An efficient new method for calculating eigenvalues and spectra of van der Waals complexes

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We present a new method of solving the Schrödinger equation for vibration–rotation levels of van der Waals complexes, which exploits a novel way of avoiding problems associated with poor convergence of radial basis sets. This “iterative secular equation” or ISE method is based on the secular equation/perturbation theory approach of Hutson and Le Roy [J. Chem. Phys. 83, 1197 (1985)]. It begins with a secular equation built from a small radial basis set which provides an initial approximation to the state of interest, and then uses a perturbation theory approach to determine optimal improvements to this initial basis set, iterating until the solution is converged. While it effectively solves the close coupled equations for the system of interest, the growth of computational effort with the number of coupled channels $N$ is distinctly slower than the $N^3$ behavior associated with conventional close coupling calculations. The present implementation also obtains solutions for a few states at a time, a feature that makes it particularly efficient when only a small number of states are of interest. The new method is illustrated by application to truly bound levels of the Ar–HCl complex and to predissociating levels of the He–HF and He–C$_2$H$_2$ complexes.

I. INTRODUCTION

The development of accurate and efficient methods for calculating rovibrational eigenvalues and eigenfunctions of van der Waals complexes and other floppy molecules is a topic of considerable current interest. This is driven partly by the progress in experimental techniques which has led to a large and growing body of spectroscopic data for these systems, much of which presents significant challenges to theory. At one level, the challenge is simply to assign the spectra. The very floppy nature of some complexes means that traditional spectroscopic methods have limited applicability, and comparisons with computed spectra implied by trial potential energy surfaces are sometimes required before the observed transitions can be assigned. Moreover, van der Waals molecules are particularly simple systems for the study of highly anharmonic and delocalized motion, where the assignment of quantum numbers becomes difficult and ergodic behavior may arise. Zeroth-order models based on such calculations may also provide approximate quantum numbers with which to label the transitions. At a deeper level, full least-squares fits to spectroscopic data are proving to be the best single means of experimentally determining the multidimensional potential energy surface governing the dynamics of such systems.

The problem of predicting the infrared spectra of weakly bound complexes from an assumed potential energy surface has several components. These include: (i) calculating the bound-state energies of the complex; (ii) calculating the energies and widths of its metastable resonance states; (iii) calculating transition intensities; and (iv) assigning exact and approximate quantum numbers to the states involved in these transitions. To allow quantitative comparisons with experiment, such calculations must be of very high accuracy, while if least-squares fits are to be used to iteratively improve the assumed potential energy surface, the computational cost must be modest. While considerable attention has been directed to all of these questions in recent years, there is currently no single approach that is able to deal with them all, even for the simple case of atom–rigid rotor complexes.

In the following, we present an efficient new method for calculating bound- and metastable-state energy levels of a weakly bound complex, and for simulating its infrared spectra. It is a basis set method, in that basis functions are used to treat both the angular and radial degrees of freedom. However, rather than use large preselected sets of radial basis functions, perturbation theory is used to numerically determine corrections to the radial behavior implied by a minimal initial basis. This solves the problem of slow convergence which plagues most basis set methods, and makes the method accurate and efficient enough to allow its use in multiparameter least-squares fits to optimize the parameters characterizing an assumed potential energy surface.

The detailed implementation of this method is described below for the case of atom–rigid rotor complexes, but its extension to more complicated cases will be quite straightforward. In order to place the new method in context, we begin in Sec. II by outlining the problem and describing previous approaches to solving it. The theory and implementation of our method is then described in Sec. III, while a number of illustrative applications are discussed in Sec. IV.

II. ROVIBRATIONAL STATES OF WEAKLY BOUND COMPLEXES

The present method may be implemented using either the body-fixed or space-fixed frames of reference. Much
recent work in this area has used body-fixed coordinates, but for the extremely high accuracy required when simulating high resolution spectra, the decoupling approximations developed for scattering calculations using body-fixed coordinates cannot be applied. When this is true, the number of angular channels which must be considered, and hence the computational effort, is usually the same for either frame. On the other hand, space-fixed coordinates provide a more natural description both of the products of complex fragmentation and of the very weakly bound complexes of particular interest to us at present. Moreover, Clary and Nesbitt state that the calculation of transition intensities is particularly simple in the space-fixed frame.

While space-fixed coordinates are used in the present work, the form of the theory is essentially the same in either frame, so a general notation applicable to either approach will be used whenever possible. Moreover, the new method promises to allow exploitation of the decoupling approximations referred to above, with no loss of eigenvalue accuracy, so its implementation in body-fixed coordinates is being pursued.

For an atom–linear molecule system, the usual Jacobi coordinates \( \mathbf{r}, \mathbf{R}, \) and \( \theta \) are used to describe the dependence of the potential energy on the internal coordinates of the complex. The vector \( \mathbf{r} \) lies on the axis of the linear molecule and is conventionally directed from its center of mass towards its most distant component atom; the vector \( \mathbf{R} \) runs from this monomer center of mass along the van der Waals bond to the adatom, and \( \theta \) is the angle between the associated unit vectors \( \mathbf{R} = \cos^{-1}(\mathbf{R} \cdot \hat{f}) \). For the sake of simplicity, the following discussion treats the component linear molecule as being rigid, so that \( \mathbf{r} \) is replaced by \( \mathbf{f} \), and the potential energy surface has no dependence on its internal stretching coordinate(s). However, to illustrate its application to more general cases, the formulation appropriate for a complex formed by an atom and a nonrigid linear molecule as being rigid, so that \( \mathbf{r} \) is replaced by \( \mathbf{f} \), and the potential energy surface has no dependence on its internal stretching coordinate(s). However, to illustrate its application to more general cases, the formulation appropriate for a complex formed by an atom and a nonrigid diatomic molecule is outlined in Appendix A.

After separating out the motion of the center of mass, the Hamiltonian for the rotational and vibrational motions of a complex formed from an atom of mass \( M_a \) and a linear molecule of mass \( M_m \) is

\[
\mathcal{H}^{(R,f)} = \frac{\mu^2 R^{-1}}{2\mu} \left( \frac{\partial^2}{\partial \mathbf{f}^2} \right) R + \frac{\mu^2 R^2}{2\mu} + V(R,\theta) + \mathcal{H}_m(\mathbf{f}). \tag{1}
\]

Here, \( \mu = M_a M_m / (M_a + M_m) \) is the overall reduced mass of the complex, \( V \) is the total angular momentum operator associated with rotation of the van der Waals bond \( \mathbf{R} \), and \( \mathcal{H}_m(\mathbf{f}) \) is the Hamiltonian associated with free rotation of a component rigid linear molecule whose moment of inertia is \( I_m \) and total angular momentum operator is \( J_m \). The eigenvalues \( E_{m,j} \) of \( \mathcal{H}_m \) may then be specified either by empirical inertial and centrifugal distortion rotational constants, or by a list of known eigenvalues for the species in question.

To place the present method in context, we will now briefly describe two classes of approach to the problem of determining the eigenvalues and eigenfunctions of this Hamiltonian, and summarize their current limitations and capabilities. More detailed discussions of these methods may be found in Ref. 20 and in the excellent recent reviews by Hutson and Byclic and Light. Section II C then describes the "secular equation with perturbation theory correction" or SEPT method for improving a given secular equation matrix result, which is the basis of the present procedure.

### A. Coupled-channel methods

The study of collision phenomena has stimulated the development of accurate methods for computing the \( S \)-matrix elements which characterize the coupling among the continuum states of the Hamiltonian of Eq. (1). Such methods involve expanding the total wave function for the system in terms of a complete set of channel basis functions \( \{ \Phi_{aMP}(R,R) \} \) spanning all degrees of freedom except the intermolecular separation

\[
\psi_{MP}(R,R) = R^{-1} \sum_a \Phi_{aMP}(R,R) \chi_{m,a}(R). \tag{2}
\]

Here, \( J \) and \( M \) are the quantum numbers for the total angular momentum and its projection on the space fixed \( z \) axis, \( p \) is the parity, and \( m \) is a label which identifies the particular eigenstate of the system. For an atom plus rigid-rotor system in space-fixed coordinates \( \mathbf{a} = (j,l) \), where \( j \) and \( l \) are, respectively, the usual quantum numbers associated with the operators \( j^2 \) and \( I \), \( p = (-1)^{l+j} \), and the sum over \( \mathbf{a} \) runs over all values of \( j \) and \( l \) consistent with the chosen parity which satisfies the triangular inequality for \( j, l, \) and \( J \). In this particular case, these internal motion basis functions reduce to the familiar total angular momentum eigenfunctions

\[
\Phi_{aMP}(R,R) = Y_{j/l}^{JM} (\hat{R}, \hat{f}),
\]

\[
\equiv \sum_{m_j,m_l} C(j,l,J;J,m_j,m_l,M) Y_{j,m_j}(\hat{R}) Y_{l,m_l}(\hat{f}), \tag{3}
\]

where \( Y_{JM} \) are the usual spherical harmonic functions and \( C(j,l,J;J,m_j,m_l,M) \) are the Clebsch–Gordan coefficients. However, the more general notation will be used in most of the following.

While the channels are also labeled (in space-fixed coordinates) by \( j \) and \( l \), the only exact quantum numbers associated with the angular motion are \( J \), \( M \), and \( p \). However, since the eigenvalues are independent of \( M \), and the value of \( p \) is defined implicitly by those of \( j \) and \( l \), for the sake of simplicity, indices \( M \) and \( p \) are omitted from the following discussion. Moreover, since all eigenstates are associated with particular values of \( J \), this label is also omitted in most of the following.

Substituting the expansion of Eq. (2) into the Schrödinger equation implied by the Hamiltonian of Eq. (1), premultiplying in turn by the complex conjugate of each of the internal motion basis functions \( \Phi_{aMP}^{(R,R)} \), and integrating...
over the angular coordinates (and any internal degrees of freedom) yields the set of coupled equations for this problem\cite{19,23}
\[
\begin{align*}
\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + U_{a,a}(R) - E_m\right] \chi_{ma}(R) \\
= - \sum_{a'} U_{a',a}(R) \chi_{ma'}(R),
\end{align*}
\]
where the prime on the summation indicates exclusion of the term \(a'=a\),
\[
U_{a',a}(R) = \left[ \frac{l(l+1)\hbar^2}{2\mu R^2} + E_m(J) \right] \delta_{a',a} + V_{a',a}(R) \quad (4)
\]
and for an atom plus linear rigid rotor in space-fixed coordinates,
\[
V_{a',a}(R) = V_{j',j}(R)
- \int \mathcal{P}^{(j',j)}(\hat{R},\hat{\theta}) \mathcal{V}(R,\theta) \mathcal{P}^{(j,j)}(\hat{R},\hat{\theta}) \, d^2\hat{R} \, d^2\hat{\theta}.
\]
(6)

If the potential is expanded in a Legendre series
\[
V(R,\theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\theta),
\]
the integrals in Eq. (6) may be evaluated in closed form and expressed in terms of the Percival-Seaton coefficients \(f(j',j',j,j,J)\),
\[
V_{a',a}(R) = \sum_{\lambda} f(j',j',j,j,J) V_{\lambda}(R).
\]
(8)

The expansion of Eq. (7) does not always converge rapidly and more compact parametrizations are often obtained by defining the potential in some other form. However, the orthogonality of the Legendre polynomials means that numerical quadratures may be used to convert other forms to that of Eq. (7) to any desired accuracy. Thus, for any arbitrary form for the potential \(V(R,\theta)\), the matrix elements of Eq. (5) may be readily generated.

The exact solutions to our multidimensional Schrödinger equation are now expressed as solutions to an infinite set of coupled differential equations in one dimension. Truncating this set to include only channels whose asymptotes lie close to that associated with the eigenstate of interest is known as the close coupling approximation. Efficient methods for solving these equations have been developed for both bound states and metastable or scattering states. The most successful are those based on matrix Numerov methods for propagation of the log derivative of the radial wave function.\cite{28,29} Metastable scattering states can be found in this approach by calculating the \(S\)-matrix eigenphase sum at a range of energies\cite{30} and iteratively converging on the resonance.\cite{31} This gives definitive results for the energies, widths, and fragmentation branching ratios for metastable states, but it can be computationally tedious and the spectroscopic identity of the state in question is not always apparent. Moreover, this approach does not readily yield wave functions and hence cannot be used to predict spectral line intensities.

For truly bound states, the most efficient close coupling computational procedures are those developed by Johnson\cite{32,33} and Manolopoulos,\cite{28} as implemented in a widely distributed computer program by Hutson.\cite{34} This approach yields rapid convergence to the eigenvalue closest to the initial trial energy, but does not produce wave functions and hence cannot predict spectral intensities. However, when combined with a finite difference technique developed by Hutson,\cite{35} it may still generate the expectation values required for predicting many properties of a molecular complex.

Close-coupling calculations yield the definitive eigenvalue and predissociation rate results against which all other methods are tested. However, for the simulation and analysis of spectroscopic data, they have a number of shortcomings. In particular, they yield results for one eigenstate at a time and offer no natural internal procedure for generating reasonable initial trial eigenvalues for other states of interest. Moreover, the computational effort increases as the cube of the number of coupled channels, a growth rate which can make accurate calculations for strongly coupled high angular momentum states prohibitively expensive. In addition, the fact that the most efficient methods do not yield wave functions, which are needed to predict spectroscopic transition intensities, hampers their use in helping to assign features of poorly understood experimental spectra.

### B. Matrix methods

We discuss two classes of basis-set (matrix) methods. In radial basis set methods, the coupled equations of Eq. (4) are solved by expanding the radial channel functions in terms of a finite set of known basis functions \(\{\phi_{n}^{a}(R)\}\), which may (or may not) be different for each channel \(a\),
\[
\chi_{ma}(R) = \sum_{n} c_{mn}^{a} \phi_{n}^{a}(R) \quad (9)
\]
and solving the Schrödinger equation variationally by diagonalizing the resulting Hamiltonian matrix. In the earliest applications of this approach to van der Waals molecules, Le Roy et al.\cite{8,20,36} defined these radial basis functions as the numerically determined eigenfunctions of an isotropic "basis-generating" potential which was defined as the leading (isotropic) contribution to Eq. (7) plus the centrifugal term
\[
V_{\text{basis}}(R) = V_{0}(R) + (l+1)\hbar^2/2\mu R^2.
\]
(10)

In later work, \(V_{0}(R)\) was replaced by the diagonal radial channel potential \(V_{\text{rad}}(R)\) of Eq. (6).\cite{37,38} In practice, the small number of bound states supported by such potentials for weakly bound van der Waals systems limits the variety of radial behavior which can be represented in this way, restricting the practical utility of such bases to weak-anisotropy systems such as the \(H_2^{+}\) (rare gas) complexes. However, this restriction is removed by the simple step of
adding a potential wall or applying an exponential log-derivative boundary condition to $V_{\text{basis}}(R)$ at moderately large distance, and the resulting sets of basis functions proved capable of yielding accurate predictions of spectra for a wide range of systems.\textsuperscript{18,36,39}

Considerable success has also been achieved using analytic orthonormal basis sets involving Morse-oscillator-like functions, harmonic oscillator functions or Sturmian functions.\textsuperscript{10,40-42} However, even with the variational optimization of the Hermite or Morse-like function exponent parameter, the radial behavior of these basis functions is usually not very similar to that of natural eigenfunctions of the Hamiltonian. As a result, relatively large basis sets are required, particularly when very high accuracy is desired.

An alternate procedure has involved the use of nonorthogonal basis sets of distributed Gaussian functions.\textsuperscript{43} However, most practical applications of that approach have simply used contracted sets of those functions as effective stretching basis functions, defined by the requirement that they satisfy the one-dimensional Schrödinger equation associated with the nonrotating isotropic potential $V_0(R)$ of Eq. (7).\textsuperscript{18,45,46} In other words, they are simply the eigenfunctions of a basis-generating potential based on the combination of $V_0(R)$ with a log-derivative boundary condition at large distances.\textsuperscript{47} This makes them precisely equivalent to the numerical basis functions referred to above,\textsuperscript{36,39} except that the absence of the centrifugal distortion term included in Eq. (10) means that these contracted basis sets will tend to converge more slowly for high angular momentum states.

Several impressive calculations have been carried out using a transformation of the angular (and sometimes radial) basis set to an equivalent discrete variable representation (DVR).\textsuperscript{11,48-50} These calculations have employed several of the radial basis sets described above. The DVR, together with a stepwise approach to the problem, allows efficient basis sets to be constructed. The collocation method, developed for these systems by Yang and Peet\textsuperscript{51} and extended by Cohen and Saykally,\textsuperscript{52} is another matrix-based method that avoids the computation of matrix elements by combining the basis set expansion with a set of discrete points at which the Schrödinger equation is required to be satisfied. It has been used successfully in a least-squares determination of a potential energy surface for Ar–H$_2$O.\textsuperscript{52}

One advantage of basis set methods is that many eigenstates may be obtained at once, and their ordering facilitates the assignment of effective quantum numbers. This in turn facilitates the computation of simulated spectra, although it may have limited importance when only a few bound states of a given symmetry exist or are required. In addition, these methods always give the wave functions required for calculating expectation values and transition intensities. This availability of wave functions also offers the tantalizing possibility of using the Hellman–Feynman theorem to generate efficiently the partial derivatives of transition frequencies required for least-squares fits to optimize a trial potential energy surface. While this latter capability has been limited use in this field to date,\textsuperscript{8} the very substantial savings in computer time and improved partial-derivative accuracy would certainly increase the feasibility of performing proper multiparameter fits to data for strongly anisotropic systems.

Unless the basis used is quite small, matrix methods tend to yield many solutions lying above the dissociation limit of the complex. While most of these roots are unphysical, others are associated with the untractable resonance states of the system. Techniques have been developed for distinguishing between the true resonance states and other positive energy solutions,\textsuperscript{50} but in order to calculate accurate widths or energies for these resonances, somewhat tedious "relaxation" methods involving repeated calculations with slightly differing basis sets are required.\textsuperscript{39,53,54}

The main weakness of most radial basis set methods is that they are very slowly convergent when there is moderate-to-strong coupling between the different degrees of freedom. If the basis functions are eigenfunctions of some basis-generating potential,\textsuperscript{8,18,20} their ability to efficiently and accurately represent eigenfunction is implicitly limited to the "classically accessible" range of $R$ associated with those basis functions. For strong-anisotropy systems where very different effective radial potentials can be associated with different angular momentum states, these basis sets can be very inefficient and indeed may never converge at all. While this difficulty can be avoided by the use of more general analytic basis sets, the ability of the latter to represent a wide range of radial behavior over a very broad range of $R$ is only achieved at the cost of requiring the use of very large basis sets. In either case, the associated computational effort can make some types of studies, such as iterative fits to optimize potential energy surfaces for strong-anisotropy systems, prohibitively expensive.

C. The "secular equation with perturbation theory correction" (SEPT) method

One attempt to overcome the shortcomings of radial basis set methods gave rise to the "secular equation with perturbation theory correction" (or SEPT) method.\textsuperscript{38,55} It begins as a standard radial basis set method, with a small basis of functions $\{\phi_{ij}(R)\}$ defined as the lowest (few) eigenfunctions of basis-generating potentials associated with the contributing channels. As implemented,\textsuperscript{38,55} this potential was chosen to be the diagonal or "distortion" potential seen in Eq. (4)

$$V_{\text{basis}}(R) = V_{\text{a}}^D(R) = V_{\l,i,lj}(R) + \left(\frac{l(l+1)}{2\mu R^2}\right),$$

but other choices could serve equally well. The usual variational treatment then yields the "secular equation" eigenvalues $E_{m}^{\text{SEPT}}$ and eigenfunctions $\psi_{m}^{\text{SEPT}}(\textbf{R},\textbf{r})$ as

$$\psi_{m}^{\text{SEPT}}(\textbf{R},\textbf{r}) = R^{-1} \sum_{a} \Phi_{l,i,lj}(\textbf{R},\textbf{r}) \chi_{m}^{\text{SEPT}}(\textbf{R})$$

$$= R^{-1} \sum_{\alpha,\nu} c_{\alpha,\nu}^{m} \Phi_{\alpha}(\textbf{R},\textbf{r}) \phi_{\nu}^{a}(R).$$
Perturbation theory is then used to determine the first order correction \( \chi^{(1)}(R) \) to the (contracted) zeroth-order function \( \chi^{\text{SE}}(R) \) representing the contribution of channel \( a \) to the initial secular equation solution for state \( m \). Following Hutson and Howard,\(^5^6\) these correction functions were determined by solving a one-dimensional (uncoupled) linear inhomogeneous differential equation for each contributing channel (see below). As discussed in Ref. 38, there is no first-order energy correction, and the second- and third-order energies are readily calculated from the first-order wave function obtained in this way.\(^5^7\)

This approach certainly yielded better results than the compact basis set itself, but even for only moderate-anisotropy systems such as Ar–HCl, it was not fully satisfactory.\(^5^8\) In an effort to improve it further, Hutson showed that one could achieve better results by treating the first-order correction functions as basis functions on their own, and repeating the Hamiltonian diagonalization step with one more radial basis function associated with each channel.\(^5^9\) This did yield better results with quite compact radial bases, but for moderate-to-strong coupling cases, the overall accuracy was still not adequate. Moreover, in the resulting composite radial basis, the eigenfunctions of a one-dimensional basis-generating potential were mixed with one (per channel) quite different type of function, and a means of further extending this approach was not immediately evident. However, this SEPT method has provided the key to the efficient and fully convergent method described below.

III. THE "ITERATIVE SECULAR EQUATION" OR ISE METHOD

A. Formalism

The formalism underlying the ISE method may be presented in terms of a partitioning of the Schrödinger equation into "basis set" and "nonbasis set" portions. The basis set portion corresponds to that part of the problem included in the secular equation, while the nonbasis set portion is that part of the problem dealt with by perturbation theory. This type of partitioning scheme was introduced by Löwdin\(^3^8\) and has been discussed by McWeeny.\(^3^9\)

Using Dirac notation, we may define a projection operator \( \mathcal{P} \) onto an finite orthonormal basis set \( \{ | b \rangle \} \) as

\[
\mathcal{P} = \sum_{\text{basis}} | b \rangle \langle b |.
\]

(13)

The projector onto the remainder of Hilbert space is then the complement of \( \mathcal{P} \),

\[
\mathcal{O} = 1 - \mathcal{P}.
\]

(14)

The idempotency and completeness properties of such projection operators then imply

\[
\mathcal{P} \mathcal{P} = \mathcal{P},
\]

(15)

\[
\mathcal{O} \mathcal{O} = \mathcal{O},
\]

(16)

\[
\mathcal{P} + \mathcal{O} = 1,
\]

(17)

\[
\mathcal{P} \mathcal{O} = 0.
\]

(18)

On replacing \( \psi_m \) by \( (\mathcal{P} \mathcal{O}) \psi_m \) and operating from the left with \( \mathcal{P} \) and \( \mathcal{O} \), the Schrödinger equation

\[
\mathcal{H} \psi_m = E_m \psi_m
\]

may be rewritten as the two equations

\[
(\mathcal{P} \mathcal{H} - E_m) \mathcal{P} \psi_m = -\mathcal{P} \mathcal{H} \mathcal{O} \psi_m,
\]

(20)

\[
(\mathcal{O} \mathcal{H} - E_m) \mathcal{O} \psi_m = -\mathcal{O} \mathcal{H} \mathcal{P} \psi_m.
\]

(21)

Our general scheme for solving the Schrödinger equation consists of the iterative self-consistent solution of these two equations.

If the term \( \mathcal{O} \psi_m \) on the right-hand side of Eq. (20) is neglected, solving the resulting equation in a basis associated with projection operator \( \mathcal{P} \) yields a zero-order wave function \( \psi^{\text{SE}} \) and eigenvalue \( E^{\text{SE}} \),

\[
(\mathcal{P} \mathcal{H} - E^{\text{SE}}) \psi^{\text{SE}} = 0,
\]

(22)

where we have used the fact that \( \mathcal{P} \psi^{\text{SE}} = \psi^{\text{SE}} \). Replacing \( E_m \) by \( E^{\text{SE}} \) and \( \mathcal{P} \psi_m \) by \( \psi^{\text{SE}} \) in Eq. (21) then gives an approximate equation for the part of the wave function not accounted for by the basis set \( \mathcal{P} \psi_m \approx \psi^{(1)} = \mathcal{O} \psi^{(1)} \),

\[
(\mathcal{O} \mathcal{H} - E^{\text{SE}}) \psi^{(1)} = -\mathcal{O} \mathcal{H} \psi^{\text{SE}}
\]

(23)

To solve Eqs. (20) and (21), a basis set is chosen and the secular equation of Eq. (22) is solved to yield an initial approximate solution \( \psi^{\text{SE}} \). Equation (23) is then solved to yield the correction function \( \psi^{(1)} \). This correction function is then used to augment the original basis set, and Eq. (22) solved in this new basis set to generate a new eigenvalue and eigenfunction, and the process iterated to convergence. On each cycle, the neglected term on the right-hand side of Eq. (20) is approximately equal to \( (E^{\text{SE}} - E^{(1)}) \psi^{\text{SE}} \), and inclusion of \( \psi^{(1)} \) in the basis set is equivalent to making the substitution \( \mathcal{O} \psi_m \approx \psi^{(1)} \) on the right-hand side of Eq. (20). Thus, the error will decrease from cycle to cycle as the current (augmented) secular equation eigenvalue \( E^{\text{SE}} \) approaches the true eigenvalue \( E_m \) until this iteration procedure yields self-consistent solutions of Eqs. (20) and (21).

The above discussion is completely general and formal. The particular nature of our problem will now be considered, and a channel-by-channel implementation of this iteration scheme described.

B. Application to van der Waals complexes

1. Defining the initial radial basis functions

In the present context, the basis vectors \( | b \rangle \) are products of radial and angular functions and are labeled by two sets of indices

\[
| b \rangle = | a, n_a \rangle = | a \rangle | n_a \rangle = \Phi_a(R) \hat{R} | n_a \rangle(R).
\]

(24)

Following a convention introduced by Hutson,\(^1^2\) the notation \( | ) \) is used to denote a function which depends on only some, and not all coordinates of the system. Thus, while the quantity \( \langle f | A | f' \rangle \) has the form of a Dirac inner product, it implies integration over only the variables associated with the labels \( f \) and \( f' \), and the result will in general be a function of the other variables of the system. For example,
in this notation, the potential matrix elements of Eq. (6) would be written \( V_{\alpha',\alpha}(R) = (\alpha' | V(R,\theta) | \alpha) \) and the orthonormality of the angular basis functions would be
\[ (\alpha' | \alpha) = \delta_{\alpha'\alpha}. \]

The iterative secular equation method blends the coupled channel and radial basis set methods by focusing attention on the problem of finding an accurate and compact basis representation of the radial channel functions \( \chi_{ma}(R) \) of Eqs. (2) and (4). As in any close coupling calculation, one begins by selecting the set of angular channel \( \{|a\} \) to be included in the wave function expansion of Eq. (2). The next step is to determine an initial set of radial basis functions for use in a preliminary secular equation calculation for the eigenstate(s) of interest. In the present implementation, these basis functions are defined as the first few numerically determined eigenfunctions of the radial Schrödinger equation for the distortion potential \( V'(R) \) of Eq. (11)
\[ \left[ \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + U_{a,a}(R) - E_{n_a}^0 \right] \phi_{n_a}^a(R) = 0. \] (25)

Other reasonable choices for this basis-generating potential are certainly possible, such as the exact radial potential \( V(R,\theta) \) at some fixed angle \( \theta \), but the distortion potential seems most appropriate for the moderate-anisotropy systems of particular interest here. In any case, this one-dimensional Schrödinger equation may be efficiently and accurately solved using standard methods to obtain as many eigenvalues \( E_{n_a}^0 \) and (numerical) radial eigenfunctions \( \phi_{n_a}^a(R) = | n_a \rangle \) as desired.

The number of radial functions required for this initial basis is typically quite modest; one function for each stretching eigenstate up to the highest one of interest should usually suffice. In practical calculations for most systems of interest, this means between one and three initial radial basis functions per channel. Moreover, there is no need for the same number of functions to be used for all channels. The projection operator of Eq. (13) is then defined in terms of the set of initial basis functions \( \{|a| n_a \rangle \}. \)

As in any radial basis set procedure, a Hamiltonian matrix is formed by applying the Hermitian conjugate of these basis functions to Eq. (22) and integrating over all variables. Diagonalizing the resulting matrix then gives the secular equation eigenvalue \( E_m^{SE} \) and the eigenfunction \( \psi_m^{(1)} \) of Eq. (12), along with analogous approximate eigenvalues and wave functions for other states associated with the range of channels included in the basis. While these results take account of much of the coupling among these channels, the overall accuracy will tend to be limited due to the small radial basis set used.

2. Correcting the secular equation solution

As in the SEPT method, the initial wave function of Eq. (12) is improved by solving a set of uncoupled linear inhomogeneous differential equations to determine radial behavior not included in the original basis set. To define these equations, we first introduce a channel expansion for the wave function correction being sought
\[ \psi_m^{(1)}(R) = R^{-1} \sum_{\alpha'} \Phi_{a'}(\hat{R},\hat{\theta}) \chi_{ma}^{(1)}(R). \] (26)

Substituting Eq. (26) into Eq. (23), multiplying from the left by the conjugate angular basis function \( | a \rangle \), and integrating over the angular coordinates then yields
\[ \phi_{n_a}^a(R) = \begin{cases} \sum_{a'} \left[ \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + U_{a,a}(R) - E_m^{SE} \right] \chi_{ma}^{(1)}(R) \\ + \begin{cases} \sum_{a'} U_{a,a'}^{(1)} \chi_{ma}^{(1)}(R) - g_{ma}(R) \\ \sum_{a'} U_{a,a'}^{(1)} \chi_{ma}^{(1)}(R) - g_{ma}(R) \end{cases} \right] \] (27)

where
\[ g_{ma}(R) = \phi_{n_a}^a(R) - \chi_{ma}^{(1)}(R) \]

If the coupling neglected in Eq. (22) is included to first order only, the summation may be deleted from the left-hand side of Eq. (27), and we are left with a separate differential equation for the correction function for each channel. However, the projection operator on the left-hand side of Eq. (27) makes it difficult to solve, except for the trivial case in which no radial functions for this channel were included in the original basis (in which case \( \phi_{n_a}^a(R) \)). Rather than attempt to solve these equations exactly, we therefore neglect this operator and solve the resulting set of linear inhomogeneous equations
\[ \left[ \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + U_{a,a'}(R) - E_m^{SE} \right] \chi_{ma}^{(1)}(R) = -g_{ma}(R). \] (30)

The price paid for this simplification is that the solution \( \chi_{ma}^{(1)}(R) \) is not necessarily orthogonal to the existing radial basis set for this channel. The solutions to Eq. (30) must therefore be orthogonalized to this basis before being used to either augment it or [in the substitution approach (see below)] being contracted with existing basis functions for that channel. We emphasize, however, that the approximations leading to Eq. (30) do not lead to approximations in the method as a whole, which is formally exact.

The simple linear inhomogeneous differential equation of Eq. (30) is the basic expression underlying the SEPT and ISE methods. Since the coupling function \( g_{ma}(R) \) is known, being determined by the (known) solution to the existing secular equation problem, this equation may readily be solved for each angular channel included in the basis. This is done using a simple numerical procedure developed for this type of problem by Hutson and Howard, which is precisely analogous to that used for the homogeneous equation of Eq. (23), and has been
shown to be much quicker and more accurate than conventional basis-set methods for one-dimensional problems.\textsuperscript{56,63}

In the SEPT method, the correction functions \( \{ \phi_{m}^{(i)}(R) \} \) are substituted into the conventional perturbation energy expressions\textsuperscript{57} to calculate the second- and third-order corrections to the secular equation eigenvalues \( E_{m}^{\text{SE}} \). In the “augmented secular equation” or ASE method proposed by Hutson,\textsuperscript{55} these correction functions are normalized and added to the basis set, and the secular equation solved a second time. However, the fact that this correction procedure can readily be repeated iteratively was not recognized earlier; this point is the key to the present method.

3. Calculating \( g_{ma}(R) \) and the iteration procedure

While the form of \( g_{ma}(R) \) may appear daunting, the fact that the initial \( \{ \phi_{m}^{(i)}(R) \} \) radial basis functions are eigenfunctions of a basis-generating potential [see Eq. (25)] reduces the right-hand side of Eq. (28) to a sum of terms involving the known potential coupling functions and the known radial basis functions of the initial secular equation problem\textsuperscript{58,64}

\[
g_{ma}(R) = \sum_{a} U_{aa'}(R) \chi_{m,a}^{\text{SE}}(R) - \sum_{b} \phi_{m}^{(i)}(R)
\times \sum_{a'} \int_{0}^{\infty} \phi_{a}^{(i)}(R') U_{a,a'}(R') \chi_{ma}^{\text{SE}}(R') dR'. \tag{31}
\]

This simplification made the initial application of Eq. (30) in the SEPT and ASE methods relatively straightforward. However, if we include the orthonormalized correction functions obtained from Eq. (30) in the radial basis for each channel, and repeat the secular equation diagonalization step, this simplification does not apply to the augmented contributions to these new \( \chi_{ma}^{SE}(R) \) functions. This is the reason that further extensions of the SEPT and ASE approaches had seemed unlikely.

The key to the present ISE method is the simple observation that one can also determine the \( g_{ma}(R) \) functions by applying Eq. (28) directly as written. In other words, rather than attempt to utilize special properties of the contributing basis functions, one simply evaluates the second derivatives of the contracted \( \chi_{ma}^{SE}(R) \) functions numerically. The \( \phi_{a}^{(i)} \) projection operator in Eq. (28) may then be accounted for by applying normal Gram–Schmidt orthogonalization to the resulting function. In this approach, the computational effort required for generating the \( g_{ma}(R) \) functions is independent of the source of the basis functions comprising the \( \chi_{ma}^{SE}(R) \) solutions, and in practice it is no greater than that associated with the application of Eq. (31). Thus, iterative application of Eqs. (22) and (23) becomes a very straightforward matter.

In summary, use of ISE method begins with a selection of the angular channels to be included and then proceeds to the determination of a minimal radial basis set for each channel of interest. While further experience will be needed before one can make reliable general prescriptions, this initial basis need not be the same size for all angular channels, and it appears that one basis function for each effective radial stretching vibrational state up to the eigenstate of interest will suffice. Solving the secular equation problem of Eq. (22) in this basis then yields an initial set of secular equation eigenvalues \( \{ E_{m}^{SE} \} \) and radial channel functions \( \{ \chi_{ma}^{SE} \} \). The next step is to apply Eq. (30) to each angular channel to obtain a radial correction function \( \chi_{ma}^{(i)}(R) \) contributing to the solution of interest. In this step, we may also choose to include angular channels which were omitted from the initial basis and are to be included only from this point onward. As mentioned above, these functions are then made orthogonal to all existing radial basis functions for that channel, normalized, and included in an augmented basis set then used to give an improved secular equation solution to Eq. (22). This cycle is repeated until convergence is achieved.

As an illustration, consider a case in which \( k \) initial basis functions are used for each of \( N \) angular channels (typically \( k = 1-3 \)). In this case, the associated Hamiltonian matrix is of order \( N \times N \) and the resulting eigenfunctions are those of Eq. (12). After the first correction cycle (the ASE step), the basis set and new Hamiltonian matrix have order \( N \times (k+1) \), while after \( c \) such correction cycles, this order has only increased to \( N \times (k+c) \). In applications of this method to date, we typically find that \( c = 3 \) or 4 suffices to give convergence to better than 0.001 cm\(^{-1} \). The resulting basis size of (say) \( N \times (k+4) \) is far smaller than the sizes (20 to 40) \( \times N \) typically needed to obtain accurate results using conventional fixed radial basis sets.\textsuperscript{13,14} Moreover, since the dimension of the Hamiltonian matrix generated in the present work remains modest, most computational effort is associated with preparing the \( g_{ma}(R) \) functions using Eq. (28) and with solving the (uncoupled) one-dimensional equations (25) and (30). Thus, its rate of growth with the number of angular channels \( N \) should be between linear and quadratic. This is a marked contrast to the \( N^{3} \) growth in computational expense associated with close coupling calculations.

In conclusion, we note that the ISE approach has the same structure as the Davidson method for finding a few roots of large matrices,\textsuperscript{65} used commonly in configuration interaction calculations. However, here it is implemented in a channel-by-channel fashion. Also, while the Davidson method uses a predefined primitive basis set to form the perturbation theory equations, here we generate the new augmenting numerical basis functions in situ.

4. Calculation of spectroscopic transition intensities

The final converged eigenfunction yielded by the ISE method is a simple angular-radial product expansion of the form of Eq. (12). It is therefore a straightforward matter to combine pairs of such wave functions with the appropriate expression for the dipole moment to calculate reliable transition intensities. This has been done by Clary and co-workers\textsuperscript{18,46} who combined more conventional radial basis set expansions with the assumption that the dipole moment of the complex was simply the projec-
tion of the permanent dipole of the monomer on the axis of the complex. While the radial parts of these integrals are quite straightforward to calculate, the angular factors can be quite complicated. However, Hutson has now presented general expressions for the angular factors due to permanent dipoles or quadrupoles on a component monomer molecule, or to charge-, dipole-, and quadrupole-induced contributions to the net dipole, and expressed these results in both space-fixed and body-fixed coordinates.

As a practical consideration, we note that storing the entire grid of values for each of the radial channel functions \( x_{nm}(R) \) could require a large amount of disk space. Fortunately, only a fraction of these values are needed for computing the overlap integrals required for defining the intensities. In the present studies, which mainly involve the lowest stretching states, a set of ten representative radial quadrature points proved sufficient. However, a more efficient approach would be to represent each of these radial functions by a modest set of distributed Gaussian functions.

C. Treatment of metastable or resonance states

Although the properties of truly bound states can be calculated to virtually any desired accuracy by the iterative approach described above, some approximations are required to deal with resonances. In general, there are two kinds of metastable behavior. The first involves “quasibound” or “tunneling predissociation” states associated with a given angular channel. These are states that lie above the asymptote associated with that monomer energy level \( E_n(j) \), but are bound by a potential barrier (usually centrifugal in origin) associated with the distortion potential \( V_d(R) \) [see Eq. (11)] for the dominant \( l \) channel. In this case, the predissociation rate is determined by the rate of tunneling through this effective one-dimensional potential barrier, and it tends to increase rapidly as the level is pushed towards and above the barrier maximum by increases in the orbital angular momentum.

The second type of metastable behavior is “Feshbach predissociation,” which occurs when an eigenstate associated with a given angular channel lies above the dissociation threshold \( E_n(j') \) of some other channel to which it is coupled by the intramolecular coordinate dependence of the intermolecular potential [i.e., by potential matrix elements \( V_{aa'}(R) \) off diagonal in \( J \)]. In this case, the level width is a measure of the degree of mixing of the metastable and continuum channel components of the wave function.

Quantitative radial basis set techniques for treating resonances do exist, but they require a series of calculations in which the basis sets are continuously adjusted, which makes them relatively tedious. More approximate techniques have been used by Choi and Light, but their accuracy was so low that they served only to distinguish between resonance states and unbound scattering states. On the other hand, perturbation theory techniques have proved quite successful for calculating resonance widths for moderately strongly coupled systems. These techniques are described below and implemented in our ISE method. While they are approximate, for the systems studied to date they are often accurate enough to allow quantitative comparisons between experimental linewidths and for values calculated in this way to contribute to the optimization of potential energy surfaces.

1. Quasibound levels and tunneling predissociation

For effectively one-dimensional isotropic molecular interactions, efficient and accurate techniques for calculating the energies and widths of quasibound levels are well developed. These involve the use of an Airy function boundary condition at the outermost classical turning point to determines the level energy, combined with a uniform semiclassical calculation of the tunneling rate to determine its width. The level widths obtained in this way are typically accurate to a few percent, while the level energies are accurate to within a few percent of the width. This is as good as the accuracy with which the widths and positions of predissociation-broadened lines can be measured experimentally, and hence is more than sufficient for present purposes.

As in earlier work in this laboratory, quasibound levels of van der Waals complexes may be treated by using these same techniques to define the energies and (basis) eigenfunctions of the associated zeroth-order (distortion potential) basis function solutions to Eq. (25). The ISE calculation then proceeds as usual. Upon convergence, the tunneling level width is obtained by performing the usual one-dimensional uniform semiclassical calculation at the converged energy on the potential barrier associated with the distortion potential for the dominant \( l \)-channel contributing to the wave function.

2. Feshbach resonances

In order to calculate the energy and width of Feshbach resonances, a two-step procedure is employed. First, a bound-state calculation is carried out as described above, with all open channels omitted from the basis set. The shift and broadening of the resulting eigenstate due to interaction with open channel states is then calculated using a Feshbach formalism as described and implemented in earlier work on the SEPT method. The level width part of this procedure is essentially a golden rule calculation, and both it and the level shift calculation involve a sum over the independent contributions from all open channels.

As in the quasibound level calculations, the errors in the resulting level shifts are expected to be a fraction of the widths, while the calculated widths are usually accurate to within a fraction of their size. The main exceptions to this situation will occur when the shifts and widths are made extremely small because the open channel asymptote lies so far below the state of interest that the integrals in question are dominated by oscillatory cancellation effects, a type of situation often associated with vibrational predissociation. When this occurs, these golden rule widths may be more than an order of magnitude in error, and the same could be true of the level shifts. However, in this case, the true
values of both will be so small that they would have little
effect on the observed spectroscopic line positions or
widths, the latter being dominated by instrumental effects.
As a result, we have the fortunate situation that the
widths, the latter being dominated by instrumental effects.

Some reassuring tests of the accuracy of these proce-
dures have been reported\textsuperscript{37,38} and others will be presented
below. The fact that these metastable states may be readily
accounted for within the same framework as the truly
accounted for within the same framework as the truly

D. Variations and details of the ISE method

We have examined several variants of the ISE method.
The basic procedure described in Sec. III B is straightforward
for a single state, but there is considerable redundancy
when calculations are to be performed for two or more \( \{n,l\} \) states corresponding to the same values of \( J \), \( j \),
and \( \rho \), where \( \rho \) denotes the atomic stretching quantum
number associated with the state of interest. For each of those
states, one starts with the same basis set of \( k \) radial func-
tions for each angular channel and solves the same secular
equation problem. In the next step, a correction function
for each channel is computed for each of the states of
interest and used to augment the basis used in the new
secular equation problem for that state. However, the cor-
rection functions for a given channel calculated for the
different \( \{n,l\} \) states generally are very similar in form,
and the several independent \( \{n,l\} \) calculations usually give
effectively the same eigenvalues for all of the other states
associated with that \( \{J,j,\rho\} \).

To exploit these observations, a “no recontraction”
(see below) variant of the method was developed in which
results for all states associated with a particular \( \{J,j,\rho\} \)
are calculated at the same time, using common radial
bases. To choose the most appropriate basis-augmenting
function for each channel, a correction function is calcu-
lated from Eq. (30) for each of the \( m=\{n,l\} \) states of
interest and used to generate the associated perturbation
theory energy correction.\textsuperscript{38} The one which causes the larg-
est energy shift is then deemed the most representative, and
it is incorporated in the radial basis for this channel used in
subsequent calculations. As it is by definition orthogonal to
all of the existing basis functions, this approach is expected
to converge for all of these \( \{n,l\} \) states, in spite of the fact
that the correction function incorporated on each iteration
is really “ideal” for only one of them.

A remaining concern is associated with the size of the
arrays which have to be stored in the course of a calcula-
tion. If there are \( k \) initial basis functions for each of \( N \)
angular channels, after \( c \) cycles of iteration the program
would have to store and deal with \( N \times (k+c) \) individual
radial basis functions. When \( N \) is large, this tends to re-
quire inconveniently large amounts of memory and makes
the method somewhat unwieldy. One way of reducing this

problem is to “recontract” the basis set after the secular
equation part of each cycle, and we have investigated both
complete and partial contraction procedures.

In complete contractions, the radial contributions to
the wave function of Eq. (12) are combined after each
secular equation step to form a single contracted basis
function for each channel

\[
\tilde{\phi}_{m}^{(k+1)}(R) = \sum_{n=1}^{k+2} c_{nm}^{k} \phi_{n}^{R}(R),
\]

(32)

where \( \phi_{n}^{R}(R) \) is the orthonormalized function constructed
from the correction function \( \chi_{m}^{(k)}(R) \). As the iteration
procedure continues, the order of the Hamiltonian matrix re-
mains \( 2N \) with the two basis functions for each channel
being \( \phi_{1}^{R}(R) = \tilde{\phi}_{m}^{(k)}(R) \), the contracted function yielded
by the previous cycle, and the new correction function for that
channel generated from Eq. (30). Of course, this approach
is applicable only when one is interested in the lowest van
der Waals stretching state. However, it has proved to be
very efficient for dealing with the \( n = 0 \) states of both Ar-
HCl and the He complexes considered below.

We have also investigated the use of partial contrac-
tion, where the \( k \) initial radial functions are retained in
the basis, but the iteratively generated correction functions are
recontracted into a single basis function following each
secular equation step. In this case, the order of the Hamil-
tonian matrix grows from its initial value of \( N \times k \) to
a maximum of \( N \times (k+2) \) on the second and all subsequent
iterations. In the later iterations, the basis functions for
each channel are the \( k \) initial functions, the contracted
correction function obtained on the previous iteration

\[
\tilde{\phi}_{k+1}^{(m)}(R) = \sum_{n=1}^{k+2} c_{nm}^{k} \phi_{n}^{R}(R)
\]

(33)

plus the new correction function generated from Eq. (30),
which yields the new \( \phi_{k+2}^{(m)}(R) \) function.\textsuperscript{71} When this
approach was implemented for the \( k = 1 \) case, it was found to be
no more effective than the full recontraction procedure
described above. However, it may prove somewhat more
useful when \( k > 2 \).

A third problem which sometimes arises, particularly
with the recontraction variants of the method, is that of
keeping track of the state being calculated as the iteration
proceeds. This is not a problem if one simply wishes to
solve for all states and simulate the overall spectrum. How-
however, it does become a concern when individual lines are
assigned and fits to the simulated spectrum are being used
to improve the potential energy surface. The problem oc-
curs because each time the secular equation is solved many
eigenvalues are produced, and the solution(s) of interest
must be properly and consistently identified if convergence
is to be achieved. We have experimented with several pos-
sible algorithms for carrying out this identification.

A method that works well when \( j \) and \( l \) are reasonably
good quantum numbers (Bratoz and Martin's “case 1"
complexes\textsuperscript{13,72}) is to select the solution having the greatest
contribution from the initial basis function for the channel
of interest, which has the appropriate number of radial
nodes. This procedure can break down if there is very strong mixing between basis functions, in which case, an alternative scheme is required. However, it was effective for the Ar–HCl calculations described below, and in any case, all complexes become case 1 at a sufficiently high total angular momentum,\textsuperscript{12} so this may be the single most generally useful scheme. Another possible approach would be to assume that the energy ordering of the matrix eigenvalues preserved the identity of a solution from one iteration cycle to the next. However, the best method is system dependent and may also depend on the recontraction scheme used (if any).

A few other points regarding our implementation of the ISE method should be noted. Eigenvalues and eigenfunctions of the linear homogeneous differential equation (25) were generated using a standard subroutine package,\textsuperscript{62} based on that developed by Cooley,\textsuperscript{61} which uses a Numerov integration procedure. The linear inhomogeneous equation of Eq. (30) is also solved with a Numerov integration scheme, using the linear inhomogeneous differential equation (LIDE) subroutine developed by Hutson.\textsuperscript{56,63} Finally, the effect of applying the kinetic energy operator to the radial functions $\chi_{m\alpha}(R)$ in Eq. (28) is computed using a fourth-order finite-difference method. Thus, all three methods are fourth order.

IV. TESTS AND ILLUSTRATIVE APPLICATIONS OF THE ISE METHOD

A. Applications to Ar–HCl

A number of features of the ISE method are now illustrated by applications to the Ar–HCl bimer, which has become a prototype system for calculations on anisotropic van der Waals complexes. The first detailed calculations of the eigenstates of Ar–HCl were performed by Dunker and Gordon\textsuperscript{73} in order to test four previously proposed\textsuperscript{74} anisotropic (two-dimensional) potential energy surfaces for this system. A number of improved potentials based largely on spectroscopic data have been reported since,\textsuperscript{75–79} all but one of which considered only the two-dimensional ($R$ and $\theta$) nature of these surfaces. The most recent and most accurate of these surfaces\textsuperscript{79} takes account of the dependence on the diatom bond length indirectly by allowing the potential parameters to depend on the mass-reduced vibrational quantum number of the diatom. However, since more extensive comparative results are available for Hutson’s earlier $H6(3)$ surface,\textsuperscript{78} the latter was used in the present calculations.

Hutson has reported close coupling calculations of a range of properties of eigenstates of the $H6(3)$ surface, which have come to be benchmark or reference points for other computational methods.\textsuperscript{18,50} Clary and Nesbitt used “conventional” radial basis set methods to perform calculations for states of total angular momentum up to 25, and they also reported detailed simulations of the associated infrared spectra.\textsuperscript{18} The eigenvalues they obtained were converged to 0.001 cm$^{-1}$ for some of the lower states, but to only 0.02 cm$^{-1}$ on average.\textsuperscript{50} Choi and Light demonstrated the power of the DVR method by performing calculations on bound and resonance states of this system for selected $J$’s up to 60.\textsuperscript{50} Their bound state eigenvalues were converged to 0.0001 cm$^{-1}$, but their widths for the resonance states showed dependence on the position at which the flux operator is evaluated, and had uncertainties of the order of a factor of 4. In any case, this body of results certainly justifies use of this Ar–HCl potential as a benchmark system.

It should be remembered that the present ISE implementation uses space-fixed coordinates. For Ar–HCl, it is commonly accepted that body-fixed coordinates are more appropriate since the projection of the total angular momentum on the axis of the complex is a nearly good quantum number, at least for states of low-to-moderate total angular momentum. A body-fixed implementation should thus be more efficient for this case, particularly with respect to the problem of following the eigenstate(s) of interest during the iteration procedure. Thus, the effectiveness of the method as implemented here is perhaps a further indication of its strength.

The ISE calculations on Ar–HCl described below included all rotational channels of appropriate parity for $J_{\text{max}} \leq 7$. The numerical integration utilized a radial interval from 2 to 15 Å and a step length of 0.04 Å. Numerical quadratures were used to express Hutson’s $H6(3)$ potential as an 11-term linear Legendre expansion [see Eq. (7)]. For the states considered, these conditions are sufficient to allow absolute convergence to 0.0001 cm$^{-1}$.

1. Calculations for individual bound states

We begin by examining the convergence behavior of the method using the “no-recontraction” variant of the ISE procedure, with one initial basis function per channel. For the ground $j=l=J=0$ state (square points) and the lowest state for $j=l=J=1$ (triangular points). Fig. 1 shows how the error in the calculated energies depends on the total number of radial basis functions used for each channel $k_{\text{max}}$ (the number of iterative ISE cycles being
TABLE I. For two states on the H6(3) potential surface for Ar–HCl (Ref. 78), comparison of energies (in cm⁻¹) yielded by no-recontraction ISE calculations with those obtained using "conventional" vibrational basis sets (see the text), as a function of the total number of radial basis functions per channel $k_{\text{max}}$.

<table>
<thead>
<tr>
<th>$k_{\text{max}}$</th>
<th>ISE basis</th>
<th>Vibrational basis</th>
<th>ISE basis</th>
<th>Vibrational basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−116.5237</td>
<td>−116.524</td>
<td>−83.5717</td>
<td>−83.572</td>
</tr>
<tr>
<td>2</td>
<td>−117.7182</td>
<td>−117.388</td>
<td>−83.7665</td>
<td>−83.667</td>
</tr>
<tr>
<td>3</td>
<td>−117.8127</td>
<td>−117.708</td>
<td>−83.7712</td>
<td>−83.728</td>
</tr>
<tr>
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<td>−117.787</td>
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</tr>
<tr>
<td>5</td>
<td>−117.8214</td>
<td>−117.808</td>
<td>−83.7713</td>
<td>−83.760</td>
</tr>
<tr>
<td>6</td>
<td>−117.8214</td>
<td>−117.814</td>
<td>−83.7713</td>
<td>−83.763</td>
</tr>
</tbody>
</table>

$k_{\text{max}} - 1$). The solid points joined by solid lines are the results for ISE calculations, where the additional basis functions (those for $k > 1$) were generated by solving Eq. (30). The resulting ground-state energy is converged to $10^{-3}$ cm⁻¹ after four cycles of iteration, while for the $J=1$ state, the same accuracy is achieved after only three iterations. This improved convergence for the latter case may reflect the trend towards free internal rotor behavior with increasing $j$. In these calculations, largest matrix diagonalized was approximately $40 \times 40$.

The linear logarithmic convergence of the ISE results seen in Fig. 1 is typical of results yielded by this method. This suggests that improved eigenvalue accuracy may be obtained by extrapolation on a plot of this type, and an extrapolation procedure based on this behavior has been implemented in our ISE code. Of course, this correction is not applied unless the eigenvalue correction decreases monotonically from one iteration to the next, but this almost always occurs, especially with larger numbers of iterations. For all of the states considered by Choi and Light with stretching quantum numbers $n=0$ and 1, the present approach converged to their result within four iterations when this extrapolation procedure was applied.

For the sake of comparison, Fig. 1 also shows the convergence behavior of "conventional" matrix method calculations using fixed direct-product bases in which the radial basis functions were ordinary vibrational eigenfunctions of the distortion Hamiltonian of Eq. (25). These results are plotted as open points joined by dashed lines. The energies computed using these "vibrational" basis sets are compared to the ISE results for the same radial basis set sizes (denoted by $k_{\text{max}}$) in Table I. It is clear that the ISE basis set is far more efficient, and it is not clear that the vibrational basis results will ever converge.

The reason for the poorer convergence behavior achieved with the conventional vibrational basis sets is illustrated by the differences between the two sets of radial basis functions for the ground $j=l=0$ state seen in Fig. 2. The heavy solid curve labeled $n=0$ is the lowest energy eigenfunction of the distortion potential, which is the initial radial basis function common to both procedures. The dashed curves are then the radial wave functions for the higher vibrational levels of that distortion potential, which were successively added to the conventional vibrational basis.

sis. The solid curves labeled cor($i$) are the orthonormalized basis functions generated from the correction functions $\chi^{(i)}(R)$ yielded by the first three iterations of the ISE method. While each cor($i$) function has the same qualitative structure as the vibrational wave function for $n=i$, the two sets of functions have markedly different overall radial behavior. In particular, the nodes of the ISE functions lie at relatively smaller distances and their inner loops have relatively greater amplitudes. The origin of these functions makes it clear that this behavior is required to represent accurately the true radial channel function $\chi_{\text{rad}}(R)$, and it is evident that the vibrational basis will only very slowly (if ever) become able to represent this short range behavior. This ability to generate basis functions which extend into the classically forbidden region of the basis-generating potential is one of the strengths of the ISE method.

As another test of the efficiency of the present procedure, ISE calculations were compared with those performed using Hutson's close coupling program BOUND for the lowest bound state of Ar–HCl associated with total angular momentum values ranging from $J=0$ to 8. The same 11-term Legendre expansion for the potential and the same angular bases were used in both sets of calculations. The states of interest all correlate with $j=0$, and since the angular basis set is truncated at $J_{\text{max}}=7$ (see above), the number of angular channels does not increase beyond $J=7$, where it reaches $N=36$. Both approaches employed the same equally spaced grid of points to describe the radial behavior of the system, and the implementations we compared both use a space-fixed coordinate representation.

Both the ISE and coupled channel methods are solved iteratively in an attempt to satisfy a predetermined convergence criterion, although the ISE calculations also utilized the extrapolation procedure mentioned above. The comp-
TABLE II. For \( j=0, n=0, l=J \) states on the \( H6(3) \) potential surface for Ar–HCl (Ref. 78), comparison of eigenvalues and CPU times required to obtain converged results using the full-recontraction ISE method and using Hutson’s close coupling program BOUND (Ref. 34).

<table>
<thead>
<tr>
<th>Number of channels</th>
<th>CPU time(s)</th>
<th>Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J )</td>
<td>BOUND</td>
<td>ISE</td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>34</td>
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<tr>
<td>3</td>
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<td>58</td>
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<td>87</td>
</tr>
<tr>
<td>5</td>
<td>33</td>
<td>115</td>
</tr>
<tr>
<td>6</td>
<td>35</td>
<td>139</td>
</tr>
<tr>
<td>7</td>
<td>36</td>
<td>160</td>
</tr>
<tr>
<td>8</td>
<td>36</td>
<td>144</td>
</tr>
</tbody>
</table>

mon convergence criterion, the difference between the energy after successive iterations, was fixed at \( 10^{-2} \) cm\(^{-1}\), and the resulting energies were accurate to at least \( 10^{-3} \) cm\(^{-1}\). The initial ISE basis consisted of a single radial function per channel, and a variant of the method using full recontraction after each correction step was employed. The time taken by the coupled-channel calculation depends on the externally supplied initial guess for the energy (no such initial guess is needed by the ISE method). Since the BOUND calculations were usually found to require four iterations for initial guesses in error by 0.1 to 1 cm\(^{-1}\), whenever this was not so, the actual computation times were scaled to make them correspond to values for four iterations in order to make the results presented below internally consistent. Similarly, the times reported for the ISE method all assume four correction iterations.

The eigenvalues and computational times determined in this way using the ISE and BOUND methods are compared in Table II and the times are plotted in Fig. 3. While the speeds of the two methods are comparable for small numbers of channels, the time required by the ISE calculations grows much more slowly with the size of basis. Thus the present method appears to be much more efficient than coupled channel calculations for large angular basis sets.

2. Calculation of Infrared spectra

Infrared spectra of the Ar–HCl complex have been calculated using a "no-recontraction" variant of the ISE method, in which the radial basis size for each angular channel increases with each ISE iteration, and all states associated with a given monomer eigenvalue \( j \) and \( J \) and \( p \) are obtained simultaneously. The formulas used for the intensities are those given by Clary and Nesbitt in their calculations of the infrared spectra of rare gas–hydrogen halide complexes.\(^{18}\)

Figure 4 shows a spectrum for Ar–HCl calculated for a temperature of \( T=10 \) K, while including total angular momentum states up to \( J=40 \), with the two most intense bands being shown on expanded scales in the inserts; the abscissa scale shows frequencies relative to the HCl vibrational band origin. In view of the low temperature, this calculation considered only absorption from sublevels associated with \( j=0 \) and in the ground van der Waals stretching state. The calculation included transitions to states associated with \( j=0, 1, \) and 2, and van der Waals stretching quantum number \( n=0 \) and 1, so the initial radial basis consisted of two functions per angular channel. The energy levels obtained were accurate to at least 0.002 cm\(^{-1}\), as confirmed by comparison with the energies of Choi and Light\(^{50}\) and by more extensive convergence tests with our program. These results are considerably more accurate than those of Clary and Nesbitt.\(^{18}\)

The efficiency of the present ISE procedure is illustrated by consideration of a version of this calculation which was scaled down to make it approximately equiva-
lent to a computation for Ne–HCl reported by Clary and Nesbitt. In our approach, an independent calculation is needed for each set of values of $J$, $j$, and $p$, but for each of these cases, all $(n_l,l)$ eigenstates are obtained simultaneously. Thus, each calculation for $j=0$ yields two eigenstates, while those for $j=1$ and 2 yield, respectively, two or four, and four or six (depending on parity) eigenstates. (Recall, however, that the angular basis contains channels up to $j_{\text{max}}=7$.)

In view of its shallower well and smaller reduced mass, Ne–HCl will have fewer bound states than Ar–HCl, so these calculations considered only total angular momentum quantum numbers up to $J=25$. Clary and Nesbitt reported that a calculation of this size for Ne–HCl required three hours on a VAX 8600. Using our implementation of their method, an Ar–HCl calculation of this same size (i.e., with $J_{\text{max}}=25$) required 90 min on one processor of our Silicon Graphics 4D/340 computer, and yielded eigenvalues accurate to $(\text{average}) 0.02 \text{ cm}^{-1}$. In contrast, calculating this same spectrum using the ISE method required only 60 min on this same computer, and the associated eigenvalues were accurate to $\sim 0.002 \text{ cm}^{-1}$. In general, increasing the accuracy of a fixed radial basis set calculation (such as that of Clary and Nesbitt) by an order of magnitude would require a massive increase in the number of basis functions, which very greatly increase its cost. Thus, for quantitative calculations of high accuracy, the ISE method appears to have substantial advantages over fixed basis set methods.

In spite of this success, substantial further improvements in the efficiency of our implementation of the ISE method may be possible. For example, the fact that highly accurate results for $j=2$ states are usually obtained from calculations for $j=0$ or $j=1$ states, which couple to $j=2$ channels, suggests that it may not be necessary to perform independent calculations for states with the same $J$ and $p$, but different values of $j$. This and other possible improvements are under investigation.

### B. Applications to predissociating helium complexes

While it is perhaps the most extensively studied (rare gas)–(hydrogen halide) system, other than the abrupt breakoff at $J=60$ in the 127 K rotational spectrum seen by Howard and Pine, there have been no direct observations of Ar–HCl line broadening due to predissociation. On the other hand, in the high resolution spectra of He–HF reported by Lovejoy and Nesbitt, 11 of the 14 observed lines involve transitions to metastable states and are clearly broadened. Thus, helium complexes seem particularly appropriate systems to use for studying the reliability of schemes for treating metastable levels. As a result, tests are reported below for He–HF, as defined by the HDF1–M2 potential energy surface of Lovejoy and Nesbitt, and for He–C$_2$H$_4$, using the HDF-type potential of Danielson et al.

All of these calculations assume a rigid-rotor model for the molecular component of the complex, so only tunneling predissociation and Feshbach predissociation by internal rotation can occur. The approximate treatment of Feshbach predissociation used by the ISE method is known to be at best semiquantitative for the very much slower process of vibrational predissociation, in which the internal vibration of the rotor couples to the radial ($R$) degree of freedom. However, these processes are usually so slow that measurable line broadening arising from it is very difficult to observe.

Table III compares the energies and widths of all bound and metastable levels of the He–HF complex (with widths $<0.5 \text{ cm}^{-1}$) calculated using the full recontraction version of the ISE method, with those obtained by Lovejoy and Nesbitt. Their bound state energies were generated using a version of Clary’s fixed radial basis set program, while their results for metastable states were generated using conventional close coupling calculations. In this table, quasibound resonances are identified by the superscript “$F$,” and Feshbach resonances by the superscript “$F$.” The second to last column in the table shows the discrepancy in the resonance energies yielded by the ISE method as a fraction of the exact (close coupling) resonance widths $\Gamma_{\text{e}}$, while the last column is the ratio of the ISE widths to those yielded by the close coupling calculations.

For metastable states, close coupling techniques are conventionally assumed to be exact, and it is gratifying to see that the ISE method gives metastable level energies accurate to within a few percent of the width, and widths which are typically only 10% too small. These discrepancies are distinctly smaller than the experimental uncertainties in the positions and widths of these broadened lines, so our method is entirely adequate for use in least-squares fits to improve this potential energy surface. Moreover, the entire ISE calculation required less than one minute of central processing unit (CPU) time on our Silicon Graphics 4D/340.

As an illustration of the importance of the effect of the open channels on these resonance energies, Table III also lists the total perturbation theory corrections to the level energies obtained in this way $\Delta E^F_{\text{ISE}}$. These shifts are roughly the same size as the widths themselves, which makes them an order of magnitude larger than the errors in the resulting corrected energies. This shows that the open-channel level shift correction is a very important part of the ISE treatment of resonance states, since without it, the eigenvalue errors would be of the order of the level width, which would make it difficult to utilize such levels in fits to optimize a potential energy surface. It is also important to remember that all aspects of the spectrum for this system—frequencies, widths, and intensities—are produced by a single method. Overall, therefore, the ISE method is very well suited for use with extremely weakly bound, but moderately strong-anisotropy systems such as this.

While the He–HF results are very encouraging, we must report that the ISE method is not always that successful, at least not as implemented at present. This point is illustrated by Table IV, which compares the resonance energies and widths for the metastable states of the recently proposed DMKD potential energy surface for He–
TABLE III. The bound and resonance states of the HFJDI-M2 potential surface for He–HF as calculated by Lovejoy and Nesbitt using a matrix method for the bound states and close coupling calculations for the resonances (Ref. 81), and by the ISE method. ΔE_{ISE} is the Feshbach level shift due to the open channels. F is the Feshbach resonance and Q is the quasibound resonance.

<table>
<thead>
<tr>
<th>State (Jf-Jp)</th>
<th>Lovejoy and Nesbitt</th>
<th>Full-recontraction ISE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (cm⁻¹)</td>
<td>Γ∞ (cm⁻¹)</td>
</tr>
<tr>
<td>(000 -)</td>
<td>-7.347</td>
<td>...</td>
</tr>
<tr>
<td>(011 -)</td>
<td>-6.572</td>
<td>...</td>
</tr>
<tr>
<td>(022 -)</td>
<td>-3.043</td>
<td>...</td>
</tr>
<tr>
<td>(033 -)</td>
<td>0.812</td>
<td>...</td>
</tr>
<tr>
<td>(044 -) +0.01</td>
<td>0.003</td>
<td>0.039²</td>
</tr>
<tr>
<td>(111 -)</td>
<td>30.725</td>
<td>0.144F</td>
</tr>
<tr>
<td>(101 -)</td>
<td>31.124</td>
<td>0.118F</td>
</tr>
<tr>
<td>(112 -)</td>
<td>32.109</td>
<td>0.091F</td>
</tr>
<tr>
<td>(123 -)</td>
<td>33.776</td>
<td>0.067F</td>
</tr>
<tr>
<td>(134 -)</td>
<td>36.124</td>
<td>0.045F</td>
</tr>
<tr>
<td>(145 -)</td>
<td>39.071</td>
<td>0.026F</td>
</tr>
<tr>
<td>(121 -)</td>
<td>34.508</td>
<td>0.018F</td>
</tr>
<tr>
<td>(132 -)</td>
<td>36.565</td>
<td>0.030F</td>
</tr>
<tr>
<td>(143 -)</td>
<td>39.294</td>
<td>0.033F</td>
</tr>
<tr>
<td>(111 +)</td>
<td>34.112</td>
<td>b</td>
</tr>
<tr>
<td>(122 +)</td>
<td>35.597</td>
<td>b</td>
</tr>
<tr>
<td>(133 +)</td>
<td>37.736</td>
<td>b</td>
</tr>
<tr>
<td>(144 +) 40.371</td>
<td>0.019Q</td>
<td>...</td>
</tr>
</tbody>
</table>

¹Treated as a bound state in Ref. 81. ²Truly bound level whose predissociation is parity forbidden. ³Reference 81.

C₂H₂,¹⁷,²⁺ as generated by the full-recontraction ISE method, and by close coupled calculations using MOLSCAT.³⁰

For the Feshbach resonances of He–C₂H₂, the errors in the ISE energies are on average ~ 1/5 of the resonance widths. While more than twice as large as those for He–HF, these discrepancies are still a small fraction of the width itself (for most cases), which means that meaningful fits to experimental data can be based on ISE calculations of the frequencies of transitions involving such states. In contrast, the errors in ISE energies of tunneling-predissociation levels range from zero to nine times the actual width, which makes it inappropriate to include transitions involving such levels in fits, unless these widths are quite small (which is often the case here).

TABLE IV. Resonance states of the DMKD potential energy surface for He–C₂H₂ as calculated using the MOLSCAT close-coupling program (Ref. 30) and by the full-recontraction ISE method. ΔE_{ISE} is the Feshbach level shift due to the open channels. F is the Feshbach resonance and Q is the quasibound resonance.

<table>
<thead>
<tr>
<th>State (Jf-Jp)</th>
<th>Close coupling</th>
<th>Full-recontraction ISE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E{oc} (cm⁻¹)</td>
<td>Γ∞ (cm⁻¹)</td>
</tr>
<tr>
<td>(202 +)</td>
<td>0.582</td>
<td>0.06F</td>
</tr>
<tr>
<td>(055 )</td>
<td>0.729</td>
<td>0.03Q</td>
</tr>
<tr>
<td>(213 -)</td>
<td>1.417</td>
<td>0.13F</td>
</tr>
<tr>
<td>(211 -)</td>
<td>2.170</td>
<td>0.55F</td>
</tr>
<tr>
<td>(224 +)</td>
<td>2.348</td>
<td>0.16F</td>
</tr>
<tr>
<td>(222 +)</td>
<td>2.572</td>
<td>0.61F</td>
</tr>
<tr>
<td>(155 -)</td>
<td>2.839</td>
<td>0.004Q</td>
</tr>
<tr>
<td>(154 -)</td>
<td>3.238</td>
<td>0.12²</td>
</tr>
<tr>
<td>(220 +)</td>
<td>3.316</td>
<td>1.63F</td>
</tr>
<tr>
<td>(233 -)</td>
<td>3.711</td>
<td>0.47F</td>
</tr>
<tr>
<td>(235 -)</td>
<td>4.037</td>
<td>0.71F</td>
</tr>
<tr>
<td>(231 -)</td>
<td>4.485</td>
<td>0.101F</td>
</tr>
<tr>
<td>(244 -)</td>
<td>4.345</td>
<td>0.32F</td>
</tr>
<tr>
<td>(242 -)</td>
<td>6.185</td>
<td>0.70F</td>
</tr>
<tr>
<td>(255 -)</td>
<td>7.618</td>
<td>0.19FQ</td>
</tr>
<tr>
<td>(253 -)</td>
<td>7.889</td>
<td>0.03²Q</td>
</tr>
<tr>
<td>(254 -)</td>
<td>7.837</td>
<td>0.05Q</td>
</tr>
</tbody>
</table>
For Feshbach predissociation, the level widths generated from our ISE calculations are typically a factor of 2 too small, while for tunneling predissociation, this discrepancy becomes as large as a factor of 10. This would make it impossible to use such calculated widths in fits to experimental data. Thus, the present ISE procedure is able to identify these resonances and give their energies reasonably accurately, but is only able to provide a qualitative estimate of their width.

In view of the fact that He–HF and He–C$_2$H$_2$ have similar ground state energies ($-7.3$ vs $-6.2$ cm$^{-1}$) and similar numbers of levels, the quite different accuracies of the level width calculations for these two cases may seem somewhat surprising. However, the fact that (with one explainable exception$^{33}$) that the ISE widths are always too small suggests that there is a systematic reason for these discrepancies, and that they can be corrected for. Consideration of the manner in which the tunneling widths are calculated suggests both a reason for these errors and a possible way of reducing them.

For quasibound levels, the ISE method obtains the tunneling predissociation rate from a uniform semiclassical calculation of the permeability of the barrier on the isotropic “distortion” potential at the converged energy of the state in question. However, for strongly anisotropic systems, the size of the barrier to tunneling will tend to vary substantially with relative orientation, and most of the predissociation flux will occur at angles where the barrier is the smallest. Close coupling calculations take account of this fact implicitly, but the tunneling calculation in the (present) ISE program uses an angle-averaged potential which will have a larger barrier than that impeding most of the predissociation flux. This explains both why the present quasibound level widths are always too small,$^{33}$ and why the discrepancies are much larger for He–C$_2$H$_2$ than for He–HF, since the former’s larger Feshbach widths show that its potential anisotropy is much stronger.

While the situation for the Feshbach widths is more complicated, similar sorts of arguments should also apply, and efforts to improve the accuracy of the width calculations are under way. However, even at the present stage, the eigenvalue discrepancies are only a small fraction of the level widths, so this difficulty would not prevent use of transition frequencies involving such states in fits to optimize the potential energy surface.

V. DISCUSSION AND CONCLUSIONS

The iterative secular equation (ISE) method presented herein exploits the strengths of both the coupled channel and matrix methods. It focuses on the problem of finding the best possible compact basis representation of the exact radial channel functions $\chi_{m/l}(R)$ of Eq. (2). Calculations are performed for one or a few states at a time, and optimized numerical correction functions are determined for each radial channel function contributing to a given eigenstate. This optimization ensures that the size of the basis set remains modest and the wave functions obtained allow accurate simulation of spectra. Moreover, the computational effort grows relatively slowly with the number of channels and with the order of correction, so extensive accurate calculations are feasible for quite strongly anisotropic systems.

The results presented for Ar–HCl show that the method can converge reliably and efficiently for the bound states of such systems, and they suggest that it will prove to be more efficient than Hutson’s widely used close coupling code BOUND$^{34}$ for large numbers of coupled channels. Moreover, the ISE method gives wave functions which may be used for calculating transition intensities and other properties, while BOUND does not. The natural ability of the method to include some angular channels in the secular equation basis and treat more weakly coupled channels by perturbation theory is also an advantage not shared by close coupling techniques.

In its ability to treat metastable states, the method to date shows mixed success. For Feshbach resonances in both strong- and weak-anisotropy systems, it appears able to generate level energies accurate to within a small fraction of the level width, which allows transitions involving such levels to be included in least-squares fits to improve a trial potential energy surface. For the weak-anisotropy species He–HF, this is also true both for the widths of Feshbach resonances and the energies and widths of tunneling-predissociation levels. However, for the more strongly anisotropic species He–C$_2$H$_2$, the level widths obtained for both Feshbach and tunneling resonances are distinctly too small. A means of improving on the tunneling width calculation by determining a more appropriate estimate of the effective barrier to predissociation is currently being investigated, as are analogous possible improvements in the calculation of Feshbach widths. However, it is also important to recall that the energy and width of a particular resonance level do not have a unique definition, as Franck-Condon overlap arguments show that values for a given resonance yielded by different experiments may differ by a fraction of the width.

In any case, the ISE method is clearly an efficient new procedure for performing accurate calculations on van der Waals molecules, particularly for cases where many coupled channels must be considered. While it will certainly benefit from further development work, particularly with regard to its treatment of metastable states, its combination of high accuracy and relatively modest CPU requirements with the ability to provide wave functions and to treat weakly coupled channels by perturbation theory makes it a very promising tool.

APPENDIX A: CALCULATIONS OF ATOM PLUS VIBRATING ROTOR ENERGY LEVELS

The ISE procedure described above may be readily modified to handle the case of atom-plus-vibrating rotor or vibrating rotor-plus-vibrating rotor systems. In the following, we briefly summarize the changes necessary for the case of an atom-plus-vibrating diatom.

The essential changes are simply that the monomer Hamiltonian $\hat{H}_m$ and the potential energy function $V(R,\theta)$ in Eq. (1) will now also depend on the magnitude...
of the monomer bond length $r$, and that the internal motion basis functions $\{\Phi^{\text{IM}}_a\}$ will now also depend on the internal vibrational degree of freedom

$$\Phi^{\text{IM}}_a(\mathbf{R},r) = \mathcal{O}^{\text{IM}}_{ij}(\mathbf{R},\mathbf{r}) \Phi_{a_j}(r), \quad (A1)$$

where the channel label $a = (v, j, l)$ now also includes the monomer internal vibration quantum number $v$, and $\Phi_{a_j}(r)$ is a radial eigenfunction of the free-monomer Hamiltonian

$$\mathcal{H}^{\text{IM}}_m(\mathbf{r}) [\Phi_{a_j}(r)] \mathcal{O}^{\text{IM}}_{ij}(\mathbf{R},\mathbf{r}) = E^{\text{IM}}_m(v, j) \mathcal{O}^{\text{IM}}_{ij}(\mathbf{R},\mathbf{r}) \Phi_{a_j}(r) \quad (A2)$$

Subject to these new definitions of $a$ and $\Phi^{\text{IM}}_a$, the form of the coupled equations of Eq. (4) and of almost all of our subsequent formalism remains unchanged. The only remaining point concerns the specification of the potential matrix elements $V_{a',a}(R)$ or $V_{a',a}(R)$,

$$V_{a',a}(R) = V^{\text{IM}}_{a' a}(R) = \int d^2r \int d^2R \mathcal{O}^{\text{IM}}_{j'j}(\mathbf{R},\mathbf{r}) \mathcal{O}^{\text{IM}}_{ij}(\mathbf{R},\mathbf{r}) \times \int_0^\infty \phi_j(r') V(R,r,\theta) \phi_j(r) dr, \quad (A3)$$

which are in principle quite straightforward to evaluate.20

The main effect of the additional degree of freedom is that the number of coupled channels which must be considered simultaneously rises by a factor equal to the number of monomer vibrational states considered. Fortunately, in most cases this internal degree of freedom is very weakly coupled to the others, so that terms off diagonal in $v$ or due to more than one value of $v$ (at a time) need not be included in either the secular equation basis set or the sum over channels of the perturbed wave function of Eq. (26) or the coupling function of Eq. (28). Thus, its main effect is felt through the dependence of the diagonal potential terms $V_{a'a}(R)$ on $v$. Exceptions to this situation will arise if the vibrational predissociation becomes rapid enough to give rise to significant level broadening, but this is not the case in the detailed studies of fully resolved van der Waals molecule spectra reported to date.

ACKNOWLEDGMENTS

We are grateful to Dr. Jeremy M. Hutson for providing us with copies of his coupled channel bound-state program BOUND, of his subroutine for generating the $H_6(3)$ potential, and of his LIDE subroutine, and we are grateful to Claudio Chuaqui for many helpful discussions. Funding for this research has been provided by the Network of Centres of Excellence in Molecular and Interfacial Dynamics, one of the 15 Networks of Centres of Excellence supported by the Government of Canada.

Note that the "case 1" coupling within which the distortion potential is the most natural choice for \( F'(R) \) becomes most appropriate for all van der Waals molecules at sufficiently high values of \( \ell \) and \( J \) (Ref. 12).


\[ Note too that the "case 1" coupling within which the distortion potential is the most natural choice for \( F'(R) \) becomes most appropriate for all van der Waals molecules at sufficiently high values of \( \ell \) and \( J \) (Ref. 12). \]


\[ This expression differs slightly from Eq. (13) of Ref. 38 in that the second set of sums there should only run over the index \( \kappa \) and not also over the angular channels \( \omega \). \]


\[ Note that for \( \kappa > k \), the basis functions are specific to a given state \( m \), since they are obtained as solutions of Eq. (30). \]


\[ The last state listed in Table III is a quasibound level whose width will be very sensitive to the distance below the effective barrier maximum. For this relatively weak-anisotropy case, the ISE width should be quite accurate, and the larger value of \( \Gamma_{IE} \) merely reflects the fact that the close coupling energy is slightly lower than the ISE value. \]


