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The collocation method for calculating vibrational bound states of molecular systems—with application to Ar-HCl

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The ability of the collocation method to calculate vibrational bound states of molecules is investigated. The technique is simpler to implement than conventional variational methods; no integration over the basis functions is involved. We apply the method to the weakly bound complex Ar-HCl, a real multidimensional system of considerable physical interest, and find the procedure to be of equivalent accuracy to the corresponding variational approach at all times. This confirms the conclusions of our previous studies on one-dimensional test problems [W. Yang and A. C. Peet, *Chem. Phys. Lett.* **153**, 98 (1988)]. Both low lying and highly excited states are examined and the conclusions hold even for levels very close to the dissociation limit. A test of the wave functions obtained also finds these to be of good accuracy and very similar to the ones given by the variational procedure.

I. INTRODUCTION

Developments in molecular beam techniques and rapid improvements in laser technology are leading to well resolved spectra for many more species than was previously possible. As these experimental advances take place, systems are being studied which exhibit dynamics of considerable complexity. Although such studies have the capability of yielding much information, the spectral analysis has become an increasingly difficult task. Simple formulas traditionally used to analyze spectra¹ often no longer work and a full consideration of the relevant dynamics on a good potential surface is required before agreement between predicted and recorded spectra is obtained. There is thus a need to develop theoretical techniques which are capable of yielding accurate bound states for systems of a very general nature. In particular, simple reliable procedures for dealing with complexes which possess many strongly coupled anharmonic or floppy motions are required.

Many methods have been proposed for calculating bound states of such systems.^{2,3} The vast majority of these have relied upon the Rayleigh-Ritz variational principle in which the algebraic eigenvalue problem is set up by calculating integrals of the Hamiltonian over the basis set. However, the integrals over the potential function are often difficult to evaluate, especially for multidimensional systems, and so the task is a considerable one. Of the techniques which do not employ the traditional Rayleigh-Ritz approach, the coupled channel method⁴ is perhaps the most commonly used. However, this technique is very intricate since it involves both the evaluation of integrals over the potential and the numerical solution of a set of coupled differential equations. The complicated nature of all these methods has often led to the feeling that the calculation of energy levels for a general system should be left to specialist theoretical chemists and is outside the realm of experimental workers.

The problems caused by the presence of multidimensional integrals may be avoided by using a pointwise representation.^{3,5-11} This replaces the integrals over the potential function by the value of the potential on a grid in space. The

best known of this class of techniques is the finite difference scheme.¹⁰ However, this usually has poor convergence properties due to the use of an inadequate representation for the kinetic energy operator. Recently, it has been found that increased accuracy may be achieved by retaining a basis set for the kinetic part.^{3,5-9} Such methods hold much promise and have already been used to carry out some very impressive calculations.^{3,8} In particular, Bačić and Light have combined a pointwise description (the discrete variable representation) for the angular variable with a basis set representation for the stretching coordinates to yield an extremely efficient method for calculating vibrational energy levels of triatomic systems. They have used the techniques to calculate high lying levels of the molecules KCN, HCN, and H₂O (Ref. 3).

In a recent paper⁹ we have investigated another of these pointwise approaches, the collocation method.^{9,11} This classical technique for solving differential equations is based upon a fitting procedure for the wave function and has the advantage that it is extremely simple to implement. Application to the Morse oscillator test problem also showed the method to be as accurate as the conventional variational procedure.⁹ This combination of accuracy and ease of implementation suggests that the method may provide a simple way for experimentalists to calculate accurate vibrational bound states from a given potential surface for a wide range of systems.

The object of the present work is thus to extend the study of the collocation method to a multidimensional system and ascertain its accuracy when compared with the corresponding variational technique. We choose the Ar-HCl van der Waals complex for this investigation as it has been of considerable interest to both experimental and theoretical chemists, being a simple system whose dynamics are sufficiently complicated for simple normal mode theories to be very poor. In the next section we present the collocation method as applied specifically to an atom-diatom system. The method is then applied to Ar-HCl and the results presented in Sec. III where they are compared with those car-

ried out using the variational procedure. The conclusions from these studies are given in Sec. IV.

II. METHOD

The collocation method was discussed in general terms in Ref. 9. Here we present the method as applied specifically to a nonrotating ($J = 0$) atom-rigid-diatom system. The Hamiltonian may be written in Jacobi coordinates as

$$H = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \left(B_e + \frac{\hbar^2}{2\mu R^2} \right) \hat{j}^2 + V(R, \theta), \quad (1)$$

where R is the distance from the atom to the center of mass of the diatom and θ is the angle between R and the diatom bond axis. The system is characterized by the collisional reduced mass $\mu = mM/(m+M)$ (where m is the mass of the atom and M is the mass of the diatom), the rotational constant of the diatom B_e and the intermolecular potential V . The angular momentum operator for the diatom \hat{j} has the property

$$\hat{j}^2 P_j(\cos \theta) = j(j+1) P_j(\cos \theta), \quad (2)$$

where P_j is a normalized Legendre polynomial of order j .

We must now expand the wave function in a basis set which can provide a good description of the dynamics. Here we choose a product basis of Legendre polynomials in $\cos \theta$ and distributed Gaussians in R ,

$$\psi = \sum_{i=1}^{N^R} \sum_{j=0}^{N^\theta-1} c_{ij} \phi_i(R) P_j(\cos \theta), \quad (3)$$

where

$$\phi_i(R) = \left(\frac{2A_i}{\pi} \right)^{1/4} \exp[-A_i(R-R_i)^2]. \quad (4)$$

and the parameters A_i are given by the prescription of Hamilton and Light,¹²

$$A_1 = c^2/(R_2 - R_1)^2; \quad A_i = 4c^2/(R_{i+1} - R_{i-1})^2, \\ A_{N^R} = c^2/(R_{N^R} - R_{N^R-1})^2. \quad (5)$$

The quantity c is left as a parameter which may be used to vary the widths of the Gaussians. This basis is chosen due to its great adaptability and simple nature. In addition, a similar basis has been successfully employed in calculating infrared spectra of several rare gas-halogen halide systems.¹³

Inserting the trial wave function (3) into the Schrödinger equation gives

$$\sum_{i=1}^{N^R} \sum_{j=0}^{N^\theta-1} (H - E) \phi_i(R) P_j(\cos \theta) c_{ij} = 0. \quad (6)$$

For a truncated (i.e., noncomplete) basis the equality will not in general be satisfied. Coefficients and energy levels which approximately satisfy the equation are then sought. The traditional way to do this, which we do not follow here, is to multiply on the left by $\phi_{i'}(R) P_{j'}(\cos \theta)$ and integrate over coordinate space. This yields a set of algebraic eigenvalue equations, the variational equations, which may be solved numerically to give energy levels and wave functions. As N^R and N^θ are increased the basis becomes more complete¹² and the values converge to the exact ones.

A much simpler way to set up the algebraic eigenvalue equations, the collocation method, is to force Eq. (6) to be exact at $N^R \times N^\theta$ points. This yields the collocation equations,

$$\sum_{i=1}^{N^R} \sum_{j=0}^{N^\theta-1} (H - E) \phi_i(R_i) P_j(\cos \theta_j) c_{ij} = 0; \\ i' = 1, \dots, N^R; \quad j' = 0, \dots, N^\theta - 1, \quad (7)$$

which may be written in general matrix notation as

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0. \quad (8)$$

For the Hamiltonian of Eq. (1), the quantities contained in this equation are

$$H_{ij,j} = \left[-\frac{\hbar^2}{2\mu} \phi_i''(R_i) - \frac{\hbar^2}{\mu R_i} \phi_i'(R_i) + \left\{ \left(B_e + \frac{\hbar^2}{2\mu R_i^2} \right) j(j+1) + V(R_i, \theta_j) \right\} \phi_i(R_i) \right] P_j(\cos \theta_j), \quad (9)$$

where ϕ' and ϕ'' are the first and second derivatives of the functions with respect to R , and

$$S_{ij,j} = \phi_i(R_i) P_j(\cos \theta_j). \quad (10)$$

The matrix equation (8) is in the form of a general unsymmetric eigenvalue problem which may be solved numerically using standard techniques to give the set of eigenvalues and their corresponding eigenvectors.

It should be noted that the formalism presented above is not a unique application of the collocation method; other coordinate systems and basis sets could clearly have been used. For example, expansion (3) could have been defined with a factor of $1/R$ present which, on multiplication of Eq. (6) by R would have removed the ϕ' term in the collocation equations (9). In addition, the method may be made more efficient by the use of a suitable nondirect product basis. In relation to this we note that in the DVR-DGB method of Bačić and Light³ only the angular coordinate is discretized allowing different radial basis sets to be used at each angle.

This is, in effect, an elegant way of choosing a nondirect product basis and allows fewer basis functions to be used than in the collocation method presented here. Unfortunately, discretizing only the angular coordinate does not confer similar basis set flexibility on the collocation method since the Hamiltonian is in a mixed representation (pointwise and basis set). However, it may be possible to choose a more efficient nondirect product basis in another manner and similar savings may then be afforded. Here we do not pursue this possibility but rather emphasize the simplicity of the collocation method which is clearly its most attractive feature.

We should also mention how symmetry may be used in conjunction with the collocation method, although it is not involved in the present calculations on Ar-HCl. As is well known, in the variational approach one constructs basis functions which transform as irreducible representations of the molecular symmetry group. Functions spanning different irreducible representations are not mixed by the Hamiltonian and so the problem is partitioned into several smaller

ones. In the collocation method we similarly construct symmetrized basis functions. However, we must now make an appropriate choice of points as well. This is done by selecting the points from the smallest region of space which is transformed onto the whole of coordinate space by successive symmetry transformations. In all calculations we must have the same number of collocation points as basis functions.

The process may be illustrated by considering the explicit example of an atom-diatom complex in which the diatom is homonuclear. For $J = 0$ the symmetry operation of interest is $\theta \rightarrow \pi - \theta$. If Legendre polynomials are used for the angular basis, as above, they are already symmetrized with respect to this operation and we merely need to partition them into even and odd j . The collocation points in θ are then conveniently chosen such that the $\{\cos \theta_j\}$ are Gauss-Legendre points of the same order as the highest j in the basis. Initially, this gives twice as many collocation points as there are basis functions of a particular symmetry. However, the points in the range $\pi/2$ to π lead to the same collocation equations (6) as are obtained from the points between $\pi/2$ and π . (This follows from the fact that the collocation points are placed symmetrically about $\theta = \pi/2$ and that both the potential and the basis functions are unchanged in magnitude by the operation $\theta \rightarrow \pi - \theta$.) Hence, only the collocation points in the range 0 to $\pi/2$ need be used to construct the collocation equations and we have the same number of points as functions in the calculation.

III. TEST CASE: Ar-HCl

We test the collocation method by calculating the bound states of the van der Waals complex Ar-HCl. This species is chosen as it is a benchmark in the study of anisotropic intermolecular forces and as such represents a realistic test problem for any new technique. Furthermore, a realistic intermolecular potential for this system has recently been determined from high-resolution spectroscopy by Hutson.¹⁴ Most notably, this surface should be reliably determined over the whole range of θ due to the input of data from far-infrared spectroscopy. The system has a linear Ar-H-Cl equilibrium geometry but also possesses a secondary minimum at the linear form Ar-Cl-H. The well depth of the potential is about 175 cm^{-1} with the secondary minimum having a depth of around 140 cm^{-1} .

As well as determining a potential surface for the Ar-HCl complex Hutson also calculated all the levels of the system with energies up to 1 cm^{-1} below the dissociation limit. This provides us with a good check on our implementation and also gives an illuminating comparison of basis set methods with the coupled channel techniques he used. To aid this we have used the same values of the collisional reduced mass 18.93246 amu , and the rotational constant of the HCl monomer 10.44019 cm^{-1} as were used in Ref. 14.

In all the calculations presented below, we chose the collocation points $\{R_r, \theta_r\}$ such that the $\{R_r\}$ were the centers of the Gaussians and the $\{\cos \theta_r\}$ were Gauss-Legendre points of the same order as the highest Legendre polynomial used in the basis set. The selection of collocation points was discussed in our previous paper and the work indicated that the present choice should provide an accurate

description of the system. In the variational calculations, which are presented for comparison, the integrals over the potential were carried out using a global trapezium rule in R and a Gauss-Legendre quadrature scheme for θ . In all cases, the quadratures present in the variational scheme were checked for convergence, which we take to be a determination of the energy levels to better than 0.001 cm^{-1} . The parameter c of Eq. (4), which controls the widths of the Gaussians, was set to 0.5 for the collocation method and 0.7 for the variational approach. These values were chosen as they had previously been found to give efficient and reliable basis sets.⁹

A. Lower levels

We first investigate the basis set convergence of the lowest 11 levels of the system. In Fig. 1(a) we give the errors in the ground, fifth excited, and tenth excited states as the num-

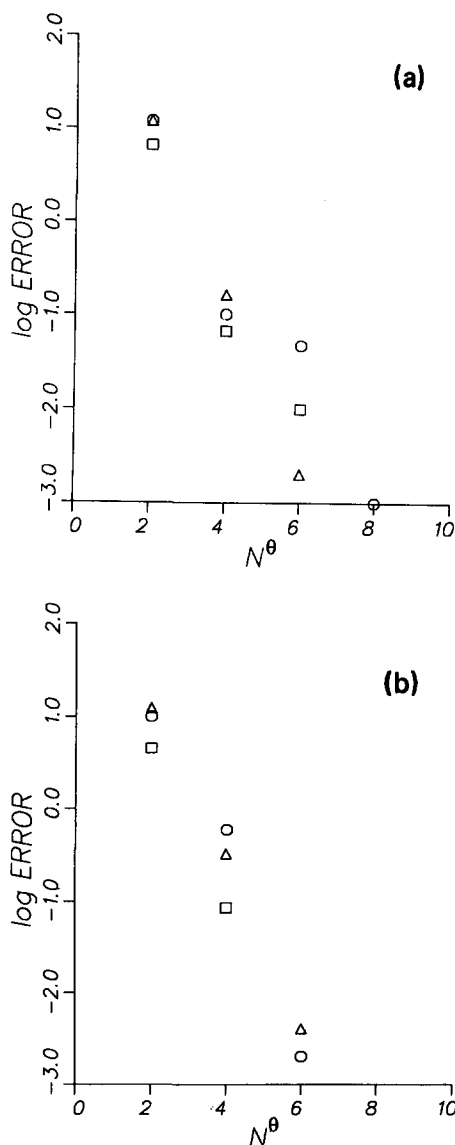


FIG. 1. Log_{10} of the absolute error in the ground (squares) fifth excited (circles) and tenth excited (triangles) states of Ar-HCl against size of angular basis set for (a) the collocation method and (b) the variational method.

ber of Legendre functions in the angular basis set is increased. For comparison Fig. 1(b) shows the errors in these states obtained from the corresponding variational calculation. Both sets of studies used a radial basis of 30 Gaussians distributed evenly in R between 3.0 and 7.0 Å, a basis which was sufficient to converge all levels under consideration. Comparing Figs. 1(a) and 1(b) we see that the convergence of the collocation and variational techniques is very similar.

Now, keeping the angular basis set fixed at the converged value of ten Legendre functions we vary the number of Gaussians in the radial coordinate. Figure 2(a) shows the errors in the same three states as we increase from 10 to 30 Gaussians placed evenly between 3.0 and 7.0 Å. Figure 2(b) shows the errors obtained from a variational calculation using the corresponding basis sets. From Figs. 2(a) and 2(b) we again see that the collocation method is of the same accuracy as the variational method throughout.

Having found the energy levels to be evaluated to high

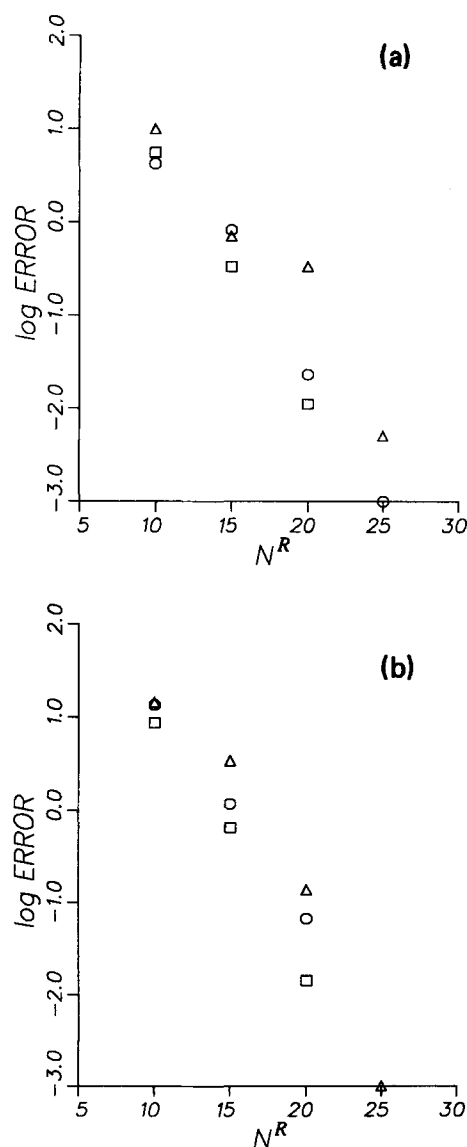


FIG. 2. \log_{10} of the absolute error in the ground (squares) fifth excited (circles) and tenth excited (triangles) states of Ar-HCl against size of radial basis set for (a) the collocation method and (b) the variational method.

accuracy by the collocation method it is also of interest to consider the wave functions produced. To do this we calculated the expectations $\langle P_1(\cos \theta) \rangle$ and $\langle P_2(\cos \theta) \rangle$ which may be determined experimentally from dipole moments and nuclear quadrupole coupling constants. The values obtained from the collocation and variational methods agreed to within four significant figures for the lowest 11 levels using the converged basis set of 30 Gaussians and 10 Legendre functions. The expectations, which are given in Table I, also agree well with the values obtained by Hutson¹⁴ who evaluated them by introducing the operators as perturbations to the potential and then determining the energy shift. Such a procedure was necessary in his case as the wave functions were not explicitly available from the coupled-channel method used.

B. High lying levels

As the levels approach the dissociation limit, the outer classical turning point occurs at increasingly large values of R while the curvature of the wave function in the well region changes little from one state to the next. It is thus most appropriate to present the convergence characteristics of the high lying levels by fixing the spacing between the Gaussians and increasing their number. The density we choose is 7.5 per Å which corresponds to about 30 in the range 3.0 to 7.0 Å. In Table II we present the eigenvalues of the 13th and 14th excited states as the radial basis is increased from 30 to 70 functions. The results of this table clearly demonstrate the collocation method to be of the same accuracy as the variational procedure for these high lying states.

We note that the need to put basis functions out at least as far as the classical turning point dictates that a considerably larger basis is required to converge the states which lie close to the dissociation limit. Fewer than 35 Gaussians were required to converge the lowest 13 levels compared with 55 functions for the 14th excited state. Furthermore, if states above this are required the basis becomes prohibitively large. However, the extra functions required are all being placed at large values of R where the wave function is varying very slowly. Hence, more widely spaced, broader Gaussians should be used in this region.

TABLE I. Expectation values of the operators $P_1(\cos \theta)$ and $P_2(\cos \theta)$ for the lowest 11 vibrational ($J=0$) states of Ar-HCl.

| I | $\langle P_1(\cos \theta) \rangle$ | $\langle P_2(\cos \theta) \rangle$ |
|-----|------------------------------------|------------------------------------|
| 0 | 0.651 | 0.342 |
| 1 | -0.469 | 0.316 |
| 2 | 0.555 | 0.307 |
| 3 | -0.444 | 0.299 |
| 4 | 0.517 | 0.248 |
| 5 | -0.078 | 0.182 |
| 6 | -0.301 | 0.323 |
| 7 | 0.370 | 0.195 |
| 8 | -0.086 | 0.248 |
| 9 | 0.118 | 0.152 |
| 10 | -0.048 | 0.253 |

TABLE II. Convergence of the 13th and 14th excited levels with respect to number of distributed Gaussians used in the basis set for the collocation and variational methods. The Gaussians were placed at a density of 7.5 Gaussians per Å from a minimum distance of 3.0 Å. An angular basis of ten Legendre functions was used.

| N^R | $E_{13} \text{ (cm}^{-1}\text{)}$ | | $E_{14} \text{ (cm}^{-1}\text{)}$ | |
|-------|-----------------------------------|-------------|-----------------------------------|-------------|
| | Variational | Collocation | Variational | Collocation |
| 30 | -4.980 | -4.974 | 0.948 | 0.956 |
| 40 | -5.468 | -5.468 | -1.604 | -1.602 |
| 50 | -5.471 | -5.471 | -1.879 | -1.879 |
| 60 | -5.471 | -5.471 | -1.893 | -1.893 |
| 70 | -5.471 | -5.471 | -1.893 | -1.893 |

C. Semiclassical spacing of the Gaussian functions

Hamilton and Light¹² suggested that an efficient basis would be provided by distributing the Gaussian functions according to the nodal structure of the wave function, which may be predicted on semiclassical grounds. We have adapted their technique to provide a simple prescription for choosing the positions of the Gaussians. The procedure is given in an appendix so as not to obscure the objective of this section, which is to demonstrate the reliability of the collocation method when used with a basis set of Gaussians which have a great variety of widths and spacings.

Choosing the positions according to the procedure given in the Appendix allowed the 14th excited level to be converged with just 45 Gaussians, 30 placed evenly between 3.0 and 7.0 Å and 15 placed semiclassically beyond 7.0 Å. The use of semiclassical spacing also allowed a further bound state, above the 14th excited, to be located and converged. This state, at -0.363 cm^{-1} , required only 50 distributed Gaussian functions to converge its value, in comparison with 90 equally spaced functions. Additional bound states, even closer to the dissociation limit, undoubtedly exist, however, we have not converged these. A full list of the converged bound states is given in Table III.

At all times, variational calculations were carried out in

TABLE III. A list of bound states for Ar-HCl ($J=0$) converged by the present calculations.

| I | $E_I \text{ (cm}^{-1}\text{)}$ |
|-----|--------------------------------|
| 0 | -117.821 |
| 1 | -94.168 |
| 2 | -85.394 |
| 3 | -67.012 |
| 4 | -59.746 |
| 5 | -48.971 |
| 6 | -41.859 |
| 7 | -38.071 |
| 8 | -25.910 |
| 9 | -22.854 |
| 10 | -17.071 |
| 11 | -11.810 |
| 12 | -7.882 |
| 13 | -5.471 |
| 14 | -1.893 |
| 15 | -0.363 |

parallel with the collocation ones and the two were found to give results of very similar accuracy. This is despite the fact that in some calculations the widths of the Gaussians varied by over an order of magnitude within the range covered. Furthermore, although complex eigenvalues can occur in nonsymmetric eigenvalue problems, none were found during any of the calculations presented in Secs. III A-III C. The collocation method is clearly very robust.

IV. CONCLUSIONS

We have investigated the ability of the collocation method to calculate bound states of a multidimensional system. The technique may be thought of as a fitting procedure in which a trial wave function, written as a linear combination of basis functions, is constrained to satisfy the Schrödinger equation at a chosen set of points. As such, the method is extremely simple to implement and has the advantage over the variational approach in that it does not require the evaluation of any integrals over the basis set. At the same time it retains all the advantages of a basis set method such as yielding many bound states in one calculation and providing the wave function in a convenient form.

Application to the weakly bound system Ar-HCl on a realistic potential showed the collocation method to be of equivalent accuracy to the variational method at all times. This held true for both low lying states and levels which were very close to the dissociation limit. The technique was found to be well behaved even when used with basis sets which included distributed Gaussian functions of many different widths. Further tests showed the wave functions obtained by collocation and variational techniques to be of the same high accuracy. The collocation method should thus be very useful for calculating a variety of molecular properties, especially spectral intensities.

The general message which we wish to convey is that, using the collocation method, it is a simple task to obtain accurate vibrational bound states for realistic systems of a few dimensions. The computer program for the Ar-HCl problem was less than 150 lines long, excluding the potential generating routine and the "canned" program for solving the algebraic eigenvalue problem.¹⁵ It should thus be a realistic venture for someone with little experience of computation to carry out such calculations.

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APPENDIX

In this Appendix we describe the procedure used to construct the distributed Gaussian basis sets of Sec. III C. The technique relies upon an approximation to the semiclassical

formula for the wave function and is adapted from a procedure given by Hamilton and Light¹² We present the method initially for a one-dimensional problem and afterwards extend it to a multidimensional system for which Gaussians are distributed only in one degree of freedom.

In one dimension, the semiclassical approximation to the wave function has the form¹⁶

$$\psi = e^{iS(R)/\hbar}, \quad (\text{A1})$$

where $S(R)$ is the classical action,

$$S(R) = \int p(R) dr \quad (\text{A2})$$

and $p(R)$ is the classical momentum $p^2(R) = 2\mu[E - V(R)]$. Thus, if a node exists in the wave function at R_i then the semiclassical prescription predicts one at R_{i+1} where

$$\hbar\pi = \int_{R_i}^{R_{i+1}} \sqrt{2\mu[E - V(R)]} dR. \quad (\text{A3})$$

We could integrate this expression from the inner classical turning point and find the positions of all the nodes, then place the Gaussians accordingly. However, we do not wish to carry out the integral (A3) explicitly as this must be done by quadrature.

In Sec. III B, we noted that only at large values of R is a semiclassical spacing likely to produce a significant reduction in the basis set. In this region, the potential is very flat and we may make the approximation, $V(R) \approx V(R_i)$. We may now integrate Eq. (A3) explicitly to give the simple formula,

$$R_{i+1} = R_i + \frac{\hbar\pi}{\sqrt{2\mu[E - V(R_i)]}}. \quad (\text{A4})$$

In practice, we require more than one Gaussian in between each pair of nodes to properly describe the wave function. This may be achieved by multiplying the final term in expression (A4) by a constant between 0 and 1 and taking the R_i to be the centers of the Gaussians.

At present, we implement the procedure by defining an inner region in which the Gaussians are equally spaced and choose the constant so as to make the first spacing in the outer region the same as the ones in the inner region. Hence, we have

$$R_{i+1} = R_i + \frac{h\sqrt{2\mu[E - V(R_n)]}}{\sqrt{2\mu[E - V(R_i)]}}, \quad i = n+1, \dots, N^R, \quad (\text{A5})$$

where R_n is the final point of the inner region and h is the spacing between the Gaussians there. The energy E is then taken to be that of the dissociation limit, in this case 0. The constant h should be varied to check convergence. However, a good value may usually be obtained from equal spacing calculations which give the lower levels accurately.

The foregoing analysis has been concerned with a particle moving in one dimension. However, we may readily adapt it to a multidimensional system for which Gaussians are distributed only in the dissociation coordinate, as in the present studies on Ar-HCl. We first define a suitable one-dimensional radial potential, for the Ar-HCl system this may be taken to be a cut passing through the potential minimum ($\theta = 0$). The Gaussians are then placed in the outer region according to Eq. (A5), with the potential $V(R_n)$ referring to the 1D cut. The quantity h which is the spacing in the inner region should be taken as the value which converges the levels of multidimensional problem not the 1D cut.

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