

The secular equation/perturbation theory method for calculating spectra of van der Waals complexes

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A new method for calculating vibrational wave functions and level energies for van der Waals molecules is proposed. It consists of a minimal secular equation calculation, including only strongly coupled basis functions, followed by perturbation theory corrections to take account of the effects of weakly coupled channels. The method is very efficient, and gives results accurate to $\pm 0.001 \text{ cm}^{-1}$ for Ar-H₂. It is also readily applicable to predissociating states of van der Waals molecules, and gives calculated level widths more accurate than any previous approximate method. The method obviates the resonance search problem associated with direct coupled channel methods for characterizing predissociating states, and is readily extendable to more strongly anisotropic systems.

I. INTRODUCTION

The infrared spectra of van der Waals molecules are of great importance in the determination of potential energy surfaces for atom-molecule and molecule-molecule systems. More than a decade ago, Le Roy and Van Kranendonk¹ used the infrared spectra of McKellar and Welsh² to determine a three-dimensional potential energy surface for Ar-H₂. Although other types of experimental data have since become available,³ the infrared spectra remain the most comprehensive single source of information on this important prototype system. More recently, with the advent of laser and molecular beam techniques, high-resolution infrared spectra have become available for systems such as (HF)₂,⁴ (CO₂)₂,⁵ and Ar-HCl;⁶ these data undoubtedly contain detailed information on the intermolecular potentials concerned, although the computational problems involved have so far prevented its extraction.

In order to determine an intermolecular potential from infrared spectra, the potential surface must be parametrized and the parameters determined by least-squares fitting to the experimental frequencies. The major problem is the calculation of the energy levels of the van der Waals complex from a trial potential surface; many methods exist for performing such calculations,⁷⁻²⁴ but there is an inevitable trade-off between accuracy and computational expense. The purpose of the present paper is to introduce a new approximate method which allows accurate van der Waals level energies to be calculated considerably more cheaply than was previously possible. The new method also gives a natural breakdown of the total energy and wave function into contributions from zeroth order and perturbing channels, so that it is easy to understand the physical effects determining the level energies and properties.

The need for a new method may be illustrated by considering the rare gas-H₂ systems, for which McKellar²⁵ has recently remeasured the infrared spectra at higher resolution and resolved many new lines. The "secular equation" (SE) method used for calculating level energies in earlier analy-

ses^{1,7,8} gave results accurate to $\pm 0.03 \text{ cm}^{-1}$, which was acceptable when interpreting the older infrared spectra, whose linewidths were around 0.5 cm^{-1} . However, such errors would obscure some of the information content of the most recent spectra, where the linewidths are about 0.1 cm^{-1} . If the basis set is extended to the point where the accuracy is acceptable, SE calculations become unwieldy, and prohibitively expensive for use in least-squares fitting of potential parameters. However, the secular equation/perturbation theory (SEPT) method described here provides the required accuracy at a very modest computational cost.

The structure of this paper is as follows. Section II describes the theoretical background, and Sec. III derives the new approximate method proposed here. Section IV describes our implementation of the method for the rare gas-H₂ complexes, and tests it by comparison with close-coupling calculations on Ar-H₂. Section V then describes the application of the method to the calculation of hyperfine frequencies, which also contain important information on the potential anisotropy for the rare gas-H₂ systems. A subsequent paper³ will describe the results of using this new method to fit potential energy surfaces to the best available experimental data for Ar-H₂, Kr-H₂, and Xe-H₂.

II. THEORETICAL BACKGROUND

After separating out the motion of the center of mass, the full Hamiltonian for a van der Waals complex may be written

$$H(\mathbf{R}, \mathbf{q}) = -(\hbar^2/2\mu)R^{-1}(\partial^2/\partial R^2)R + l^2/2\mu R^2 + V(R, \mathbf{q}) + H_i(\mathbf{q}), \quad (1)$$

where \mathbf{R} is the vector of length R joining the centers of mass of the monomers, \mathbf{q} represents their vibrational and rotational coordinates, $\mu = m_a m_b / (m_a + m_b)$ is the effective reduced mass associated with the interaction of monomers of masses m_a and m_b , l^2 is the angular momentum operator associated with the rotation of the unit vector $\hat{\mathbf{R}}$, and $H_i(\mathbf{q})$ is the sum of the vibration-rotation Hamiltonians of the isolated monomers.

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The exact eigenfunctions of this Hamiltonian may be expanded as

$$\psi_m^{JM}(\mathbf{R}, \mathbf{q}) = R^{-1} \sum_a \Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) \chi_{ma}^J(R), \quad (2)$$

where J and M are the quantum numbers for the total angular momentum and its space-fixed projection, and m is an index identifying a particular eigenstate of the system. The functions $\{\chi_{ma}^J(R)\}$ are the radial channel wave functions, and $\{\Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q})\}$ are a complete set of channel basis functions spanning the space of all coordinates except R , with quantum numbers collectively denoted a . The J and M labels will often be omitted from channel specifications in the following sections, and are to be taken to be included in a when not specified explicitly.

Substituting Eq. (2) into the total Schrödinger equation, premultiplying by $\Phi_{a'}^{JM}(\hat{\mathbf{R}}, \mathbf{q})^*$ and integrating over \mathbf{q} and $\hat{\mathbf{R}}$ yields the usual set of coupled equations for a van der Waals complex,

$$\sum_a \left[-\delta_{a'a} (\hbar^2/2\mu) d^2/dR^2 + U_{a'a}^J(R) - E_m^J \delta_{a'a} \right] \chi_{ma}^J(R) = 0, \quad (3)$$

where E_m^J is the total energy of the system and $U_{a'a}^J(R)$ are the matrix elements of the channel basis functions with the operator $U(\mathbf{R}, \mathbf{q})$,

$$U_{a'a}^J(R) = \langle a' | U(\mathbf{R}, \mathbf{q}) | a \rangle, \quad (4)$$

where

$$U(\mathbf{R}, \mathbf{q}) = l^2/2\mu R^2 + V(\mathbf{R}, \mathbf{q}) + H_i(\mathbf{q}), \quad (5)$$

and the Dirac bracket notation containing only channel labels implies integration over \mathbf{q} and $\hat{\mathbf{R}}$ but not R .

Sets of coupled equations such as Eq. (3) can be solved directly, using methods such as those of Dunker and Gordon,⁹ Shapiro,¹⁰ Johnson,¹¹ and Danby.¹² These procedures are accurate and reliable, but are usually too expensive to use in a least-squares fitting routine for determining potential energy surfaces, and are also difficult to automate to find specific bound states. It is therefore necessary to devise an alternative method which is both accurate and computationally inexpensive.

Approximate methods which have been used in the past fall into three main categories. First, there are methods based on distortion approximations,¹³⁻¹⁷ in which all off-diagonal terms in Eq. (3) are ignored. A distortion approximation alone is seldom adequate, and it is usual to reintroduce the off-diagonal terms using perturbation theory. The best way of doing this is by solving the Rayleigh-Schrödinger perturbation equation directly as a second-order inhomogeneous differential equation.¹⁸ This form of perturbation theory has the major advantage that the correction to the wave function is determined directly, rather than being represented by a sum over some inevitably incomplete radial basis set. Such distortion/perturbation approximations are qualitatively useful, but they are not sufficiently accurate when several channels lie close together or share the same threshold, as is the case for most states of atom-diatom van der Waals complexes.

The second category consists of the secular equation

(SE) methods, which are based on straightforward matrix diagonalization in a basis set formed from products of angular and radial functions.^{1,7,8,19} These give good results if convergence with respect to the basis set of radial functions is fast; for example, in previous work on determining potential energy surfaces for rare gas-H₂ systems,^{1,7,8} it was found to be sufficient to include only one radial basis function in each channel. However, such a restricted basis set does not give results accurate enough to account for high resolution spectra, and the SE methods become quite expensive when many radial functions must be included.

Thirdly, there are "adiabatic" methods, which attempt to find a "best" basis set for describing the angular motion at each value of the intermolecular distance R .²⁰⁻²⁴ These methods have proved very useful for the ground states of highly anisotropic systems such as Ar-HCl^{22,23} and (HF)₂,²⁴ but the nonadiabatic correction terms are too large for them to be useful for the rare gas-H₂ systems.¹⁶ The adiabatic methods are also not very accurate for excited states of the van der Waals bending and stretching vibrations, so that they will be of limited use in interpreting infrared spectra.

III. THE SEPT METHOD

The method proposed here first uses a minimal secular equation calculation to deal accurately with couplings between nearby channels, and then uses the "linear inhomogeneous differential equation" (LIDE) form of perturbation theory¹⁸ to take account of functions not included in the original basis set. This procedure will be referred to as the "secular equation/perturbation theory" (SEPT) method.

We choose the basis set for the SE calculation as a (small) set of eigenfunctions of the distortion Hamiltonian H^D ,

$$H^D = \sum_a |a\rangle \langle a| \left(-\hbar^2/2\mu \right) R^{-1} (d^2/dR^2) R + U(\mathbf{R}, \mathbf{q}) |a\rangle \langle a|, \quad (6)$$

where the projection operator $|a\rangle \langle a|$ projects onto channel a . The eigenfunctions of this Hamiltonian will be denoted $\psi_{an}^D(\mathbf{R}, \mathbf{q}) = R^{-1} \Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) \chi_{an}^J(R)$, and are represented in Dirac notation as $|an\rangle$. The functions $\{\chi_{an}^J(R)\}$ are easily calculated from the diagonal channel potentials $U_{aa}^J(R)$ using the Cooley algorithm.²⁶

The secular equation Hamiltonian may be written

$$H^{\text{SE}} = H^D + H^M, \quad (7)$$

with

$$H^M = \sum_{an} \sum_{a'n'} (1 - \delta_{a'a}) |a'n'\rangle \langle a'n'| U(\mathbf{R}, \mathbf{q}) |an\rangle \langle an|, \quad (8)$$

where sums over a and n are restricted to the product functions to be explicitly included in the basis set. This convention will be used throughout this paper, wherever indices a and n (with or without primes) are summed over simultaneously. Thus H^{SE} includes the off-diagonal terms between the product functions in the basis set, as well as all the diagonal terms in the Hamiltonian. The difference H' between H^{SE} and the exact Hamiltonian H is due solely to the trunca-

tion of the sums in Eq. (8). The eigenvalues of H^{SE} are denoted E_m^{SE} , and its eigenfunctions are

$$\psi_m^{\text{SE}}(\mathbf{R}, \mathbf{q}) = R^{-1} \sum_{an} c_{man} \Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) \chi_{an}^J(R). \quad (9)$$

If the remainder of the total Hamiltonian, $H' = H - H^{\text{SE}}$, is now reintroduced by Rayleigh-Schrödinger perturbation theory, the equation defining $\psi_m^{(1)}$, the first-order correction to ψ_m^{SE} , is

$$(H^{\text{SE}} - E_m^{\text{SE}}) \psi_m^{(1)} = -(H' - E_m^{(1)}) \psi_m^{\text{SE}}. \quad (10)$$

Since H' has no matrix elements between the secular equation basis functions, $H' \psi_m^{\text{SE}}$ is orthogonal to all of them. Consequently, $E_m^{(1)}$ is zero, and $\psi_m^{(1)}$ is also orthogonal to the basis functions. Equation (10) thus reduces to

$$(H^D - E_m^{\text{SE}}) \psi_m^{(1)} = -H' \psi_m^{\text{SE}}. \quad (11)$$

In terms of explicit channel functions, $H' \psi_m^{\text{SE}}$ may be written

$$H' \psi_m^{\text{SE}} = R^{-1} \sum_a \Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) g_{ma}(R), \quad (12)$$

where

$$g_{ma}(R) = \sum_{a'n'} (1 - \delta_{aa'}) U_{aa'}^J(R) c_{ma'n'} \chi_{a'n'}^J(R) - \sum_{a'n''} \chi_{a'n''}^J(R) \sum_{a'n'''} \int \chi_{a'n'''}^J(R') \delta_{a'a} \times (1 - \delta_{aa'}) U_{aa'}^J(R') c_{ma'n'''} \chi_{a'n'''}^J(R') dR'. \quad (13)$$

The second term in this equation simply ensures that the result is orthogonal to any SE basis functions in channel a . If we now write

$$\psi_m^{(1)}(\mathbf{R}, \mathbf{q}) = R^{-1} \sum_a \Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) \chi_{ma}^{(1)}(R), \quad (14)$$

then projecting Eq. (11) onto each perturbing channel in turn yields the uncoupled equations

$$\left[(-\hbar^2/2\mu) d^2/dR^2 + U_{aa}^J(R) - E_m^{\text{SE}} \right] \chi_{ma}^{(1)}(R) = -g_{ma}(R). \quad (15)$$

All the functions contributing to $g_{ma}(R)$ are known once the secular equation problem has been solved. Thus Eq. (15) may be solved for each channel function $\chi_{ma}^{(1)}(R)$ in turn, using the numerical method described in Ref. 18. The second-order perturbation correction to the SE eigenvalue is simply given by

$$E_m^{(2)} = \int \psi_m^{\text{SE}} H' \psi_m^{(1)} d\tau = \sum_a g_{ma}(R) \chi_{ma}^{(1)}(R) dR. \quad (16)$$

This procedure allows nearby perturbing channels to be accurately accounted for, even if they are strongly coupled to the zeroth-order channel. For well-separated channels (such as those differing in v), it is not necessary to include any basis functions explicitly in the diagonalization, and the second term in Eq. (13) vanishes. If the channel separation is large compared to the van der Waals stretching frequency, the appropriate correction function $\chi_{ma}^{(1)}(R)$ may be approximated¹⁸:

$$\chi_{ma}^{(1)}(R) = \frac{-g_{ma}(R)}{U_{aa}^J(R) - U_m^{\text{eff}}(R)}, \quad (17)$$

where $U_m^{\text{eff}}(R)$ is some "effective" potential for the zeroth-order state. This approximation is particularly useful for evaluating the small shifts due to channels with asymptotic energies which differ considerably from that of the zeroth-order state, since it is then appropriate to make the further approximation

$$\chi_{ma}^{(1)}(R) = \frac{-g_{ma}(R)}{E_{vj} - E_{v'j'} + (\hbar^2/2\mu) [l(l+1) - l'(l'+1)]}, \quad (18)$$

where E_{vj} and $E_{v'j'}$ are the monomer vibration-rotation level energies corresponding to the perturbing and zeroth-order channels, and l and l' are their respective end-over-end angular momenta.

Open channels require careful treatment, particularly if the width due to predissociation into them is important. Two situations may be distinguished: the state of interest may itself be quasibound, in which case E_{an}^D lies above the dissociation threshold of the supporting channel potential; or the effect of an open perturbing channel may be required. These situations will be treated separately below, although they often occur together.

In the first case, where the zeroth-order channel is open, little modification to the scheme described above is necessary. Quasibound solutions of H^D may be defined using an Airy function boundary condition at the third turning point R_t ²⁷; these solutions are then treated as being square-integrable on the range $0 < R < R_t$, and simply used as basis functions $\chi_{an}^J(R)$ in the SEPT calculation. The only difference in procedure from the bound state case is that there is now a contribution to the width from tunneling through the centrifugal barrier; this may be calculated using a uniform semiclassical approach, which in the single-channel case gives widths accurate to a few percent.²⁷ Such a treatment of quasibound levels is in principle approximate in the SEPT framework, for two reasons. First, the Airy function boundary condition may yield resonance energies in error by up to 20% of the tunneling width, even in the single channel case,²⁷ and any such error is naturally propagated into the SEPT results. Secondly, the use of the Airy function boundary condition collapses bound state character which was originally spread over the resonance width to a single central energy, and such an approximate treatment may have effects on the SE eigenvalues. However, as will be seen below, the resulting errors in level energies and widths are only a fraction of the widths themselves.

The case of open *perturbing* channels also requires careful consideration, even if a large part of their effect is taken into account by including a quasibound basis function in the SE diagonalization as described above. For the open channel case, Eq. (15) has continuum solutions, which cannot be obtained by the method of Ref. 18. However, it is still possible to obtain the width and shift contributions using a Green's function method, as described in Ref. 16. The outgoing Green's function for (open) channel a is²⁸

$$G_a^+(R, R') = -\pi (RR')^{-1} \\ \times [\chi_a^r(R) \chi_a^i(R') + i \chi_a^r(R) \chi_a^r(R')] , \quad \text{for } R < R' \\ G_a^+(R, R') = -\pi (RR')^{-1} \\ \times [\chi_a^i(R) \chi_a^r(R') + i \chi_a^r(R) \chi_a^i(R')] , \quad \text{for } R > R' . \quad (19)$$

where $R^{-1} \chi_a^r(R)$ and $R^{-1} \chi_a^i(R)$ are the independent regular and irregular eigenfunctions of the distortion Hamiltonian H^D for channel a at energy E_m^{SE} , normalized to delta functions of energy. This Green's function may be used to solve Eq. (15) for the open channel case, giving

$$\chi_{ma}^{(1)}(R) = - \int G_a^+(R, R') g_{ma}(R') dR' . \quad (20)$$

The width and shift contributions from channel a , Γ_{ma} and Δ_{ma} , may then be obtained from²⁸

$$\Gamma_{ma} = -2 \text{Im } \bar{\mathcal{E}}_{ma} , \quad (21)$$

$$\Delta_{ma} = \text{Re } \bar{\mathcal{E}}_{ma} , \quad (22)$$

where $\bar{\mathcal{E}}_{ma}$ is just the contribution to $E_m^{(2)}$ from channel a [Eq. (16)], which is now a complex quantity

$$\bar{\mathcal{E}}_{ma} = \int g_{ma}(R) \chi_{ma}^{(1)}(R) dR . \quad (23)$$

When written explicitly in terms of $\chi_a^r(R)$ and $\chi_a^i(R)$, this gives the usual Golden Rule expression for the width

$$\Gamma_{ma} = 2\pi \left[\int g_{ma}(R) \chi_a^r(R) dR \right]^2 , \quad (24)$$

while the shift breaks down into two terms,

$$\Delta_{ma} = -\pi \int g_{ma}(R) \chi_a^i(R) \\ \times \left[\int_0^R \chi_a^r(R') g_{ma}(R') dR' \right] dR \\ - \pi \int g_{ma}(R) \chi_a^r(R) \\ \times \left[\int_R^\infty \chi_a^i(R') g_{ma}(R') dR' \right] dR . \quad (25)$$

Equation (25) is not expensive to evaluate numerically, requiring only two passes through the equally spaced R array. The regular function $\chi_a^r(R)$ and the first integral over R' are evaluated and stored at the mesh points on the first (outwards) pass, and then $\chi_a^i(R)$, the second integral over R' , and the integrals over R are performed on the second (inwards) pass. In the present work, $\chi_a^r(R)$ and $\chi_a^i(R)$ were calculated numerically, by Numerov integration. This is in contrast to earlier work,^{16,17} where the uniform Airy approximation was used, and allows the widths and shifts due to perturbing channels with centrifugal barriers to be treated properly. This was not possible previously, since the uniform Airy approximation cannot be applied when the supporting potential has three classical turning points.

This procedure for calculating the level shift achieves the same advantage for the open channel case as the LIDE method provides for closed channels. All (bound and continuum) levels of the perturbing channel are implicitly included in a single operation, so that the question of convergence of a radial basis set does not arise.

IV. RESULTS FOR Ar-H₂

The rare gas-H₂ van der Waals complexes are weakly anisotropic systems whose eigenstates are well described by space-fixed quantum numbers. Their states are characterized by the total angular momentum J , the diatom vibration and rotation quantum numbers v and j , the end-over-end angular momentum of the complex l , and the stretching quantum number of the van der Waals bond n . The rigorously conserved quantities (neglecting nuclear hyperfine effects) are J and the parity $p = (-)^{j+l}$, but the other quantum numbers are also nearly conserved. The appropriate channel basis functions are thus products of H₂ vibration-rotation eigenfunctions and space-fixed total angular momentum eigenfunctions, $\Phi_a^{JM}(\hat{\mathbf{R}}, \mathbf{q}) = r^{-1} \phi_{vj}(r) \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$.

The states observed in the spectra of the rare gas-H₂ systems are all $n = 0$ van der Waals stretching states, with H₂ in states correlating with $v = 0$ and 1 and $j \leq 3$. The dominant coupling occurs between zeroth-order states of the same n but different l within each (v, j, J) manifold. We have therefore implemented the scheme described in Sec. III as follows: for each total J , parity p , and diatom (v, j) level, the $n = 0$ eigenvalues and eigenfunctions of the distortion Hamiltonian [Eq. (6)] are calculated using the Cooley method.²⁶ The SE Hamiltonian matrix is then constructed in a basis set consisting of these $n = 0$ levels (including quasibound levels, if any) for all allowed values of l . This matrix (which is no bigger than 4×4) is then diagonalized to obtain the SE eigenvalues $\{E_m^{\text{SE}}\}$ and eigenvectors $\{c_{man}\}$. The additional contributions due to the channels so far included are then evaluated using Eqs. (13), (15), and (16), with the numerical method of Ref. 18, and those due to the open channels using Eqs. (24) and (25). Finally, the shifts due to closed channels differing in j and/or v and due to open channels differing in v are calculated from Eqs. (18) and (16), and the widths and shifts due to open channels differing in j are calculated using Eqs. (24) and (25).

The fundamental constants used in the present work are summarized by the single number $\hbar^2/2 = 16.857\,630$ amu cm⁻¹ Å². The matrix elements of the H₂ stretching coordinate ξ between vibration-rotation functions, $\langle v, j | \xi^k | v', j' \rangle$, were calculated from the potential curve of Schwartz and Le Roy;²⁹ these matrix elements and the H₂ level energies used here are listed in Ref. 30. For Ar-H₂, the effective reduced mass was taken to be 1.918 865 04 amu, and the differential equations were solved on an equally spaced radial mesh of 183 points from $R = 2.2$ to 9.5 Å.

In order to test this method, we have performed calculations on states of Ar-H₂ correlating with H₂ in its $v = 1$, $j = 2$ level. These are the excited states involved in the $S_1(0)$ band of the Ar-H₂ spectrum, which is the band most sensitive to the potential anisotropy. The calculations described below use the $BC_3(6, 8)$ potential of Le Roy and Carley,⁸ for which close-coupling calculations of these levels have been performed previously.¹⁶ In order to allow direct comparison with the results of Ref. 16, the basis sets used in this test were restricted to channels correlating with H₂ in $v = 1$, with $j = 0$ and 2. However, the effects of extending the basis set were also examined, and will be described later in this sec-

TABLE I. Comparison of distortion (D), secular equation (SE), and secular equation/perturbation theory (SEPT) level energies and widths with the close-coupling (CC) results of Ref. 16, for Ar-H₂ ($v=1, j=2$) levels on the $BC_3(6, 8)$ potential of Ref. 8. These calculations include only those channels correlating with H₂ ($v=1, j=0$) and ($v=1, j=2$). Level energies are given in cm⁻¹ relative to the $v=1, j=2$ threshold of H₂.

l	J	E_m^D	E_m^{SE}	E_m^{SEPT}	E_m^{CC}	Γ_m^{SEPT}	Γ_m^{CC}
0	2	-23.028	-23.234	-23.239	-23.238	0.0393	0.0394
1	1	-22.671	-22.685	-22.653	-22.653	0.0546	0.0530
1	3	-22.127	-22.239	-22.238	-22.237	0.0414	0.0414
2	0	-20.801	-20.801	-20.728	-20.727	0.1126	0.1103
2	2	-19.470	-19.292	-19.310	-19.311	0.0235	0.0235
2	4	-20.006	-20.083	-20.078	-20.078	0.0420	0.0420
3	1	-17.293	-17.279	-17.244	-17.243	0.0556	0.0551
3	3	-16.011	-15.927	-15.942	-15.943	0.0237	0.0237
3	5	-16.770	-16.829	-16.822	-16.823	0.0411	0.0411
4	2	-12.879	-12.852	-12.828	-12.828	0.0410	0.0408
4	4	-11.617	-11.567	-11.580	-11.580	0.0219	0.0219
4	6	-12.482	-12.530	-12.523	-12.523	0.0388	0.0388
5	3	-7.537	-7.508	-7.489	-7.490	0.0322	0.0319
5	5	-6.288	-6.253	-6.265	-6.265	0.0191	0.0191
5	7	-7.214	-7.252	-7.249	-7.249	0.0351	0.0351
6	4	-1.347	-1.319	-1.306	-1.306	0.0246	0.0244
6	6	-0.129	-0.103	-0.113	-0.113	0.0156	0.0156
6	8	-1.080	-1.115	-1.109	-1.109	0.0298	0.0298
7	5	5.465	5.489	5.498	5.496	0.0687	0.0647
7	7	6.576	6.594	6.589	6.580	0.1596	0.1484
7	9	5.677	5.649	5.656	5.651	0.0825	0.0766
8	6	12.761	12.783	12.792	12.633	1.234	1.088
8	8	13.933	13.950	13.950	13.654	1.951	1.587
8	10	12.954	12.931	12.936	12.763	1.335	1.140

tion; fully converged basis sets were used in the actual fitting of potential surfaces.³

The SEPT results for both level energies and widths are compared with the close-coupling results in Table I. It may be seen that the largest error in the level energies is about 0.001 cm⁻¹ for levels which cannot predissociate by tunneling, and a fraction of the width for those which can. The larger error for quasibound states simply reflects the errors inherent in the Airy function boundary condition method for locating quasibound states.²⁷ The calculated widths are also accurate to about 1% except for the quasibound states. This accuracy is entirely adequate for performing fits to McKellar's most recent infrared spectra,²⁵ which have esti-

mated errors in the line positions of less than 0.02 cm⁻¹. The complete set of calculations summarized in Table I took only 24 s on a VAX 11/750.

As mentioned above, the shifts due to perturbing channels differing in v and j also requires investigation. The SEPT level energies may be broken down into a sum of a zeroth-order (secular equation) part and contributions from different perturbing channels

$$E_m^{SEPT} = E_m^{SE} + E_m^l + E_m^{j-} + E_m^{j+} + E_m^{v-} + E_m^{v+}. \quad (26)$$

Here, E_m^l is the contribution from channels of the same v and j as the zeroth-order state, excluding those ($n=0$) levels

TABLE II. Contributions of different perturbing channels to level energies for representative states of Ar-H₂ ($v=1, j=2$).

l	J	E_m^{SE}	E_m^l	E_m^{j-}	E_m^{j+}	E_m^{v-}	E_m^{v+}	E_m^{SEPT}
0	2	-23.2342	-0.0282	0.0237	-0.0138	0.0059	-0.0137	-23.2603
2	0	-20.8006	0.0	0.0721	-0.0153	0.0079	-0.0190	-20.7549
2	1	-20.2406	0.0	0.0	-0.0136	0.0056	-0.0128	-20.2613
2	2	-19.2917	-0.0332	0.0150	-0.0101	0.0038	-0.0083	-19.3245
2	3	-19.1745	-0.0172	0.0	-0.0105	0.0037	-0.0081	-19.2066
2	4	-20.0832	-0.0193	0.0240	-0.0134	0.0058	-0.0135	-20.0996
4	2	-12.8522	-0.0051	0.0291	-0.0123	0.0057	-0.0134	-12.8481
4	3	-12.0809	-0.0171	0.0	-0.0100	0.0039	-0.0086	-12.1127
4	4	-11.5670	-0.0273	0.0146	-0.0088	0.0034	-0.0075	-11.5926
4	5	-11.6377	-0.0165	0.0	-0.0094	0.0034	-0.0075	-11.6676
4	6	-12.5301	-0.0148	0.0216	-0.0120	0.0052	-0.0121	-12.5421

already in the SE basis set; E_m^{j-} is the contribution from channels with $v' = v$ and $j' < j$ (only $j' = j - 2$, which gives open channels, contributes in the present case); E_m^{j+} is the contribution from channels with $j' > j$ (again, only $j' = j + 2$ contributes in the present case); and E_m^{v-} and E_m^{v+} are the contributions from channels with $v' < v$ and $v' > v$, respectively.

Examples of these different contributions to the level energies of Ar-H₂ ($v = 1, j = 2$) on the BC₃ (6, 8) potential are given in Table II. Apart from zeros arising from the absence of perturbing channels in certain categories, all the sources of level shifts are significant compared to the experimental uncertainty. As might be expected, the largest of the correction terms are those involving coupling to excited van der Waals stretching states within the same (v, j) manifold. The lack of cancellation between E_m^{v-} and E_m^{v+} is at first sight surprising; it arises because the diatom matrix elements $\langle v, j | \xi^k | v', j' \rangle$ are very different for $v' = v + 1$ and $v' = v - 1$. This is true even for a harmonic oscillator: for example, the harmonic oscillator matrix element $\langle v, 0 | \xi | v + 1, 0 \rangle$ is proportional to $(v + 1)^{1/2}$, so that the negative shift due to perturbing channels of higher v will tend to be larger than the positive shift due to those of lower v . Thus the overall level shift due to perturbing channels off-diagonal in v is always likely to be negative.

V. HYPERFINE SPECTRA

The hyperfine spectra of van der Waals molecules provide valuable additional information on the anisotropy of the intermolecular potential. For the rare gas-H₂ systems, proton hyperfine spectra have been observed by Waaier and Reuss,³¹ and a method for calculating the spectra, based on a limited secular equation calculation, has been described by Waaier *et al.*³² However, the SEPT procedure provides a rather more efficient means of calculating the spectra, and also takes account of some contributions neglected by Waaier *et al.*

For complexes of ortho-H₂ with rare gases, the total nuclear spin of the H₂ molecule ($I = 1$) couples with the total mechanical angular momentum J to form a resultant F which can take values $J - 1, J$, and $J + 1$. States of the same v, j, l , and J , but different F , are split by the hyperfine Hamiltonian H^{HF} , and transitions between them with $\Delta F = \pm 1$ are allowed.

The hyperfine Hamiltonian may be written as a sum of spin-spin and spin-rotation terms,

$$H^{\text{HF}} = H^{\text{SS}} + H^{\text{SR}}. \quad (27)$$

The matrix elements of H^{SS} and H^{SR} in the space-fixed basis set have been given in Ref. 32. They are diagonal in F and its space-fixed projection M_F , and are independent of M_F :

$$\begin{aligned} \langle j l J M_F | H^{\text{SS}} | j' l' J' M_F \rangle &= \delta_{ll'} \delta_{JJ'} (-1)^{l+F} \frac{1}{2} d \\ &\times [30(2j+1)(2j'+1)(2J+1)(2J'+1)]^{1/2} \\ &\times \begin{Bmatrix} J & J' & 2 \\ 1 & 1 & F \end{Bmatrix} \begin{Bmatrix} J & J' & 2 \\ j' & j & l \end{Bmatrix} \begin{pmatrix} j & 2 & j' \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned} \quad (28)$$

$$\begin{aligned} \langle j l J M_F | H^{\text{SR}} | j' l' J' M_F \rangle &= \delta_{ll'} \delta_{JJ'} (-1)^{l+F+j+1} c \\ &\times [6(2J+1)(2J'+1)(2j+1)j(j+1)]^{1/2} \\ &\times \begin{Bmatrix} J' & J & 1 \\ 1 & 1 & F \end{Bmatrix} \begin{Bmatrix} J & J' & 1 \\ j & j & l \end{Bmatrix}. \end{aligned} \quad (29)$$

For H₂, the spin-rotation and spin-spin coupling constants c and d are³³

$$\begin{aligned} c &= 113.904 \text{ kHz}, \\ d &= 288.355 \text{ kHz}. \end{aligned} \quad (30)$$

The resulting matrix elements are typically 10⁵ times smaller than the smallest separation between different $n = 0$ levels for Ar-H₂, so that effects which are second order in H^{HF} are completely negligible. The hyperfine energy of a state may thus be evaluated simply by calculating the expectation value of H^{HF} over the SEPT wave function. Expanding this by perturbation theory in orders of H' yields

$$\langle H^{\text{HF}} \rangle^{\text{SEPT}} = \sum_k \langle H^{\text{HF}} \rangle^{(k)}, \quad (31)$$

where the leading terms are

$$\langle H^{\text{HF}} \rangle^{(0)} = \int \psi_m^{\text{SE}} H^{\text{HF}} \psi_m^{\text{SE}} d\tau, \quad (32)$$

$$\langle H^{\text{HF}} \rangle^{(1)} = 2 \int \psi_m^{\text{SE}} H^{\text{HF}} \psi_m^{(1)} d\tau, \quad (33)$$

$$\langle H^{\text{HF}} \rangle^{(2)} = \int \psi_m^{(1)} (H^{\text{HF}} - \langle H^{\text{HF}} \rangle^{(0)}) \psi_m^{(1)} d\tau. \quad (34)$$

Each of these simplifies considerably when written in terms of explicit channel functions. Since ψ_m^{SE} is restricted to components with $j = 1$, differing only in l , and H^{HF} has no matrix elements off-diagonal in l , the zeroth-order term simplifies to

$$\langle H^{\text{HF}} \rangle^{(0)} = \sum_{an} c_{an}^2 W(l, J, F), \quad (35)$$

where l and J are the quantum numbers corresponding to channel a , and

$$W(l, J, F) = \langle 1 l J M_F | H^{\text{HF}} | 1 l J M_F \rangle. \quad (36)$$

The first-order correction has no contribution from perturbing channels with $j = 1$, since $\chi_{ma}^{(1)}(R)$ is orthogonal to all the $\{\chi_{an}^j(R)\}$ functions included in the SE basis set for channel a , and H^{HF} has no matrix elements off-diagonal in l . However, there are matrix elements of H^{SS} connecting channels of the same l and J but different j (only $j = 3$ contributes here). The first-order correction thus takes the form

$$\begin{aligned} \langle H^{\text{HF}} \rangle^{(1)} &= 2 \sum_{ln} c_{m1ln} Y(l, J, F) \\ &\times \int \chi_{1ln}^j(R) \chi_{m3ln}^{(1)}(R) dR, \end{aligned} \quad (37)$$

where the subscripts a have been explicitly replaced by j, l , and J , and

$$Y(l, J, F) = \langle 1 l J M_F | H^{\text{SS}} | 3 l J M_F \rangle. \quad (38)$$

The second-order correction formally contains contributions from perturbing channels with $j = 1$ and 3, but in practice only those for $j = 1$ are significant. Once more, since H^{HF} has no matrix elements off diagonal in l , the second-order term reduces to

TABLE III. Calculated hyperfine frequencies for Ar-H₂ ($v = 0, j = 1$) using the $BC_3(6, 8)$ potential (kHz).

l	J	F	F'	SE	First-order corr.	Second-order corr.	SEPT	Ref. 31 (calc)	Ref. 31 (expt)
0	1	0	1	495.61	0.0	-0.045	495.56	497.12	489.94(15)
0	1	1	2	37.92	0.0	-0.015	37.90	38.42	35.92(15)
1	2	1	2	304.78	0.255	-0.034	305.00	305.15	303.68(15)
2	1	2	1	114.33	-0.045	-0.017	114.27	114.77	112.30(15)
2	3	2	3	264.65	0.254	-0.034	264.87	264.89	264.25(15)

$$\langle H^{\text{HF}} \rangle^{(2)} = \sum_T [W(l, J, F) - \langle H^{\text{HF}} \rangle^{(0)}] \times \int [\chi_{m'l}^{(1)}(R)]^2 dR. \quad (39)$$

For the five hyperfine transitions of Ar-H₂ observed experimentally by Waaijer and Reuss, the contributions of these different terms, calculated using the $BC_3(6, 8)$ potential, are listed in Table III. It may be seen that the first-order correction terms are larger than the experimental uncertainties, so that it is important to include them. There are significant discrepancies between the calculated and experimental values; since the hyperfine frequencies are directly dependent on the anisotropy of the potential for an atom interacting with H₂ ($v = 0, j = 1$), it would clearly be desirable to include them when performing least-squares fits to determine potential energy surfaces.

The hyperfine frequencies calculated by Waaijer and Reuss³¹ for the $BC_3(6, 8)$ potential are given in Table III for comparison. They differ from the present results by up to 1.7 kHz, which is more than 10 times the experimental uncertainty. There are several reasons for this. First, our SE basis consists of eigenfunctions of the distortion Hamiltonian, whereas theirs consists of eigenfunctions of the central Hamiltonian (neglecting anisotropic terms). Thus, some contributions which appear in their formulation to arise from couplings to excited van der Waals stretching states are accounted for in zeroth order here. Their calculations on the $BC_3(6, 8)$ potential did not include such excited states, although the formalism of Waaijer *et al.*³² would have allowed them to. Our procedure of evaluating the effects of $n > 0$ functions by perturbation theory is essentially equivalent to a secular equation calculation using a fully converged radial basis set. Secondly, Waaijer *et al.* neglected the first-order terms involving perturbing states with $j = 3$; as seen above, this results in small but not negligible errors. Thirdly, the "Carley" potential used by Waaijer and Reuss differed somewhat from the $BC_3(6, 8)$ potential used here, since they used only the " $k = 0$ " term and did not carry out the proper vibrational averaging over the $v = 0, j = 1$ state of H₂.

VI. CONCLUSION

We have developed a new theoretical method for calculating level energies of van der Waals molecules. The method uses perturbation theory to correct for the incompleteness of a small "secular equation" calculation. It thus eliminates the main deficiency of secular equation methods, which is that it is usually necessary to include a large number of relatively unimportant functions in the basis set to achieve conver-

gence. The new method is very efficient, and gives results in good agreement with close-coupling calculations for Ar-H₂. It is readily extendable to more strongly anisotropic systems, simply by choosing a secular equation basis set consisting of whichever distortion eigenfunctions lie close in energy to the state of interest. This basis set will always be much smaller than that required for convergence of a simple secular equation calculation, so the new method will always give a considerable saving in computer time.

The method is applicable to both bound and predissociating states of van der Waals complexes. It does not suffer from the search problems associated with the direct numerical solution of coupled equations. The method also makes it relatively easy to identify the parentage of a particular state, and to gauge the importance of coupling to individual perturbing channels. This feature of the method will be particularly valuable when the wave functions are used to calculate molecular properties involving expectation values and spectroscopic intensities.

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