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Variationally exact rovibrational spectra of nonrigid triatomics: The HeHF van der Waals molecule

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A variationally exact method of obtaining the rovibrational levels of triatomic potentials is presented. This LC-RAMP method derives from the close-coupling approach in body-fixed coordinates, but uses optimized Morse oscillator functions to give radial basis sets for both the diatomic and complex stretching coordinates. The method is suited to the nuclear dynamics of nonrigid molecules and atom–diatom van der Waals complexes. A recent full interaction surface for HeHF is fitted and used for dynamical calculations. The binding energy of the complex increases slowly with HF vibrational excitation. Correlation between the HF and complex vibrational modes is found to be negligible.

I. INTRODUCTION

In a recent paper,[1] henceforth referred to as I, we developed a method for the solution of the rovibrational problem of "floppy" atom–diatom systems in body-fixed coordinates. Implicit in I and other theoretical works on the bound states of van der Waals dimers[2-8] is the assumption of separability between the (high frequency) vibrational mode(s) of the monomer (diatom) and the (low frequency) modes of the complex. This approximate separation is physically reasonable, but to our knowledge, has never been tested by full rovibrational calculations. Moreover, there must be some coupling between inter- and intramolecular modes in the dimer, but its magnitude and whether or not it stabilizes the dimer is still a matter for speculation. Furthermore, if calculations are to be performed on floppy triatomics it is necessary to have a method capable of treating all vibrational degrees of freedom.

Recently, Burton and Senff[9] have performed detailed *ab initio* calculations on the $(H_2)_2$ interaction potential. They obtained a van der Waals well deeper than those given by inverting a variety of empirical data and attributed this discrepancy to an increase in the vibrational zero point energy of the H_2 monomers upon complex formation. They suggest that this could effectively raise the rigid monomer potential by about 4 cm^{-1}. This effect can also be viewed as the destabilization of the dimer due to interaction with the monomer modes.

Much data on the bound states of van der Waals dimers have been obtained from combinations of dimer modes with monomer bands using infrared spectroscopy.[10,11] Typically, the diatom stretch is excited and the transitions of the complex are observed as sidebands to this intense transition. This technique is particularly powerful for the complexes of homonuclear diatomics where the complex formation itself causes the monomer band to become infrared active. In order to obtain information about the dimer potential from these infrared spectra, it is necessary to consider the effect of the monomer stretching coordinate. One approach is to fix the monomer bond lengths at suitable values.[11,12] A more sophisticated treatment was used by Le Roy and Van Kranendonk[3] to invert the experimental data on H_2-rare gas dimers. They fitted potential functions to several H_2 states (and isotopes) and thus were able to obtain potential energy surfaces (linearly) dependent on the H_2 bond length. However, they took no account of the possible correlation between monomer and complex rovibrational modes.

In this work, we extend the method developed in I for triatomic systems to include all three possible normal modes, with no separation. The method presented can be used to give rovibrational levels which are exact variational upper bounds, within the electronic Born–Oppenheimer approximation for the potential energy hypersurface. That is to say that the method does not depend on any perturbation like assumption that certain terms are small and therefore to be neglected.

The method is quite general for any triatomic system, but the coordinate system in which the Hamiltonian is expressed is specifically chosen to deal adequately with atom–diatom systems as close-coupled triatomics. Its form makes it particularly suitable, therefore, for considering atom–diatom van der Waals complexes and nonrigid systems of a similar kind, and in particular, for considering the vibration-rotation spectrum of HeHF.

Rodwell, Sin Fai Lam, and Watts[13] have recently calculated an extensive grid of potential points for the HeHF system. In this paper, we fit this with an appropriate analytic form and use it for a series of bound state rovibrational calculations which test the coupling of the HF stretch to the other modes of the complex.

In the next section we summarize the method of I and generalize it to the full triatomic problem. In Sec. III we discuss some computational aspects of these ro-

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vibrational calculations. In particular, we focus on diagonalization which is the bottleneck in dynamical calculations based on secular matrices. Sections II and III present a general computational technique for solving the nonrigid triatomic dynamical problem.

In Sec. IV we fit the HeHF surface. In Sec. V we present rovibrational calculations on He-rigid HF, the HF monomer, and the full HeHF system. Section VI gives our conclusions.

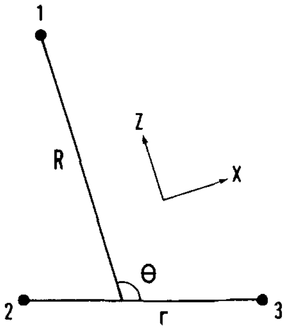

FIG. 1. Body-fixed coordinate system.

II. METHOD

In paper I we derived a Hamiltonian for the interaction of an atom with a diatom in body-fixed coordinates (see Fig. 1). In that paper we showed that a suitable trial function was of the form

$$\psi_J = \sum_{k=-J}^{J} \sum_{j,n} C^J_{jkn} \psi_n(r, R) \Theta_{jk}(\theta) \mathfrak{D}^J_{Mk}(\alpha, \beta, \gamma) . \qquad (1)$$

In equation (1) $\mathfrak{D}^J_{Mk}$ is a standard rotation matrix element[14] expressed in terms of the Euler angles α, β and γ, and Θ_{jk} is a standard associated Legendre polynomial[15] in the collision angle θ. Using this trial function we showed that it was possible to reduce the Hamiltonian for the problem to an effective radial-motion Hamiltonian In the present work, we have used a slightly different form for the functions of the Euler angles and θ than is given in Eq. (1). The form chosen here is

$$2^{-1/2}(\Theta_{jk}\mathfrak{D}^J_{Mk} + (-1)^p \Theta_{j-k}\mathfrak{D}_{M-k}), \quad k > 0 \qquad (2a)$$

and

$$\Theta_{j0}\mathfrak{D}^J_{M0} \qquad (2b)$$

which allows the functions to be grouped into parity eigenstates according to the value of p.

In terms of this choice, the radial motion Hamiltonian in the present work differs slightly from that shown in I and is given below:

$$\langle j'k' | \hat{H} | jk \rangle = \delta_{k'k}\delta_{j'j}\left[-\frac{\hbar^2}{2\mu_1 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2\mu_2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2}{2} j(j+1)\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right) + \hbar^2\frac{J(J+1)}{2\mu_1 R^2}\right] + \delta_{k'k}\langle \Theta_{j'k'} | V | \Theta_{jk} \rangle$$
$$- \hbar^2 \delta_{jj'}[\delta_{k',k} 2k^2 + \delta_{k',k+1} C^+_{Jk} C^+_{jk} (1+\delta_{k0})^{1/2} + \delta_{k',k-1} C^-_{Jk} C^-_{jk} (1+\delta_{k'0})^{1/2}]/2\mu_1 R^2 , \qquad (3)$$

with

$$C^{\pm}_{Jk} = (J(J+1) - k(k \pm 1))^{1/2} \qquad (4)$$

and

$$\mu_1^{-1} = m_1^{-1} + (m_2 + m_3)^{-1}, \quad \mu_2^{-1} = m_2^{-1} + m_3^{-1} . \qquad (5)$$

The only terms in the Hamiltonian that connect basis functions that differ in k are the last two terms in the last part of Eq. (3). These terms, which may be referred to as "Coriolis terms," have generally been found to be small[1,5,6,17] if the coordinate system has been chosen appropriately. If the off-diagonal Coriolis terms can be neglected then the secular problem becomes diagonal in k and states which differ only in parity become degenerate. This results in considerable computational savings, since it allows the secular problem for $J > 0$ to be block factorized into $2J+1$ blocks with no block larger than for the $J = 0$ case.

In paper I it was assumed that the diatomic variable r could be considered fixed, but in the present work this restriction is relaxed so that we work in a basis of *products* of radial functions

$$R^{-1}H_{n_1}(R) r^{-1} H_{n_2}(r) . \qquad (6)$$

Thus $\psi_n(r, R)$ is approximated by a linear combination of these products and thus the total trial function is a *l*inear *c*ombination of *r*adial and *a*ngular *m*omentum function *p*roducts, a type of function for which the acronym LC-RAMP was coined in a previous paper.[8] It was found in I that Morse oscillatorlike functions[18] described the motion in the R coordinate very well. Such functions would also seem to be eminently suitable for the description of the diatom in the r coordinate too, and were used in this work. It is the tradition, as explained in I, to specify these function in terms of sets of three parameters and in the present work two such sets will be needed, and are denoted as (D_1, ω_1, R_e) and (D_2, ω_2, r_e). Both sets are treated as adjustable for the purposes of basis set optimization. This makes it unnecessary to put artificial walls in the potential (see e.g., Ref. 20), as explained in I.

As in I, the potential V is expanded in the form

$$V(R, r, \theta) = \sum_\lambda V_\lambda(R, r) P_\lambda(\cos\theta) \qquad (7)$$

and the matrix elements of the potential in Eq. (3) are independent of the parity of the angular functions. The integrals over the angular functions can be done analytically and expressed in terms of the Gaunt coefficients, just as in I.

The procedures used for evaluating the integrals are straightforward generalizations of those described in I. As in that paper, all numerical integrations were done using Gauss–Laguerre quadrature[21] and the Laguerre polynomials were as defined in Ref. 19. The procedure was found to be just as satisfactory as it was found in I, even though the quadratures are, in the present case, all double quadratures.

III. COMPUTATIONAL CONSIDERATIONS

In traditional approaches[16] to the use of Eq. (3), the angular integration over the potential is completed and the resulting equations are regarded as a set of coupled differential equations. In the LC-RAMP approach it is computationally advantageous to perform the integrals over the radial variables in the potential first and to store the resulting, possibly long, list of integrals according to n_i, n_i' values for given λ. The integrals can then be read back once, sequentially, for each angular block of the problem to complete the sum over λ in Eq. (7) and obtain the matrix elements of the full potential. The other integrals in the problem can be dealt with exactly as described in I and there are no more problems in setting up the secular matrix than those described there. The two-dimensional Gauss–Laguerre quadrature scheme is computationally efficient and in the present case as in other LC-RAMP methods the major problems arise in diagonalizing the secular matrix.

In all LC-RAMP methods the size of the secular matrix generated provides a severe limitation on the problems that can be tackled since big secular problems must be solved by methods that involve the use of backing store (for instance tape or disk files). Although large secular problems are commonplace in CI calculations, the methods that have been developed in that context rely for their efficiency on the sparsity and diagonal dominance of the matrix. In the LC-RAMP approach, the matrices are not sparse, particularly if the full symmetry of the problem is used, and they are not generally dominated by their diagonal elements. There are certain special cases such as H_2–X systems (where X is a rare gas[1,3] or H[22]), where the matrices are diagonally dominant but they are too few to dictate a general choice of method. Furthermore, in CI calculations, one is usually interested only in the first one or two roots of the problem and the diagonalization methods used are efficient at this level. In LC-RAMP calculations, however, we are typically interested in the lowest ten or so roots and a CI diagonalization scheme may become very inefficient in these circumstances.

Mindful of these difficulties, we investigated four diagonalization procedures, all of which were designed to give the lowest k eigenvalues of an n dimensional symmetric matrix stored in triangular form. As a bench mark, we used the Householder tridiagonalization procedure followed by a bisected Sturm sequence.[23] We used this as bench mark because it is generally believed[24,25] to be the best method of solving the symmetric eigenvalue problem when the whole of the triangular matrix can be kept in fast store. The other three methods considered were the Shavitt–Raffenetti method of optimal relaxations[26] and two variants of the Lanczos procedure.[27,28] The Shavitt–Raffenetti method has found extensive use in CI calculations and its characteristics and properties are well described elsewhere.[29,30]

The Lanczos algorithm transforms the matrix into tridiagonal form in a cyclic fashion which means that the matrix need not be retained in core. Analytically, n iterations give a tridiagonal matrix equivalent to that given by the Givens or Householder transformations.[28] However, there are two important differences. Firstly, if only a few eigenvectors are required, it is not normally necessary to perform all n steps of the Lanczos process. Secondly, in computer applications, the Lanczos vectors rapidly lose orthogonality; this led Wilkinson to comment "it is difficult to think of any reason why we should use Lanczos' method in preference to Householder's."[31]

There are ways of circumventing this numerical problem. The traditional method is explicitly to orthogonalize each Lanczos vector to the previous one as it is generated. We refer to this method as orthogonalized Lanczos; it has the disadvantage, especially for sparse matrices, that the orthogonalization can greatly increase the time taken per cycle. Paige[32] analyzed the loss of orthogonality and developed a procedure adapted to the linear dependency displayed by the nonorthogonalized vectors. We call this Paige-style Lanczos; it has the drawback that convervence in n cycles is no longer guaranteed. There are also Lanczos algorithms based on selective orthogonalization of the Lanczos vectors,[30] but for reasons that will become apparent, we did not consider these. Both Lanczos algorithms yield tridiagonal matrices, the eigenvalues (and vectors) of which were found with a Sturm sequence using bisection and inverse iteration.[33]

Table I compares the performance of these diagonalization procedures on a 444 dimensional secular matrix (KCN with $J=1$, $p=0$, see I), with k (the required number of eigenvectors) = 10. This matrix took only 22 s to construct. In each case, at least ten figure accuracy for the eigenvalues was obtained. This accuracy is necessary for rotational transitions, which, in the case of KCN, are the differences between energies differing in only the sixth or seventh figures.

The Householder tridiagonalization plus Sturm sequence required just over 10 min to diagonalize this matrix and 800 K bytes of fast storage. In contrast, the Shavitt–Raffenetti method used 50 min and only 80 K bytes. A striking feature of the iterative procedures is the number of cycles required to achieve convergence, which is an order of magnitude greater than the number needed for the large, diagonally dominant CI matrices.[30]

The main difference between the Shavitt–Raffenetti and Lanczos processes is the time taken per cycle. Whilst the Lanczos algorithms perform only one vector matrix multiplication per cycle, independent of k, the Shavitt–Raffenetti method performs k such operations.

TABLE I. Comparison of diagonalization procedures for the ten lowest eigenvectors of a 444 dimensional secular matrix.. All timings are for an IBM 4341/2.

Method	Type	Starting vector(s)	Array area (K bytes)	Time per cycle (s)	Number of cycles	Total CPU time (s)
In core	Householder	...	797	...	...	608.7
Shavitt–Raffenetti	MOR[d,e]	a	86	19.1	156	2983.1
Lanczos	Paige style[f,g]	a	55	1.8	340	694.7
		b	55	1.8	340	698.3
	Orthogonalized	a	55	2.3[c]	220	551.3
		b	55	2.2[c]	220	545.0

[a] Unit vector(s) determined by the lowest diagonal element(s).

[b] Unit vector with $n^{-1/2}$ in every position.

[c] Cycle time increases with number of cycles, these values are averages.

[d] Reference 27.

[e] Reference 26.

[f] Reference 28.

[g] Reference 32.

This makes the Shavitt–Raffenetti procedure unattractive for cases such as ours where k is greater than 2.

Comparison between Paige-style and orthogonalized Lanczos processes shows that the reduced number of cycles required by the orthogonalized procedure more than compensates for the slight (average) increase in cycle time caused by the orthogonalization. Indeed, the orthogonalized Lanczos method proved to be faster in this case than the in core diagonalization. Because the increase in cycle time due to orthogonalization was small, we did not consider it necessary to investigate the use of selective orthogonalization.

Finally, we tested the effect of the starting vectors on the rate of convergence. The effect was to be negligible, probably because of the large number of cycles required to achieve convergence. Starting vectors of type b (see Table I) are generally favored as they allow all the matrix to be sampled immediately[28] and we have used these in our implementation of the orthogonalized Lanczos procedure.

Our LC-RAMP method for triatomics is implemented as a general computer program with the following features: Radial basis functions are set up using (D_1, ω_1, R_e) and (D_2, ω_2, r_e) as input parameters. The relevant M-point (M input) Gauss–Laguerre integration schemes are automatically generated and checked against analytic formulae for the sum of weights.[21] The angular basis set is taken as all functions for the selected J and p with $j \leq j_{\max}$ (input); for homonuclear diatomics, problems with j odd or even are treated independently. Options allow all Coriolis interactions to be computed or k to be treated as a good quantum number. The secular matrix is either retained in core (if possible) or written to disk and a choice of in core (Householder) or iterative (orthogonalized Lanczos) diagonalization is available.

A full account of and a listing of the program has been prepared by one of us (JT) for publication.[34] In Sec. V we describe the application of the program to a calculation of the rovibrational levels of He–HF, but first it is necessary to describe the fitting of the surface of Rodwell *et al.*[13] for this system.

IV. HeHF POTENTIAL ENERGY HYPERSURFACE

Rodwell *et al.*[13] performed several hundred SCF calculations[35] which gave them a grid of points in R, r, and θ for the HeHF surface. They fitted these points with a Legendre expansion [see Eq. (7)]. In this section we obtain a fully analytic representation of their SCF hypersurface by fitting an appropriate functional form for $V_\lambda(R, r)$.

Rodwell *et al.* used the hybrid Hartree–Fock SCF plus Damped Dispersion (HFD) method of Douketis *et al.*[36] to represent the dispersion forces which are neglected in an SCF calculation, thus

$$V_\lambda(R) = V_\lambda^{\mathrm{SCF}}(R) + \lambda^{\mathrm{DISP}}(R) . \tag{8}$$

The dispersion part of the surface is fully analytic and their HFD1 values (see Ref. 13) are used without further modification.[37]

Before obtaining a full hypersurface we fit the rigid-rotor result (r fixed at $1.7328a_0$) given by Rodwell *et al.* This is done using a standard fitting procedure for the SCF interaction surfaces of closed shell species[38,39] and we show how this can be generalized to the full three-dimensional surface.

The first step in fitting the rigid rotor SCF potential is to partition between long and short range interactions

$$V_\lambda^{\mathrm{SCF}}(R) = V_\lambda^{\mathrm{short}}(R) + V_\lambda^{\mathrm{long}}(R) . \tag{9}$$

At the SCF level, the long range interactions between neutral closed shell monomers is purely attractive and can be obtained from perturbation theory.

For HeHF, the long range induction forces are given by[40]

$$V_0^{\mathrm{long}}(R) = V_2^{\mathrm{long}}(R) = -\frac{\alpha_{\mathrm{He}}}{R^6}\,\mu_{\mathrm{HF}}^2 , \tag{10a}$$

$$2V_1^{\mathrm{long}}(R) = 3V_3^{\mathrm{long}}(R) = -\frac{36}{5}\,\alpha_{\mathrm{He}}\frac{\mathrm{HF}}{R^7}\Theta_{\mathrm{HF}} , \tag{10b}$$

TABLE II. Fitted coefficients $A_{\lambda i}$ for the short range part of the He–HF rigid rotor potential [Eq. (24)] in a.u.[a]

	$i=0$	1	2	3
$\lambda=0$	2.905 042 40	−1.758 714 98	−0.070 556 42	0.003 347 17
1	1.012 342 79	−1.396 333 53	−0.103 607 54	0.003 797 44
2	7.639 397 86	−6.295 872 47	1.110 519 87	−0.100 812 37
3	3.918 584 05	−3.289 399 62	0.292 443 25	−0.025 804 04
4	13.292 795 64	−11.001 758 21	2.226 629 46	−0.190 628 99
5	19.752 983 16	−15.591 595 96	3.195 656 11	−0.260 326 15
6	31.770 421 06	−24.021 548 52	5.086 739 42	−0.406 774 03
7	28.842 410 77	−21.437 144 97	4.386 388 90	−0.357 334 22
8	35.253 897 76	−27.092 543 25	5.845 643 66	−0.483 539 62

[a] 1 $a_0 = 0.529\,18$ nm; 1 hartree $= 2.1947 \times 10^5$ cm^{-1} $= 4.3598$ *aJ*.

where terms of order R^{-8} have been ignored. In Eqs. (10) α_{He} is the dipole polarizability of He, for which a value 1.38 a.u. was taken from the literature.[41] μ_{HF} and Θ_{HF} are the permanent dipole and quadrupole moments of HF, values for which were obtained by assuming the interaction energy at $R = 10a_0$ to be entirely given by the long range contribution.

For the rigid rotor potential, this gave values of $\mu_{\mathrm{HF}} = 0.82$ a.u. (Hartree–Fock limit 0.76 a.u.[42]) and $\Theta_{\mathrm{HF}} = 1.77$ a.u. (MCSCF value 1.69 a.u.[43]). Other long range terms in V_4–V_8 were neglected. They are not significantly larger than the basis set superposition error.[13]

The short range energy, defined as the difference between V^{SCF} and the long range terms given above, was then fitted, allowing inaccuracies in the long range terms to be removed by the short range fitting. Damping of the long range terms, found necessary when the long range interactions are particularly strong,[39] was not deemed necessary in the region of interest ($R > 3a_0$).

The short range energy was fitted by a modified Born–Mayer potential

$$V_\lambda^{\mathrm{short}}(R) \cong \exp\left(\sum_{i=0}^{3} A_{\lambda i} R^i\right) \tag{11}$$

using standard least squares fitting techniques. Points where the short range energy was less than 5×10^{-8} hartree were excluded from the fit. Table II gives the matrix of fit coefficients A.

The fitted potential plus dispersion terms reproduced the data on the region of van der Waals minima (Ref. 13 and Table IV) with an average error of only 0.06×10^{-5} hartree compared with a minimum in the isotropic potential of -9.32×10^{-5} or -20.5 cm^{-1}. The rigid rotor potential of Rodwell *et al.* was computed using a larger Gaussian basis set than their full potential; thus, the rigid rotor parts of these two potentials are not equivalent. Furthermore, their full potential only includes terms up to $\lambda = 6$ in the Legendre expansion. As we show, the higher Legendre terms play an insignificant role in the dynamics of the van der Waals molecule, partly because of the large HF rotational constant of about 20 cm^{-1}.

As a first step in fitting the full SCF potential, we repeated the fitting procedure described for each value of r for which calculations were performed.[13] This gave $\mu_{\mathrm{HF}}(r_i)$, $\Theta_{\mathrm{HF}}(r_i)$ and $A(r_i)$ for $r_i = 1.4827$, 1.6027, 1.7328, 1.9180, and $2.1032a_0$. Ten values of R between 3 and $10a_0$ were used in the fits, the dipoles and quadrupoles being fitted to the interaction energies at $R = 10.99a_0$.

Next, the fit coefficients were expressed as Taylor series about r_e ($= 1.7328a_0$) giving

$$\chi(r) \cong \sum_k \chi_k \zeta^k, \quad \chi = \mu_{\mathrm{HF}}, \Theta_{\mathrm{HF}} , \tag{12a}$$

$$A_{\lambda i}(r) \cong \sum_k a_{\lambda i k} \zeta^k , \tag{12b}$$

where

$$\zeta = (r - r_e)/r_e . \tag{13}$$

The coefficients of the Taylor expansion were determined by a least squares fit using the five points with the constraint that the values for $r = r_e$ were exactly reproduced. This ensured a rigid rotor surface identical to the one which would have been obtained if only $r = r_e$ data had been used.

Initially, we followed Rodwell *et al.* and used terms up to ζ^3 in the expansion. However, we found that surfaces fitted in this manner became extremely unstable only a short distance, less than $0.2a_0$, outside the range of r used in the fit. A fit up to ζ^2 was found to be much better behaved and only slightly less accurate.

When a surface is fitted to a Born–Mayer potential (11), if the coefficient of the highest power of R is negative, then the fitted potential tends to 0 as R tends to ∞, as required. If the highest power of R is positive then the polynomial must have a turning point for some critical value of R beyond which the fit is no longer valid.[39] If this critical value occurs where V^{short} is essentially zero then the Born–Mayer potential can be set to zero beyond this point without error. For the cases $\lambda = 2$ and $\lambda = 6$ in the present work, the critical value was found to be below $10a_0$, which was within the range of interest, unless V^{short} was fitted to a value of zero (10^{-9} hartree) at $R = 11a_0$. For R greater than this, any contribution from V^{short} can be neglected.

Table III gives the Taylor expansion coefficients for the dipole and quadrupole moments; for comparison it

TABLE III. Expansion coefficients for HF dipole and quadrupole moments in the form of Eq. (27). For comparison, accurate, theoretical, and some experimental values are also given.

	μ/a. u.[a]			Θ/a. u.[b]		
	Fit	MC-SCF[c]	Expt.[d]	Fit	MC-SCF[c]	Expt.[e]
$k=0$	0.8437	0.724	0.707	1.6484	1.687	1.75 ± 0.02
1	0.7874	0.468	0.549	2.1795	1.478	
2	−0.3364	−0.704	−0.093	3.6117	0.178	

[a] 1 a. u. = 2.541 74 D = 8.4778×10^{-30} cm.

[b] 1 a. u. = $1.344\,91\times10^{-26}$ esu = 4.4865×10^{-4} cm^2.

[c] Reference 43.

[d] Reference 44.

[e] Reference 45.

also gives corresponding values obtained from MC SCF calculation and experiment. Table IV gives the coefficients of the short range interaction energy. These were obtained by fitting the difference $V^{\mathrm{SCF}}(R, r_i)$ and $V^{\mathrm{long}}(R, r_i)$ given by the Taylor expansion of the permanent moments.

Our fit accurately reproduces the cuts through the potential given by Fig. 3 of Rodwell *et al.* For $r=r_e$, these potentials have van der Waals wells of 35 cm^{-1} at both $\theta=0°$ and 180°. Lengthening r deepens the well at 180° and reduces it at 0°. Compressing r makes both minima shallower. At 0°, the well is also shifted outwards by lengthening the HF bond; this of course shortens the He–H separation.

It is possible to express our potential in the form

$$V(R, r, \theta)=\sum_{\lambda}\sum_{k} P_\lambda(\cos\theta)\xi^k V_{\lambda k}(R) \qquad (14)$$

by using the series expansion for the exponential terms which depend on ξ. If terms up to ξ^2 are retained, this expansion gives a little loss of accuracy. Rodwell *et al.* give damped dispersion terms in this form.

Finally, we note that to obtain the full HFHe potential energy hypersurface, it is necessary to add a potential for the separated HF molecule to the interaction surface discussed above. There are several empirical potentials available[46,47] and we chose to use one in the form of Ogilvie[47]

TABLE IV. Fitted coefficients $a_{\lambda i k}$ for the short range part of the full HeHF potential [Eq. (27)] in a. u.

	$i=0$	1	2	3
	$k=0$			
$\lambda=0$	0.595 741 67	−0.212 088 32	−0.392 760 42	0.024 552 15
1	0.330 191 64	−0.918 102 45	−0.207 529 05	0.010 760 00
2	−14.661 100 56	9.015 075 73	−2.212 584 52	0.122 628 10
3	5.316 836 04	−4.266 796 60	0.514 961 66	−0.042 368 50
4	12.566 970 24	−10.362 754 67	2.050 378 72	−0.175 102 33
5	22.435 717 52	−16.964 726 84	3.436 101 28	−0.274 599 97
6	0.523 616 42	−0.419 520 85	−0.670 130 76	0.048 968 40
	$k=1$			
$\lambda=0$	−7.677 447 01	4.976 936 43	−0.942 893 66	0.059 387 73
1	0.884 145 36	−0.410 691 95	0.488 562 97	−0.048 258 23
2	31.078 327 31	−24.957 422 74	6.311 483 63	−0.390 861 15
3	19.706 006 59	−11.949 710 54	2.572 718 91	−0.158 832 13
4	31.782 292 18	−16.835 628 43	2.893 172 99	−0.103 380 86
5	−30.361 370 86	37.093 885 08	−11.870 920 71	1.195 110 96
6	55.671 961 02	−30.298 336 69	5.656 067 18	−0.305 615 62
	$k=2$			
$\lambda=0$	59.753 736 16	−40.542 095 49	8.546 974 30	−0.566 922 77
1	13.791 048 89	−11.732 590 84	2.550 524 91	−0.195 299 76
2	83.651 829 20	−33.170 987 27	1.609 903 88	0.064 936 63
3	−22.086 274 71	15.013 448 11	−3.237 675 85	0.192 972 13
4	132.811 922 99	−81.930 655 37	16.908 225 70	−1.229 148 19
5	509.217 336 20	−392.099 970 65	100.457 439 54	−8.557 647 03
6	−112.067 167 46	67.003 805 68	−12.831 208 33	0.696 920 75

$$V_{\mathrm{HF}}(r)=C_0 z^2\left(1+\sum_i C_i z^i\right) , \tag{15}$$

$$z=2(r-r_e)/(r+r_e) \tag{16}$$

with $C_0=203\,708$ cm^{-1}, $C_1=-1.260\,746$, $C_2=0.894\,864$, $C_3=-0.398\,54$, $C_4=-0.2025$, and $C_5=0.2103$, as this potential has no unphysical values in the range of r of interest.[48] This form of the potential does not reproduce the experimental dissociation energy of $D_e=49\,380 \pm 60$ cm^{-1}.[49]

V. DYNAMICAL CALCULATIONS

Dynamical calculations were first performed on the HeHF rigid rotor potential using the atom rigid diatom program of I. We optimized the radial R basis set for a calculation with $j \leqslant 10$ and $n_1 \leqslant 5$, giving a 66 dimensional secular problem for the only bound state with $J=0$. Starting from $R_e=6.5$ cm^{-1}, $D_e=33$ cm^{-1}, and $\omega_e=22$ cm^{-1}, values suggested by the potential, the energy was found to depend strongly only on R_e for which a value of $8.25a_0$ was optimal. A check on the basis set convergence showed that the angular basis functions with $j>3$ gave an insignificant lowering of the energy for all the bound states $J=0$, 1, 2, and 3. This was found to be true for all the potentials tested, suggesting that the higher terms in the Legendre expansion of the potential hardly effect the van der Waals complex. The relatively large HF rotational constant (21.1 cm^{-1} at $r_e=1.7328$) means that the higher j states lie well above the $j=0$ states.

As increasing the radial basis beyond $n_1 \leq 5$ had little effect, a saturated basis was given by the optimized functions with $n_1 \leq 5$ and $j \leq 3$. Table V shows all the bound states for the rigid rotor (large electronic basis set) potential (a). Also shown are the results of the calculations on the full (smaller electronic basis set) potential (b) with r fixed at r_e and $\langle r\rangle_0$, the average bond length of the HF ground vibrational state. While the results for the two potentials are similar, it is clear that the rigid rotor part of the full potential is slightly more attractive than the simple rigid rotor potential.

Lengthening r from $r_e=1.7328$ to $\langle r\rangle_0=1.7496$ (see Table VI) has two effects. Firstly, the increase in r lowers the HF rotational constant allowing increased mixing between $j=0$ and higher j basis functions. This effect can only increase the binding energy of the complex. Secondly, the increase in r allows a slightly different cut through the potential to be sampled. As the effect of stretching the diatomic bond is usually to lower the interaction potential, this effect is generally, although not necessarily, to increase the binding energy further. The levels for $r=\langle r\rangle_0$ are about 0.07 cm^{-1} lower in energy than those for $r=r_e$ with the same potential.

TABLE V. Bound levels for atom rigid diatom calculations (in cm^{-1}). a is the rigid rotor potential, b is the full potential at fixed r.

	r	$J=0$	1	2	3
a	r_e	-5.977	-5.224	-3.738	-1.562
b	r_e	-6.325	-5.562	-4.057	-1.850
b	$\langle r\rangle_0$	-6.396	-5.633	-4.126	-1.918

TABLE VI. HF zero point energy (G_0) and first two band origins (G_v), and rotational constants (B_v). Also given is $\langle r\rangle_v = (\langle v \mid r^{-2} \mid v\rangle)^{-1/2}$ for vibrational states $v=0$, 1, 2. The calculations used Ogilvie's empirical potential Refs. 47 and 48 [Eq. (30)].

	Calculation		
	Basis set	Numerical	Experiment[a,b]
G_0/cm^{-1}	2055.275	2055.221	2050.76
B_0/cm^{-1}	20.7020	20.7015	20.5596
$\langle r\rangle_0/a_0$	1.7496	1.7496	1.7556
G_1	3969.721	3969.477	3961.418
B_1	19.9206	19.9166	19.7872
$\langle r\rangle_1$	1.7836	1.7838	1.7896
G_2	7768.837	7767.586	7750.814
B_2	19.1350	19.1562	19.0328
$\langle r\rangle_2$	1.8198	1.8188	1.8247

[a] Reference 49. [b] Reference 51.

Next we optimized the basis set for r. This was done by performing calculations on the isolated HF diatom with a basis set of five functions (all $n_2 \leq 4$). Starting from $r_e=1.7328a_0$, $\omega_e=3950$ cm^{-1}, and $D_e=40\,240$ cm^{-1} we minimized the sum of the energies of the lowest three vibrational states for a calculation with $J=0$. This gave an optimum basis set with $r_e=1.7788a_0$, $\omega_e=3296.9$ cm^{-1}, and $D_e=39\,771$ cm^{-1}.

Table VI compares the results obtained for the lowest three vibrational states of HF using this basis set with the exact result for the same potential (obtained by direct numerical integration of the Schrödinger equation[50]) and the experimental values. While Ogilvie's potential gives vibrational spacings that are slightly too large, our small optimized basis set reproduces the vibrational levels and rotational constants of the exact results for this potential very satisfactorily.

Using the two optimized basis sets we performed calculations on the full HeHF potential fitted in the previous section. We are interested not only in the four bound states of the potential, but also in states which are formed by the interaction of He with HF in a vibrationally excited state. Although these states are metastable relative to He and ground state HF, they are easily obtained from our calculations as the separation of HF vibrational states (~3950 cm^{-1}) is much larger than the range spanned by the basis functions of the complex (~500 cm^{-1}). Theoretical calculations have shown vibrational predissociation in van der Waals dimers to be slow.[52]

Table VII presents the calculated binding energies of the HeHF van der Waals dimer for $v_{\mathrm{HF}}=0, 1$, and 2. Energies are relative to the calculated energies for

TABLE VII. Bound levels of the HeHF van der Waals molecules for HF in vibrational state ν_{HF}. Binding energies (in cm^{-1}) are relative to dissociated He + HF (ν_{HF}). Upper rows are for rigid HF calculations using $\langle r \rangle_{\nu_{HF}}$ and lower rows are for fully correlated calculations.

$J=0$	0	1	2	3
$\nu_{HF}=0$	−6.393	−5.630	−4.123	−1.915
	−6.393	−5.632	−4.128	−1.924
1	−6.528	−5.764	−4.256	−2.043
	−6.510	−5.751	−4.253	−2.056
2	−6.669	−5.904	−4.394	−2.178
	−6.586	−5.832	−4.341	−2.155

separated He + HF (ν_{HF}). Also shown are rigid diatom calculations performed for $r = \langle r \rangle \; \nu_{HF}$ for each state. The difference between the two calculations is due to two effects.

Formally, the rigid diatom calculations can be viewed as a full three dimensional calculation with only one basis function, the unperturbed diatom wave function, in the r coordinate. This would be exactly so if we had used the correct vibrational averages over the potential or, more simply, over a potential expanded in the form of Eq. (14) as done by Le Roy and Van Kranendonk.[3] As we have only used vibrational averages of r^{-2}, in the rigid diatom calculation, the potential sampled is not strictly the same as that sampled by the full calculation. This effect is the one discussed by Burton and Senff.[9]

Secondly, the rigid diatom calculations do not allow for the instantaneous (as opposed to time averaged) coupling between the diatom vibration and the modes of the complex. This effect, which can be regarded as inter–intra correlation, must be purely attractive and can only be represented by the full calculation.

Table VII shows that both of the calculations predict the complexes of the vibrationally excited states to be more stable. The effect, about 0.1 cm^{-1} for $\Delta\nu_{HF}=1$, is smaller than, but consistent with, the previously noted behavior.[3] The differences between the rigid diatomic and full calculations are very small, suggesting that the inter–intra correlation effects which have always previously been ignored are indeed negligible compared with accuracy of the potential.

The use of the vibrationally averaged potential with a rigid rotor calculation thus gives results very similar (to within 0.02 cm^{-1}) of the full calculation. In the language of Burton and Senff,[9] this means that the monomer zero point energy is unaffected by complex formation. This is in line with the experimental observation that monomer modes are shifted very little in the complex.[11]

VI. CONCLUSION

In this paper we have presented a method for performing *ab initio* rovibrational calculations on nonrigid triatomics. Within the usual assumptions of the variational principle and Born–Oppenheimer approximation, this method is exact for the potential under consideration. The method is appropriate for floppy triatomics as well as atom–diatom collision complexes (van der Waals molecules) with no approximate separation of vibrational modes. It has been implemented as a fully documented computer program,[34] although the requirement of a potential energy surface prevents it being used as a black box.

In particular, we have investigated several techniques for diagonalizing the secular matrix as this is the bottleneck in any LC-RAMP method. We found the iterative orthogonalized Lanczos procedures[27,28] particularly appropriate for the secular matrices typically encountered in LC-RAMP calculations and have implemented this as an alternative to the standard in-core diagonalization procedure.[25]

We have fitted the full *ab initio* HeHF potential energy surface[13] and used it to perform calculations which test the effect of fixing the HF bond length. The correlation between the HF vibrational coordinate and the complex modes, which has until now been neglected, was found to be small (less than 0.02 cm^{-1}). The effects of vibrational excitation, which have sometimes been neglected,[11,12] were found to be somewhat larger (~0.1 cm^{-1}), with complexes of the higher states being more stable. We found little evidence to suggest that the rigid monomer approximation used by experimentalists in inverting their data is a serious source of error. We would be surprised if this was the cause of the discrepancy between the empirical isotropic well depth of $(H_2)_2$ and that found *ab initio* by Burton and Senff.[9]

Finally, we note that the major expense in *ab initio* rovibrational calculations such as those outlined in this paper is the potential energy surface. To obtain a reliable potential for a nonrigid molecule in three dimensions is a formidable task. Typically, the calculation of the electronic potential at one geometry is as computationally expensive as performing all the dynamical calculations.

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$$g_n(R)=\{1-\exp[-(2.1/n)R_s-(0.109/n^{1/2})R_s^2]\}^n$$

$$f(R)=1-R_s^{1.68}\exp(-0.78\,R_s).$$

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