The use of distributed Gaussian basis sets for calculating energy levels of weakly bound complexes

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A basis set method for calculating the energy levels of weakly bound complexes is investigated. The basis is constructed from distributed Gaussian functions in both the bending and stretching coordinates. This produces a set of functions which are localized in the full internal space and allows the construction of nondirect product basis sets which model the known characteristics of the wave function. Low lying states which are restricted to a small portion of space may be described by functions placed just in the well region. Highly excited states usually occupy large regions of space but may still be efficiently described by modeling the regions of greatly differing wave function curvature. Application to the van der Waals complex $Ar-CO_2$ shows that such basis sets give a reduction of about a third in basis set size when compared with a more conventional basis of Legendre functions for the monomer rotation and distributed Gaussians for the stretching motion. Such savings should increase for larger, more anisotropic systems.

I. INTRODUCTION

The spectroscopy of weakly bound complexes has the potential to yield much information concerning intermolecular forces. In particular, systems containing polyatomic molecules should be able to yield information which may not at present be obtained from *ab initio* methods. Unfortunately, the problem of calculating bound states from a given trial potential surface, and using these states to predict a spectrum, is not a simple one. Many methods, both accurate[1,2] and approximate,[3] have been proposed for accomplishing this task but they have invariably proved adequate only for small complexes. Despite this, much has been learnt from the work on small systems[4] and the development of accurate methods for larger clusters is eagerly awaited.

Methods for calculating energy levels of weakly bound molecular complexes may generally be grouped into two categories, variational basis set approaches and coupled channel techniques.[5] In the variational methods, basis functions are used to describe all degrees of freedom. They have the advantages that many bound states are obtained in one calculation and the wave functions are given in a simple form which may be used to calculate molecular properties. However, basis set techniques have traditionally suffered from problems associated with selecting an adequate set of functions. The difficulty arises from the floppy nature of the motions involved and the strong coupling between the modes. Such dynamics are described only poorly by conventional basis sets formed from direct products of single center expansions in each dimension.

The problem may be understood by considering an atom–molecule system. As the atom moves round the molecule, the equilibrium separation of the two components changes. Hence, a single radial basis set is not optimum for describing the van der Waals stretching motion for all orientations of the monomer. Moreover, for many basis sets, this problem is severe enough to make the calculation of accurate energy levels intractable.

One way to circumvent the difficulty is to use the coupled-channel method which solves for the motion in the dissociation coordinate numerically. This has led to the coupled–channel method being considered of higher accuracy than the basis set approaches. Unfortunately, the calculations involved are carried out at a fixed energy and must be repeated several times in order to search for a given bound state. Furthermore, the wave function is not usually obtained directly and the calculation of matrix elements over the eigenfunctions is usually not a simple task. Clearly, an efficient and adaptable basis set method is preferable.

A single radial basis set which can be flexible enough to describe the van der Waals stretching motion for all orientations of the molecule, is the distributed Gaussian basis of Hamilton and Light.[6] The adaptability of this multicenter basis is demonstrated by the fact that even when employed in a direct product with diatom rotational functions it is capable of giving the whole spectrum of eigenvalues for an atom–diatom system accurately. Such methods have recently met with much success in calculating infrared spectra of rare gas–hydrogen halide systems[7] and are perhaps the best of the conventional basis set methods.

However, such techniques still suffer from the inefficiencies inherent in using a direct product basis. The van der Waals stretching motion is described by the same radial basis for each orientation of the monomer. In particular, Gaussians must be placed at small enough intermolecular distances to describe the distance of closest approach of the atom to the molecule. For systems with a large wall anisotropy, this leads to Gaussians being placed well into the classically forbidden regions at other orientations.

In order to overcome such problems in atom–diatom systems, Bačić and Light[2] transformed the basis set in the angular coordinate to a pointwise representation (the DVR). This allowed them to use a different basis of distributed Gaussians for each angle. Their simple and elegant procedure, which is essentially a way of constructing a nondirect product basis, should be very efficient, especially for high

lying states in which the diatom motion is well thought of as a hindered rotation. Unfortunately, when more than one angular motion is involved, the DVR is defined as the direct product of the DVRs in the separate angles. Thus, although one may still use a different radial basis for each point in the angular space, the set of points available is unsatisfactorily restrictive. The work has, however, shown the power of using nondirect product basis sets for systems where coupling between the different motions is strong.

The general aim of using nondirect product basis sets is to place basis set flux only in regions of the potential which warrant it. Perhaps the most obvious way to do this is to choose several appropriate points in the multidimensional space and then expand in a basis set about them. The adaptability of the basis then increases with the number of centers chosen. Furthermore, the greater the number of expansion centers, the lower the order of the basis functions required. As a limiting case of this we may use just a single multidimensional Gaussian at each point and use many points. This is the approach we wish to investigate here. We note that, in such a scheme, Gaussians are used in all internal coordinates which is a significant departure from the conventional approach of using monomer rotational functions to describe the bending motions.

Although we have mainly discussed atom–molecule systems, a major objective is to consider strongly bound dimeric complexes, which at present are not amenable to exact quantum mechanical treatments. Such systems have a very large coordinate space and this has led to much scepticism regarding their possible treatment. However, only a small part of the space is usually accessed by the wave function and if this property can be exploited, a tractable method may become available. This is the philosophy behind developing a localized basis set method. In this paper, we consider only a small complex as this affords a simple demonstration of the technique and allows us to compare it with the more conventional basis set methods available. We choose the atom-linear molecule system $Ar–CO_2$ as it is fairly anisotropic and a potential has recently been determined for the complex by Hough and Howard.[8]

The methods used to construct the basis sets for $Ar–CO_2$ are given in the next section. This is followed in Sec. III by a study of the efficiency of the basis, including comparisons with the more conventional approach. First, we investigate the ability of the method to describe states below the barrier to rotation of the CO_2 monomer within the complex, then we consider the more highly excited and delocalized states. The final part of Sec. III investigates the savings which may be obtained by placing the Gaussians semiclassically and the method is used to calculate a list of bound states for the system. In Sec. IV we discuss the results of the tests and their implications towards tackling larger systems.

II. METHOD

We consider a nonrotating $(J = 0)$ complex comprised of an atom weakly bound to a rigid linear molecule. Scattering coordinates[9] are used as they give a good description of the system for all orientations of the monomer within the complex. The vibrational Hamiltonian is then[10]

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

$$(1)$$

where R is the distance from the atom to the center of mass of the linear molecule, and θ is the angle between R and the bond axis of the monomer. The quantities μ and B_e are the collisional reduced mass and the rotational constant of the monomer, respectively.

We expand the wavefunction as a linear combination of functions which depend upon both R and θ,

$$\Psi = \sum_{k=1}^{N} c_k\phi_k(R,\theta).$$

$$(2)$$

Each basis function ϕ_k is taken to be the product of a distributed Gaussian function in R with one in θ,

$$\phi_k(R,\theta) = \left[\frac{2}{\pi}\right]^{1/2}\left[A_k^R A_k^\theta\right]^{1/4}$$
$$\times\exp\left[-A_k^R(R-R_k)^2 - A_k^\theta(\theta-\theta_k)^2\right].\,(3)$$

Gaussian functions of other variables, e.g., $\cos\theta$, could have been used. Our rationale for choosing θ was that the nodes in the semiclassical wave function are evenly spaced in θ when the potential is a constant. This indicates that Gaussians placed evenly in θ may provide a good initial description of the wave function.

The functions (3) are generalized two-dimensional Gaussians centered on the points (R_k,θ_k). We may thus distribute these functions over the two-dimensional surface in a manner which forms an optimum basis. For systems of several dimensions, however, it would be a considerable task to optimize the positions and widths of all the functions individually and, in practice, a balance between efficiency of basis and ease of implementation is required.

As a starting point, we may select a single basis set in R and one in θ,

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

$$\phi_j^\theta(\theta) = \left[\frac{2A_j^\theta}{\pi}\right]^{1/4}\exp\left[-A_j^\theta(\theta-\theta_j)^2\right],\qquad(4)$$

then form the direct product of the two sets,

$$\Psi = \sum_{i=1}^{N^R}\sum_{j=1}^{N^\theta} c_{ij}\phi_i^R(R)\phi_j^\theta(\theta).$$

$$(5)$$

This technique has the advantage that the preexponential factors may be chosen simply by the prescription of Hamilton and Light,[6] with

$$A_1^R = 4C_R^2/(R_2 - R_1)^2,$$
$$A_i^R = C_R^2/(R_{i+1} - R_{i-1})^2,$$
$$A_{N^R}^R = 4C_R^2/(R_{N^R} - R_{N^R-1})^2,\qquad(6)$$

and similarly for A_j^θ. The quantities C_R and C_θ are left as parameters which may be used to optimize the widths of the

Gaussians. Due to their structure in the R, θ coordinate system, we say that these basis sets are formed on a rectangular grid, and use this expression throughout the paper.

In this work, the rectangular grids we use are all constructed from *equally spaced* functions in R and θ. Even for these basis sets, the ability to select the range of θ covered makes the basis more flexible than a conventional basis of monomer rotational functions coupled in a direct product with radial functions,

$$\Psi = \sum_{i=1}^{N^R} \sum_{j=0}^{N^\theta - 1} c_{ij} \phi_i^R(R) P_j(\cos \theta); \qquad (7)$$

P_j is a Legendre polynomial of order j. However, the use of the rectangular region is obviously not optimum and so we seek a more efficient nondirect product basis. One way to do this is to set up the basis (5) on a rectangular grid and then discard all product functions for which $V(R_i, \theta_j) > V_{max}$, where V_{max} is some sufficiently large value of the potential. Such a basis should be quite efficient for low lying states since it models the restricted nature of the dynamics and the nodes in the wavefunction are usually fairly evenly spaced. The scheme also has the advantage that it is very simple to implement.

For states close to the dissociation limit, the wave function oscillates rapidly in the well region but very slowly at large R where the local kinetic energy is small. Basis sets constructed via an equally spaced grid are thus very inefficient for such states. Broader, more sparsely distributed Gaussians are required in R and, in addition, different basis sets in θ will be optimum at different values of the radial coordinate. This requirement for change in the spacing of functions in both R and θ is inherently a problem for a nondirect product basis and so may be efficiently treated by distributed Gaussians. The problem is discussed more in Sec. III C and a method for choosing the positions and widths of the Gaussians is presented in the Appendix.

Apart from varying the positions of the Gaussians, we may further improve the efficiency of the basis by performing basis set contractions. This may be implemented by solving some model problem and then using the resulting eigenfunctions as the basis for the complete system. Such basis set contractions may be used for both direct and nondirect product basis sets. However, for larger systems possessing several minima, it is difficult to construct a model problem which is suitable for contracting direct product basis sets. It thus seems inappropriate to consider the savings which these techniques afford on the single minimum system which we are studying here. We leave an investigation of this important topic to future studies of systems with several minima. We should mention, however, that a possible scheme for the distributed Gaussian basis would be to contract the basis in each well, and then put extra functions along the tunneling paths between the minima.

Having selected the positions and preexponential factors which define the basis set, the calculation of eigenvalues and eigenvectors proceeds by the variational principle. Algebraic eigenvalue equations are obtained in the conventional manner by inserting the trial wave function (2) into the Schrödinger equation, multiplying on the left by $\phi_k(R,\theta)$ and integrating over the coordinate space. This yields

$$\sum_{k=1}^N \langle \phi'_k | H - E | \phi_k \rangle c_k = 0 \quad k' = 1,...N, \qquad (8)$$

where the matrix element is given by

$$\int_0^\infty \int_0^\pi \phi_{k'}(R,\theta)(H - E)\phi_k(R,\theta) R^2 \sin \theta \, dR \, d\theta \qquad (9)$$

In this work we evaluate the integrals (9) by various quadrature rules[11] and make sure that the energy levels are converged with respect to the quadrature for each basis set used. This ensures that the calculations are variational and so provides a well accepted framework for comparing the different basis sets. Future implementations should avoid the need to evaluate the integrals (9) by using a suitable pointwise representation such as the collocation method.[12-14]

III. TEST CASE Ar–CO₂

We tested the relative efficiencies of the different basis sets discussed in Sec. II by calculating bound states of the van der Waals complex Ar–CO$_2$ on the AD–M potential of Hough and Howard.[8] This surface is a least squares fit to molecular beam electric resonance spectra, mixed second virial coefficients and mean-square torque measurements. The complex is T shaped at equilibrium ($R = 3.446$ Å, $\theta = \pi/2$) with the well depth being 186.8 cm^{-1}. The linear geometry is a saddle point on the potential with the barrier to rotation of CO$_2$ being 129.8 cm^{-1}. For more details on the surface and the exact functional form we refer the reader to Hough and Howard's paper.[8] In this work we assume that the CO$_2$ molecule is rigid and has a rotational constant of 0.3895 cm^{-1}. Although this approximation may be simply relaxed it is not usually a source of any significant error in the bound states and it allows us to concentrate our attention on the intermolecular dynamics.

The results of the investigation are mainly presented as graphs of the log of the error in the energy levels against basis set size, where the error is with respect to the converged values, which are given in Table I. As some nondirect product basis sets are used, all basis set sizes refer to the total number of functions rather than the number in a particular degree of freedom. The plots are most conveniently read by extrapolating the curves to the N axis, which corresponds to an error of 0.001 cm^{-1}, and reading off the basis set required to achieve this accuracy. In all the calculations carried out we use the symmetry of the CO$_2$ molecule to reduce the size of the calculation involved. This is simply done by placing the Gaussians symmetrically about $\theta = \pi/2$ and using symmetrized linear combinations of them. We use s to denote the functions which are symmetric with respect to the operation $\theta \to \pi - \theta$, and a to denote those which are antisymmetric with respect to this operation. The values of N used in the plots refer to the sizes of the symmetry reduced basis sets.

A. States below the barrier

In this subsection we consider levels which lie below the barrier to internal rotation of the CO$_2$ monomer. For clarity, we present the results for only three states, the ground

TABLE I. Energy levels of the Ar–CO$_2$ complex ($J = 0$) on the AD–M potential of Hough and Howard (Ref. 8) as obtained by the basis set of Eq. (7). The zero of energy is the lowest dissociation limit of the complex and all levels within 10 cm^{-1} of this are omitted.

Level	Symmetry	Energy (cm^{-1})	Level	Symmetry	Energy (cm^{-1})
0	s	-156.071	24	a	-40.780
1	a	-139.308	25	a	-40.194
2	s	-124.537	26	a	-38.292
3	s	-115.582	27	s	-37.052
4	a	-111.327	28	s	-35.074
5	s	-99.572	29	s	-33.866
6	a	-97.820	30	a	-31.563
7	a	-89.134	31	a	-29.361
8	s	-85.865	32	s	-28.107
9	s	-79.929	33	a	-25.923
10	s	-78.169	34	s	-25.801
11	a	-72.776	35	s	-24.170
12	a	-71.612	36	a	-23.588
13	s	-64.818	37	a	-23.039
14	s	-62.465	38	s	-22.358
15	a	-59.416	39	a	-19.380
16	a	-58.705	40	s	-18.962
	barrier	-57.000	41	a	-17.581
17	s	-55.115	42	s	-17.424
18	s	-53.624	43	s	-14.569
19	a	-52.877	44	a	-14.390
20	a	-49.266	45	s	-12.720
21	s	-45.352	46	a	-12.098
22	s	-44.917	47	s	-11.569
23	s	-40.900	48	a	-11.302

(-156.071 cm^{-1}), fifth excited (-99.572 cm^{-1}) and tenth excited (-78.169 cm^{-1}). Nearby levels were found to have similar convergence properties. All basis sets used were constructed with the same radial basis of 20 distributed Gaussians ($C_R = 0.7$) between $R_{\min} = 3.0$ Å and $R_{\max} = 5.0$ Å. These values were sufficient to converge the energies of the lowest 7 levels of s symmetry. In Fig. 1(a) we give the results obtained with a basis of Legendre polynomials in cos θ and distributed Gaussians in R [Eq. (7)]. This provides us with a benchmark against which to compare the results of various basis sets formed from distributed Gaussians in R and θ.

The states being considered are largely vibrational in nature and so it is illuminating to obtain some absolute measure of the relative abilities of the two angular basis sets (Legendre polynomials and distributed Gaussians) to describe the motion. To accomplish this, we placed Gaussians ($C_\theta = 0.75$) evenly on a rectangular grid between the limits 0 and π in θ, and $R_{\min}$ and $R_{\max}$ in R. This region is the same as that covered by the basis used to produce Fig. 1(a). The results are shown in Fig. 1(b) and a comparison of the two figures indicates that the basis sets have similar abilities to describe the angular dynamics of this system. This may not be the case for larger, more anisotropic systems where rotational basis functions provide only a poor description of the bending motion.

We now investigate the basis set reduction which may be obtained by manipulating the distributed Gaussian basis. For the moment let us keep the rectangular grid and just optimize the range in θ over which the Gaussian functions are placed. Due to the considerable barrier to rotation of the

CO$_2$ monomer, the wave functions should be very small at values of θ close to 0 and π radians. A significant saving should thus be obtained by reducing the range over which the functions are distributed. Investigating this we found a range of 0.7 π (centered on $\theta = \pi/2$) to be reasonably optimum. We consider the same three states as before and in Fig. 1(c) give their convergence as the angular basis is increased. Comparison with Fig. 1(b) shows that a reduction of about 20% in the basis set is afforded by placing the Gaussians over this restricted range.

The use of a direct-product basis of Gaussians in θ and R dictates that functions are placed well into the classically forbidden region for values of θ well away from equilibrium. As discussed in Sec. II, this may be avoided by removing all functions placed in regions where the potential is greater than a given value, $V_{\max}$. Repeating the calculation of Fig. 1(c) with $V_{\max}$ set to 100 cm^{-1} gave the results of Fig. 1(d). From Figs. 1(a) and 1(d) we see that this simple procedure for constructing a nondirect product basis of distributed Gaussians gives a saving of 35% to 40% over a direct product basis of monomer rotational functions coupled with distributed Gaussians.

B. States above the barrier

With the successes of the previous subsection, it is worth considering whether distributed Gaussian basis sets placed evenly on rectangular grids are capable of providing a competitive description of levels above the barrier to rotation of the CO$_2$. Initial feelings might be that they would not. Such states are best described as hindered rotations and should be
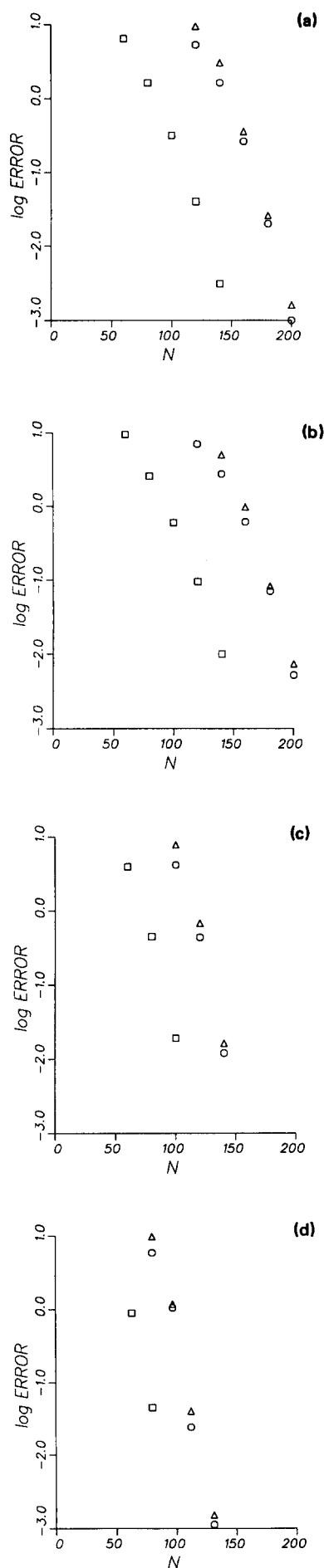
(a)

(b)

FIG. 1. Plot of $\log_{10}$ of the absolute error in the ground (squares), fifth excited (circles) and tenth excited (triangles) states of Ar–CO_2 against total basis set size for (a) a direct product basis of distributed Gaussians and monomer rotational functions; (b) a basis of Gaussians placed on a rectangular grid with a range in θ of π; (c) a basis of Gaussians placed on a rectangular grid with a range in θ of 0.7π; and (d) a nondirect product basis of Gaussians formed by removing functions from basis "c" using the criterion that the potential should be greater than 100 cm^{-1} at the center of the Gaussian.

(c)

(d)

more efficiently represented by monomer rotational functions. Furthermore, the wave function explores the whole range of θ and so we may not place Gaussians over a reduced interval in this coordinate. However, the removal of Gaussians lying in regions where the potential is greater than V_{max} should still give a significant basis set reduction since the hard wall shifts out considerably when the complex comes close to being linear. The aim of this subsection is to investigate the relative importance of these effects.

The basis of distributed Gaussian functions was constructed by placing functions evenly on a rectangular grid between 3.0 and 6.7 Å in R, and -0.05 and $1.05\,\pi$ in θ. We note that functions must be placed outside the range 0 to π to ensure completeness of the basis within the physical range. The values $C_R = 0.7$ and $C_\theta = 0.75$ were used and all functions placed where the potential is greater than 100 cm^{-1} were removed. We placed 37 Gaussians in R and varied the number of functions in θ to obtain errors in the energy levels with increasing basis. We present the error in the 28th excited energy level as a function of total basis set size in Fig. 2. We also give the values obtained by a basis with rotational functions in θ and 37 Gaussians between 3.0 and 6.7 Å in R.

From Fig. 2 we see that the basis of distributed Gaussians in R and θ does indeed provide an accurate description of the high lying states and is of virtually identical efficiency to the basis which uses monomer rotational functions in the angular coordinate. From this result we see that the advantages conferred on the monomer rotational functions by their more natural description of the motion are closely balanced by the ability of the localized basis not to venture into the classically forbidden region. Alternatively, we may say that the monomer rotational functions provide the best description of the angular motion at large R while the distributed Gaussians are more efficient at small R. This is an interesting viewpoint as it suggests that we should use the present distributed Gaussian basis at small R but improve the angular basis at large R. We address this in the next subsection.

C. Distributing the Gaussians semiclassically

Up to this point we have constructed the distributed Gaussian basis sets by initially placing the functions evenly on a rectangular grid with equal spacing in both R and θ. However, this is very inefficient for describing high lying
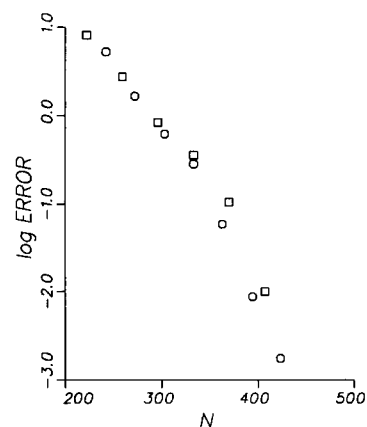

FIG. 2. Plot of $\log_{10}$ of the absolute error in the 28th excited state against basis set size for (squares) a basis of distributed Gaussians coupled with monomer rotational functions; (circles) distributed Gaussians placed on a rectangular grid with a range in θ of 1.1π and functions removed if $V > 100$ cm^{-1}.

states since the oscillation of the wave function changes from being rapid in the well region to very slow at large values of the dissociation coordinate. It is thus appropriate to consider schemes for placing the Gaussians more sparsely in the regions of large R.

Of course, such tricks may be used to reduce the size of any (direct or nondirect product) basis which uses distributed Gaussians in the radial coordinate. However, for a direct product basis, we are restricted to constructing a single optimized radial basis. To enable a fair comparison of the methods we first construct such a basis for use in a direct product with monomer rotational functions. We use a simple prescription described recently by Peet and Yang[14] and ensure that the basis is as small as possible while still giving converged (to within 0.001 cm^{-1}) results for the 28th excited state. This was found to be the case when 20 functions were placed evenly in the inner region[14] (3.0 to 5.0 Å) and the outer limit was taken to be 6.7 Å. Using this radial basis and varying the number of monomer rotational functions gave the errors presented in Fig. 3. Comparing the results with those of Fig. 2 shows that this method of modeling the wave function by the distributed Gaussians effects a saving of about 20% in the basis.

For a basis of distributed Gaussians in R and θ we could similarly construct a single efficient radial basis then combine this with a set of functions evenly spaced in θ. This would afford similar savings to those obtained by the direct product basis but would not exploit the flexibility of the local basis set to the full. A slightly better scheme would be to define separate radial basis sets at each of the selected values of θ. However, the savings from such an approach are likely to be small since the potential is fairly isotropic at large values of R where the variable spacing is used. In order to effect greater reductions in basis set size we must increase the spacing in θ as well as R at large values of the intermolecular distance.

A simple method for choosing the positions in θ may be obtained by using the fact that the potential is relatively isotropic at large R. It is therefore appropriate to space the functions evenly in θ but to choose a different spacing for each value of R. A technique for accomplishing this is described in detail in the Appendix. The basic idea is that the shape of the generalized multidimensional Gaussians [Eq. (3)] should be kept the same over all coordinate space but
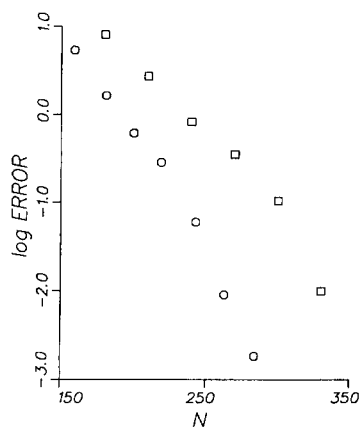
that the size should increase in regions where the wave function is slowly varying. Placing the Gaussians according to the procedure given in the Appendix (with $R_n = 5.0$ Å, $\Delta_R = 0.1$ Å, $C_R = 0.75$, and $C_\theta = 0.75$) yielded the results which are also presented in Fig. 3. We see that there is a significant saving in the basis set (about 30%) over the best direct product method. From this example we clearly see the advantages conferred by having a basis of functions localized in the complete space.

IV. DISCUSSION

We have investigated the ability of distributed Gaussian basis sets to describe the bound states of floppy molecules. The approach is an extension of a method due to Light and co-workers[2,6] who used distributed Gaussians to describe stretching coordinates. Here, we include the bending coordinates in the same scheme, yielding basis functions which are localized in the full internal coordinate space. This allows the functions to be placed in a manner which forms an efficient description of the wave function. However, in order to take advantage of this property, a reliable technique for choosing the basis set parameters must be available. In this paper, we placed an emphasis on simple schemes for accomplishing this task, with the foresight that the technique will eventually need to be used for systems of higher dimensionality.

For low lying states, we constructed basis sets by initially placing the functions on a rectangular grid and then discarding the ones lying above a given value of the potential. Tests on the Ar–CO$_2$ complex showed that a 30% to 40% reduction in the basis set size was achieved compared with a basis incorporating monomer rotational functions. More sophisticated schemes which allow a closer modeling of the wavefunction may be used but none we considered were, in our opinion, simple enough to be used in systems of many dimensions.

Highly excited states cover large regions of coordinate space and the wave function oscillates rapidly in some parts but only very slowly in others. Thus, it is essential to use a basis which more closely models the form of the wave function. We developed a straightforward technique for doing this in the atom-rigid linear molecule case and the method should be easily extended to larger systems. Tests on the Ar–CO$_2$ complex showed that a 30% reduction in the basis set size was achieved by this basis set when compared with a basis incorporating monomer rotational functions.

Distributed Gaussians clearly form an efficient basis for calculating the bound states of small, relatively anisotropic, complexes such as Ar–CO$_2$. For systems of greater anisotropy the savings over a direct product basis of single center expansions should increase greatly. The method thus holds much promise for treating complexes such as HCl dimer and H$_2$O dimer for which no exact quantum mechanical treatment is at present available.

FIG. 3. Plot of log$_{10}$ of the absolute value in the 28th excited state against total basis set size for (squares) a basis of monomer rotational functions coupled with a largely optimized basis of distributed Gaussians in R; (circles) a basis of distributed Gaussians formed by the method presented in the Appendix.

ACKNOWLEDGMENTS

APPENDIX

In this Appendix we describe the method used to select the positions of the distributed Gaussian functions used in the basis sets of Sec. III C. The method is an extension of a technique used recently for a radial basis of Gaussian functions and is adapted from similar approaches due to Light and co-workers.[6] We first define a one-dimensional radial potential as a cut through the surface at a value of θ corresponding to the potential minimum. The motion on this 1D cut is described approximately by the semiclassical wave function,[9]

$$\Psi = e^{iS(R)/\hbar} \tag{A1}$$

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

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

with $p(R)$ being the classical momentum $p^2(R) = 2\mu [E - V(R)]$.

From Eqs. (A1) and (A2) we see that if a node exists in Ψ at R_i then one will exist at R_{i+1} where

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

Now, following the procedure of Ref. 14 we define an inner region in which we place n Gaussians evenly and an outer region in which the potential is varying slowly enough to allow the approximation $V(R) \approx V(R_i)$ to be used. Integrating Eq. (A3) explicitly in the outer region then allows R_{i+1} to be obtained in terms of R_i. In practice we require more than one Gaussian per node and the spacing obtained from Eq. (A3) is multiplied by a constant. Selecting this constant to give continuity of spacing at the boundary between the two regions then yields the prescription

$$R_{i+1} = R_i + \Delta_R \frac{\sqrt{2\mu[E - V(R_n)]}}{\sqrt{2\mu[E - V(R_i)]}} \quad i = n+1,...N^R, \tag{A4}$$

where R_n is the final point of the inner region and Δ_R is the spacing there. We take the energy E to be that of the dissociation limit.

We now consider the positioning of the functions in θ. For values of R less than R_n we use a global spacing Δ_θ in θ

and treat this as a parameter to converge. Along with the distance Δ_R this then defines the positioning of the functions in the inner region. Using the formulas

$$A_i^R = C_R^2/\Delta_R^2; \quad A_j^\theta = C_\theta^2/\Delta_\theta^2, \tag{A5}$$

then totally defines the basis in the inner region.

In the outer region, the $\{R_i\}$ are given by the values on the 1D radial cut. We then associate with each R_i a basis in θ which is chosen as follows. The widths of the Gaussians in R are given by the formula,

$$A_i^R = C_R^2/(R_{i+1} - R_{i-1})^2 \tag{A6}$$

and we select the widths of the functions in θ so as to keep the shape of the multidimensional product (3) the same as in the inner region, i.e., A_i^θ is chosen to keep the ratio A_i^θ/A_i^R constant throughout space. The spacing H_i^θ of the functions in θ is then easily obtained from the formula

$$H_i^\theta = C_\theta/\sqrt{A_i^\theta}. \tag{A7}$$

Ensuring that Gaussians lie at $\theta = \pi/2 \pm H_i^\theta/2$ and excluding ones outside the range 1.05 to -0.05π, then totally defines the basis.

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