. Before transforming Eq. (4.2) to normal coordinates, this Hamiltonian is transformed to the symmetry coordinates S_i and momenta P_i , shown in Table IV, in order to remove redundant coordinate S_r .

The zero order part of this Hamiltonian is

$$H^{(0)} = \frac{1}{2} \sum_i \sum_j [P_i G_{ij}^0 P_j + S_i F_{ij} S_j]. \quad (4.3)$$

Here G_i^0 is the G matrix evaluated at the equilibrium position. This Hamiltonian is transformed to the curvilinear normal coordinates Q_i using $\mathbf{Q} = \mathbf{L}^{-1}\mathbf{S}$. As in the work of Green *et al.*,^{58(b)} the CH stretch degree of freedom is includ-

TABLE IV. Internal symmetry coordinates for CHD_3 .^a

A_1	$S_1 = r$
A_1	$S_2 = \frac{1}{\sqrt{3}} (r_1 + r_2 + r_3)$
A_1	$S_3 = \frac{1}{\sqrt{6}} (r_4 + r_5 + r_6 - r_7 - r_8 - r_9)$
E_a	$S_4 = \frac{1}{\sqrt{6}} (2r_2 - r_2 - r_3)$
E_a	$S_5 = \frac{1}{\sqrt{6}} (2r_4 - r_5 - r_6)$
E_a	$S_6 = \frac{1}{\sqrt{6}} (2r_7 - r_8 - r_9)$
E_b	$S_7 = \frac{1}{\sqrt{2}} (r_2 - r_3)$
E_b	$S_8 = \frac{1}{\sqrt{2}} (r_5 - r_6)$
E_b	$S_9 = \frac{1}{\sqrt{2}} (r_8 - r_9)$
	$S_r = \frac{1}{\sqrt{6}} (r_4 + r_5 + r_6 + r_7 + r_8 + r_9)$

^a r is defined here to be the C-H bond displacement coordinate, r_i ($i = 1-3$) the C-D bond displacement coordinate, r_{i+3} ($i = 1-3$) the D-C-H angles that include the r_i bond, r_{i+6} ($i = 1-3$) the angles opposite r_i .

ed in the normal mode analysis. We will return to this point later. The harmonic frequencies⁶⁵ ω_i of Gray and Robiette are given in Table V.

Our initial work uses the quartic force field of Gray and Robiette.⁶⁵ The kinetic anharmonic terms which arise from the functional dependence of the G -matrix elements on the internal coordinates in Eq. (4.2), were determined as follows. The kinetic energy in normal coordinates is

$$\begin{aligned} T &= \frac{1}{2} \sum_i \sum_j P_i G_{ij}(\mathbf{S}) P_j \\ &= \frac{1}{2} \sum_i \sum_m \dot{Q}_i \left[\sum_j \sum_j (L^{-1})_{ij} (L^{-1})_{mj} G_{ij}(\mathbf{S}) \right] \dot{Q}_m \\ &\equiv \frac{1}{2} \sum_i \sum_m \dot{Q}_i G_{im}(\mathbf{S}) \dot{Q}_m. \end{aligned} \quad (4.4)$$

The kinetic anharmonic terms are determined by Taylor series expanding the G_{im} in the normal coordinates using finite

TABLE V. Comparison of fundamental frequencies ν_i (in cm^{-1}) obtained from rectilinear and curvilinear second order perturbation theory for CHD_3 .

	i	ω_i^a (calc)	ν_i^a	ν_i^b	ν_i^c	ν_i^d
CH stretch	A_1 1	3128.0	2990.1	2990.1	2995.0	2984.7
CD stretch	A_1 2	2185.0	2162.3	2162.3	2162.6	2150.2
CD bend	A_1 3	1042.3	1007.1	1007.1	1006.6	1006.8
CD stretch	E 4	2336.3	2248.2	2248.2	2247.6	2244.1
CH bend	E 5	1335.6	1293.0	1293.0	1292.4	1292.5
CD bend	E 6	1070.0	1037.0	1037.0	1037.1	1037.1

^a Results of Gray and Robiette.

^b Curvilinear representation with CH included in the normal mode analysis.

^c Curvilinear representation with CH not included in the normal mode analysis.

^d Results of modified Gray and Robiette force field discussed in the text.

difference methods. This is readily implemented since the functional dependence of the G_{ij} on the internal coordinates is known, and hence is also numerically known [using Eq. (4.4)] for the normal coordinates using $Q = L^{-1}S$. This enables one to calculate the derivatives of G_{ij} , with respect to the normal coordinates and provides a very efficient method for obtaining terms in the G -matrix expansion up to fifth order.

B. Application of canonical Van Vleck perturbation theory to CHD₃

Following the prescription of Sec. II, the Hamiltonian is rewritten in the raising and lowering operators associated with the normal coordinates. As an initial test of our approximate Hamiltonian [cf. Eq. (4.2)], we transform the Hamiltonian through second order to a diagonal form [cf. Eq. (2.10)]. The resulting energies are compared to those calculated by Gray and Robiette⁶⁵ in a rectilinear representation in Table V. In contrast to the higher energy results of Green *et al.*,^{58(b)} the results for the two representations are similar. Also shown in Table V are the results of a calculation where the CH stretch is uncoupled from the remaining degrees of freedom in the normal mode analysis, and the quadratic coupling terms were included in $H^{(1)}$. Here the CH stretch is treated as a local mode. Again at the present level of analysis the results are quite similar. As in the coupled Morse oscillator case, we find that the normal mode is better converged using second order perturbation theory than the local mode basis.

In order to test the convergence of the perturbation expansion as well as to compare with other methods we focus on a restricted problem where a subset of the vibrational normal modes are included in the calculation. This calculation includes the CH stretch, the doubly degenerate CH bend, and the symmetric CD stretch. The CH stretch degree of freedom is of primary importance, since this mode initially carries the oscillator strength. Previous work has clearly demonstrated that the highly excited CH stretch is strongly coupled to the degenerate CH bend states via a 2:1 resonance.⁵⁶⁻⁵⁹ The interaction with the CD stretch has been already partially included in the normal mode analysis, as discussed by Green *et al.*^{58(b)} However, for high CH excitation this interaction may become more important, as has been noted by Bagotte and Mills⁶⁵ for the CHDCl₂ molecule.

We have modified the force field of Gray and Robiette for this calculation, the major change being to describe the CH(D) internal stretching potential with Morse oscillators (cf. Table VI). This is the only change made to the anharmonic terms. The harmonic terms, which have not been changed significantly, are indicated in Table VI. The fundamental frequencies for this force field determined by second

TABLE VI. A quartic force field of methane.

F_{ij} matrix elements	Gray <i>et al.</i>	This work
$F_{11}/\text{aJ } \text{\AA}^{-2}$	5.435	5.374 25
F_{22}/aJ	0.5845	0.578 7
$F_{33}/\text{aJ } \text{\AA}^{-2}$	5.378	5.398 25
$F_{34}/\text{aJ } \text{\AA}^{-1}$	-0.221	-0.221
F_{44}/aJ	0.5480	0.544 2
$f_{rrr}/\text{aJ } \text{\AA}^{-3}$	31.466	29.304 ^b
$f_{rrrr}/\text{aJ } \text{\AA}^{-4}$	173	123.862

^aThe notation is that which was used by Gray and Robiette (Ref. 65).

^bThe CH(D) oscillators are modeled with a Morse potential whose parameters are $a = 1.8115 \times 10^8 \text{ cm}$ and $D = 8.2162 \text{ D}^{-12} \text{ ergs}$. For the CH oscillators this gives an energy level expression in cm^{-1} of $E = 3137.44 (n + \frac{1}{2}) - 59.498 (n + \frac{1}{2})^2$.

order perturbation theory are given in Table V, and are in close agreement with the force field of Gray and Robiette. The fitting procedure used is approximate. The present goal is to test the perturbation theory on a given force field. For the higher energy results, the G -matrix elements have been expanded through second order. Only the functional dependence of the G -matrix element on the CH stretch coordinate Q_1 has been included to higher order; it has been included up to fifth order.

In all of the calculations the Cartesian representation of the doubly degenerate degrees of freedom has been employed rather than the polar (r, θ) representation.⁶⁷ Although this latter representation has a basis in which the Hamiltonian matrix is block diagonal, due the C_{3v} symmetry, the simple commutation relations of Sec. II cannot be employed. Consequently, we use the Cartesian representation to provide an effective Hamiltonian, and then take the appropriate linear combinations of the degenerate Cartesian basis functions of the effective Hamiltonian to make full use of the C_{3v} symmetry. Although this is computationally much easier, recent work by Uzer *et al.*⁶⁸ has shown that carrying out the perturbation theory in the polar representation may provide for better convergence.

The two transformations discussed in Sec. II have been performed. First we transform to a "self-consistent" representation and compare this to a calculation where, variationally obtained, prediagonal basis functions are used. We focus here for the sake of comparison, on the coupling between a select group of states $|n_1', n_2, n_1\rangle$ these being the $|0^0, 1, 4\rangle$, $|4^0, 0, 3\rangle$, $|2^0, 0, 4\rangle$, and $|0^0, 0, 5\rangle$ states. See Table V for notation. The Hamiltonian matrices have been calculated for several different orders of perturbation theory in order to examine the convergence properties of the matrix elements. The lower triangle of the Hamiltonian matrix to second order is

	$ 0^0, 1, 4\rangle$	$ 4^0, 0, 3\rangle$	$ 2^0, 0, 4\rangle$	$ 0^0, 0, 5\rangle$
$ 0^0, 1, 4\rangle$	13 383.31			
$ 4^0, 0, 3\rangle$	0	13 564.21		
$ 2^0, 0, 4\rangle$	12.20	202.37	13 677.77	
$ 0^0, 0, 5\rangle$	-70.37	0	113.13	13 727.34

to fourth order

	$ 0^0,1,4\rangle$	$ 4^0,0,3\rangle$	$ 2^0,0,4\rangle$	$ 0^0,0,5\rangle$
$ 0^0,1,4\rangle$	13 381.75			
$ 4^0,0,3\rangle$	0	13 564.95		
$ 2^0,0,4\rangle$	8.75	162.25	13 658.42	
$ 0^0,0,5\rangle$	-33.12	-.31	85.91	13 711.17

and to the sixth order is

	$ 0^0,1,4\rangle$	$ 4^0,0,3\rangle$	$ 2^0,0,4\rangle$	$ 0^0,0,5\rangle$
$ 0^0,1,4\rangle$	13 386.70			
$ 4^0,0,3\rangle$	0	13 545.11		
$ 2^0,0,4\rangle$	8.39	161.72	13 656.19	
$ 0^0,0,5\rangle$	-20.52	-.25	85.34	13 710.56

With the exception of the coupling between the $|0^0,0,5\rangle$ and $|0^0,1,4\rangle$ states, there is little difference between the fourth and sixth order calculation, and we assume that the sixth order operator Hamiltonian has successfully provided an excellent approximation to the "SCF" matrix Hamiltonian; *the second order calculation significantly overestimates the off-diagonal matrix elements.* We note that the CD stretch is only weakly coupled to the other degrees of freedom in this

normal mode perspective. In a local mode basis the coupling is more substantial.

These results are compared to a prediagonalized Hamiltonian matrix whose basis functions were obtained as follows: the CH and CD stretch states were prediagonalized individually and the CH degenerate bend states were prediagonalized together. Select elements of this matrix are given below:

	$ 0^0,1,4\rangle$	$ 4^0,0,3\rangle$	$ 2^0,0,4\rangle$	$ 0^0,0,5\rangle$
$ 0^0,1,4\rangle$	13 387.59			
$ 4^0,0,3\rangle$	0	13 542.87		
$ 2^0,0,4\rangle$	-8.01	161.99	13 650.19	
$ 0^0,0,5\rangle$	16.67	-.23	87.77	13 706.31

The agreement is surprisingly good. Clearly, for this problem, the prediagonalized wave functions and self-consistent wave functions are very similar.

We have also applied almost degenerate perturbation theory to form a block diagonal Hamiltonian where $N_i = n_5 + 2n_2 + 2n_1$. Eigenvalues and eigenvectors are compared for various levels of perturbation theory in Table VII for the block $N_i = 10$. Again the fourth and sixth order results are in close agreement. Also shown there are the results for the full nine-dimensional calculation. Here $N_i = 2(n_1 + n_2 + n_4) + n_3 + n_5 + n_6$.

The eigenvalues and eigenvectors for the full nine-dimensional problem have been obtained in the same fashion as those for the four-dimensional problem. As these additional degrees of freedom are expected to be less important, the degenerate CD stretches have only been expanded

through fourth order. The differences between the restricted and full problem are small; the main difference is the downward shift in energy of all the levels. Comparing fourth order calculations we see that the states which have substantial $5\nu_1$ character are split by 135 cm^{-1} in the four-dimensional calculation and 121 cm^{-1} in the nine-dimensional calculation. In addition, the $5\nu_1$ character is more evenly shared between the two states in the latter calculation. For the most part, however, the additional degrees of freedom do not significantly interact with the CH stretch states in this energy regime. The results demonstrate an important point. The sharing of the $5\nu_1$ state between predominantly two eigenstates does not imply that only two zero order states are involved in the Fermi resonance as some workers have speculated.⁵⁷

Selected results of the effective Hamiltonian matrix calculated through sixth order for the restricted problem are

	$ 0^0,1,4\rangle$	$ 4^0,0,3\rangle$	$ 2^0,0,4\rangle$	$ 0^0,0,5\rangle$
$ 0^0,1,4\rangle$	13 375.19			
$ 4^0,0,3\rangle$	0	13 471.65		
$ 2^0,0,4\rangle$	8.68	167.73	13 621.60	
$ 0^0,0,5\rangle$	-14.63	-.18	92.11	13 697.87

TABLE VII. Comparison of eigenvalues and three leading contributions of the eigenvectors^a of states nearly degenerate with the $\nu = 5$ overtone.

	E	First	Second	Third
Four-dimensional	13 427.5	$(-0.776)4\nu_1\nu_2^b$	$(-0.546)3\nu_1\nu_22\nu_5$	$(-0.242)2\nu_1\nu_24\nu_5$
	13 526.5	$(0.652)4\nu_12\nu_5$	$(-0.525)2\nu_16\nu_5$	$(-0.365)3\nu_14\nu_5$
Second	13 714.3	$(0.785)5\nu_1$	$(-0.452)3\nu_14\nu_5$	$(-0.358)2\nu_16\nu_5$
	13 877.8	$(0.662)4\nu_12\nu_5$	$(0.525)3\nu_14\nu_5$	$(-0.452)5\nu_1$
Fourth	13 412.7	$(-0.853)4\nu_1\nu_2$	$(-0.477)3\nu_1\nu_22\nu_5$	$(-0.179)2\nu_1\nu_24\nu_5$
	13 499.2	$(0.657)4\nu_12\nu_5$	$(-0.536)2\nu_16\nu_5$	$(0.318)3\nu_14\nu_5$
	13 674.2	$(0.782)5\nu_1$	$(-0.487)3\nu_14\nu_5$	$(-0.316)2\nu_16\nu_5$
	13 809.1	$(0.671)4\nu_12\nu_5$	$(0.529)5\nu_1$	$(0.469)3\nu_14\nu_5$
Sixth	13 421.1	$(-0.864)4\nu_1\nu_2$	$(-0.467)3\nu_1\nu_22\nu_5$	$(0.172)2\nu_1\nu_24\nu_5$
	13 500.2	$(0.659)4\nu_12\nu_5$	$(-0.538)2\nu_16\nu_5$	$(-0.318)3\nu_14\nu_5$
	13 677.6	$(0.781)5\nu_1$	$(0.490)3\nu_14\nu_5$	$(-0.316)2\nu_16\nu_5$
	13 812.1	$(-0.669)4\nu_12\nu_5$	$(-0.539)5\nu_1$	$(-0.464)3\nu_14\nu_5$
Nine-dimensional	13 356.2	$(0.785)4\nu_1\nu_2$	$(0.395)3\nu_1\nu_2^2$	$(0.308)3\nu_1\nu_22\nu_5$
	13 394.7	$(-0.647)4\nu_1\nu_2^2\nu_4^{-1}$	$(-0.472)4\nu_12\nu_5$	$(0.353)2\nu_16\nu_5$
Fourth	13 447.6	$(0.688)4\nu_1\nu_2\nu_4$	$(-0.438)3\nu_14\nu_5$	$(0.393)2\nu_16\nu_5$
	13 638.7	$(0.681)5\nu_1$	$(-0.482)3\nu_14\nu_5$	$(-0.418)4\nu_12\nu_5$
	13 760.1	$(0.663)5\nu_1$	$(0.637)4\nu_12\nu_5$	$(0.360)3\nu_14\nu_5$

^a The three leading contributions are given in terms of basis functions of the second, fourth, and sixth order effective Hamiltonian.

^b $n\nu_i m\nu_j \equiv n$ quanta in mode i , m quanta in mode j . The modes are defined in Table V. The zero order, degenerate basis functions, in the polar coordinate representation, have an angular dependence of $\exp[\pm il\phi]$ (cf. Ref. 67). Linear combinations of these states are constructed so that the states of A_1 symmetry have the form $\cos(l_4\phi_4 + l_5\phi_5 + l_6\phi_6)$, where $l_4 + l_5 + l_6$ is a multiple of 3. The l_i value of a degenerate state is denoted with a superscript with the exception of $l_i = 0$ where the superscript is absent.

We note that the interactions between states with different values of N_i in the SCF representation are small but not negligible as is made evident by a comparison of the above Hamiltonian matrix with the corresponding one for the SCF basis. Some diagonal matrix elements have been shifted by as much as 70 cm^{-1} .

The eigenvalues obtained by diagonalizing the $N_i = 10$ block are compared to two other sets of eigenvalues in Table VIII. The first set of eigenvalues were obtained by numerically applying second order Van Vleck perturbation theory to a matrix Hamiltonian of the prediagonal functions in order to decouple the $N_i = 10$ states from the remaining states of the Hamiltonian. Here all the off-diagonal couplings were

included in $H^{(1)}$. The second set of eigenvalues was also obtained using numerical second order Van Vleck perturbation theory, but here the P space was extended from $N_i = 10$ to include the states corresponding to $N_i = 9-11$.

In general, the operator approach provides a faster and more efficient method of obtaining block diagonal Hamiltonians, whereas the numerical approach is more flexible; one can use it to examine a greater variety of problems. On a VAX 8600, transforming an effective Hamiltonian to fourth order in perturbation theory takes 160 min and 29 s, respectively for the nine-dimensional and four-dimensional calculations. The final diagonalizations take significantly less time. The four-dimensional SCF calculation takes 16 s.

Other workers have used block diagonal Hamiltonians⁵⁶⁻⁵⁸ with functional forms which are assumed using ideas from low order perturbation theory.⁵⁶ Using fitting procedures the constants in the effective Hamiltonian are varied to obtain agreement with observed spectra. This provides a relatively straightforward way of obtaining force constants. The present treatment is complementary in that given the force constants, one can test the validity of the functional forms used in constructing the effective Hamiltonian. Future work on CH_4 and its deuterated analogs will specifically address this point.

V. SUMMARY

In this paper we have successfully applied Van Vleck perturbation theory to three vibrational problems, transforming to effective Hamiltonians whose solutions are easier to obtain than those of the original Hamiltonian. The prob-

TABLE VIII. Calculated eigenvalues in cm^{-1} for the restricted, four-dimensional model of CHD_3 corresponding to $N_i = n_s + 2(n_1 + n_2) = 10$.

State	E^a	E^b	E^c
1	13 421.1	13 422.8	13 423.8
2	13 500.2	13 488.8	13 493.0
3	13 677.6	13 671.2	13 673.5
4	13 812.1	13 811.6	13 812.8

^a Results of diagonalizing a block diagonal effective Hamiltonian obtained using the operator algebraic method to sixth order.

^b Results of diagonalizing the states corresponding to $N_i = 10$, where these states have been decoupled from the remaining states by applying second order Van Vleck perturbation theory to a prediagonalized Hamiltonian.

^c Same as footnote b, but here the $N_i = 9-11$ states were decoupled from the remaining states through second order perturbation theory.

lem of small divisors and divergences in the perturbation expansions is not evident for the systems studied. This is mainly due to the flexibility one has in developing the form of effective Hamiltonians. Two transformations have been discussed, the first being the transformation to a SCF-like representation, the second being the transformations to a block diagonal representation. By implementing the transformations in an operator representation, the need for large basis sets is obviated. The very cumbersome algebra is performed using FORTRAN codes.

Future work in this area will involve a thorough investigation of the CH₄ stretching dynamics along with the deuterated analogs. These ideas will also be extended to examine rovibrational dynamics. Here the vibrational Hamiltonian can be transformed using the methods discussed above; the rovibrational interactions are then transformed to the new representation. This should provide new insight on the role of rovibrational interactions, which have recently been shown to play a significant role in intramolecular dynamics.⁶⁹

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