

1968

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John P. Chesick  
*Haverford College*

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Chesick, John P. "Gaussian basis sets for model anharmonic oscillator systems." *The Journal of Chemical Physics* 49 (1968): 3772.

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Citation: *J. Chem. Phys.* **49**, 3772 (1968); doi: 10.1063/1.1670678

View online: <http://dx.doi.org/10.1063/1.1670678>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v49/i9>

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## Gaussian Basis Sets for Model Anharmonic Oscillator Systems

JOHN P. CHESICK\*

*Department of Chemistry, Haverford College, Haverford, Pennsylvania 19041*

(Received 8 July 1968)

Basis sets of equally spaced Gaussian functions are used to obtain diatomic Morse and harmonic-oscillator wavefunctions for CH and CN species. These functions are then used to obtain energy levels and eigenfunctions for model linear HCN and CH<sub>2</sub> species with both harmonic and Morse potentials for two internal coordinates.

Wilson and co-workers<sup>1,2</sup> have described a variety of approaches to the problem of calculating eigenvalues and wavefunctions for model anharmonic-oscillator systems. Such quantities for systems containing at least two internal coordinates would be useful in consideration of problems of inter- and intramolecular energy transfer relevant to chemical kinetics. For polyatomic (more than two atoms) problems, continuum states must be considered as well as bound states when the total vibrational energy exceeds the dissociation energy of a single bond. However, except for some calculations reported for a model H<sub>3</sub> species,<sup>3</sup> even the bound states for highly vibrationally anharmonic systems have not been characterized for systems other than diatomic molecules.

Endres and Wilson<sup>2</sup> compared results of using perturbation theory and expansion in a harmonic-oscillator basis set for the diatomic Morse oscillator problem. Baetzold, Tahk, and Wilson<sup>1</sup> used products of diatomic harmonic-oscillator wavefunctions as an expansion basis set for a linear triatomic harmonic-oscillator system. Endres<sup>3</sup> used such products of diatomic harmonic-oscillator functions for a linear H<sub>3</sub>-coupled Morse system with two internal coordinates. Difficulties arise in the selection of a basis set which will provide sufficiently rapid convergence for a practical basis size and which also permits convenient evaluation of matrix elements for anharmonic potential functions.

The following is a report of the trial of different sets of evenly spaced Gaussian orbitals as a basis for the Morse diatomic oscillator problem with extensions to linear Morse triatomic systems. Ease of integral evaluation with Gaussian basis functions having variable centers should permit application to a wide variety of potential functions. Although Gaussian basis sets have been frequently employed in molecular electronic calculations, their use has not previously been reported for this vibrational problem.

### DIATOMIC CALCULATIONS

A normalized basis set of the form  $x_i = (2a/\pi)^{1/4} \times \exp[-a(x-c_i)^2]$  was used. Here, the centers  $c_i$  are

\* Work performed as a National Science Foundation Science Faculty Fellow, Cambridge University (1967).

<sup>1</sup> R. C. Baetzold, C. T. Tahk, and D. J. Wilson, *J. Chem. Phys.* **45**, 4209 (1966).

<sup>2</sup> P. F. Endres and D. J. Wilson, *J. Chem. Phys.* **46**, 425 (1967).

<sup>3</sup> P. F. Endres, *J. Chem. Phys.* **47**, 798 (1967).

chosen to be equally spaced along the coordinate axis, and the exponent constant  $a$  is chosen to be the value of the quantity  $\mu(h\nu_0)/(2\hbar^2)$ . This is the exponent of the ground-state harmonic-oscillator function matching the curvature of the Morse and harmonic potentials at the potential minimum with  $\nu_0$  being the harmonic-oscillator vibration frequency. The coordinate origin is defined by the Morse potential in the form

$$V = D[1 - \exp(-cx)]^2,$$

$$c = (h\nu_0)(\mu/2D)^{1/2}\hbar^{-1}.$$

Here,  $D$  is the dissociation energy.

Table I lists the exact eigenvalues obtained for the Morse problem for a CH molecule using the parameters employed by Endres and Wilson.<sup>2</sup> Also included are sets of eigenvalues for the calculations of Endres and Wilson with a 30-term harmonic-oscillator basis set, and for sets of 15, 20, and 25 evenly spaced Gaussian functions employed in this work. The 15-term set was centered at the coordinate origin, and the 20-term set was shifted to larger coordinate values so that the seventh function was located at the origin. The 25-term set was located with the ninth Gaussian basis function at the origin. The magnitude of the interval between the basis functions is illustrated by the quoted values of  $S_{12}$ , the overlap integral between adjacent functions, for each case.

The solution of the eigenvalue problem  $|\mathbf{H} - E\mathbf{S}| = 0$  in the nonorthogonal basis was achieved by means of the Löwdin canonical orthogonalization procedure<sup>4</sup> which diagonalizes the overlap matrix  $\mathbf{S}$  and then transforms the Hamiltonian matrix to give the eigenvalue problem in the form  $|\mathbf{H}' - E| = 0$  in the new orthonormal basis. Diagonalizations of the symmetric matrices were performed with a standard library routine employing the Jacobi method. The Cambridge University TITAN computer operating with 11-12 decimal digit precision was used for all calculations. A poorly conditioned  $\mathbf{S}$  matrix results from close basis-function spacing and leads to some inaccuracies in highest eigenvalues and eigenvectors as shown by deterioration in eigenvector orthonormality for large eigenvalues. This error is the limiting factor in reducing the spacing between the Gaussian basis functions and in obtaining accurate upper energy levels and

<sup>4</sup> P.-O. Löwdin, *Advan. Phys.* **5**, 1 (1956).

TABLE I. Eigenvalues for diatomic Morse oscillator (CH molecule)<sup>a</sup> (energy×10<sup>12</sup> erg).

n	Exact Morse	30-Term harmonic osc. basis <sup>b</sup>	15-Term Gaussian basis S <sub>12</sub> =0.927	20-Term Gaussian basis		25-Term Gaussian basis S=0.916
				S <sub>12</sub> =0.927	S <sub>12</sub> =0.916	
0	0.26900	0.26900	0.26900	0.26900	0.26900	0.26900
1	0.78855	0.78854	0.78855	0.78855	0.78855	0.78855
2	1.28347	1.28345	1.28347	1.28347	1.28348	1.28347
3	1.75378	1.75376	1.75380	1.75379	1.75380	1.75379
4	2.19948	2.19942	2.19954	2.19951	2.19960	2.19952
5	2.62056	2.62353	2.62120	2.62070	2.62100	2.62065
6	3.01702	3.02666	3.02439	3.01732	3.01780	3.01712
7	3.38886	3.43153	3.42915	3.38869	3.38963	3.38909
8	3.73609	3.86548	3.91847	3.73362	3.73761	3.73731
9	4.05871	4.34537	4.41652	4.04933	4.06397	4.06238
10	4.35670	...	5.02884	4.35949	4.37443	4.363396
11	4.63008	...	6.79512	4.61999	4.66735	4.63925
12	4.87885	...	...	5.02417	5.00663	4.89081

<sup>a</sup> Molecular parameters: D = 6.014 × 10<sup>12</sup> erg; (hν<sub>0</sub>) = 0.54416 × 10<sup>-12</sup> erg; μ = 1.5436 × 10<sup>-24</sup> g.

<sup>b</sup> Reference 2.

eigenfunctions for larger Gaussian basis sets with this method. The larger of the two spacings cited for the 20-term set gives slightly poorer energies for the higher states than did the closer spacing, but numerical errors for the smaller spacing are apparent from the few eigenvalues which were slightly lower than the exact values, also given in Table I. The largest off-diagonal

eigenvector overlap integrals for the first 10 eigenvectors associated with the 10 lowest eigenvalues were 1.5 × 10<sup>-3</sup>, 2.7 × 10<sup>-5</sup>, and 8.3 × 10<sup>-5</sup> for the basis sets associated with the last three columns of Table I. The corresponding values for the first six eigenvectors were 7.0 × 10<sup>-6</sup>, 3.0 × 10<sup>-7</sup>, and 1.7 × 10<sup>-7</sup>, respectively.

TRIATOMIC SYSTEMS

TABLE II. Energy levels for linear CH<sub>2</sub> system. All potential parameters are same as those employed for CH diatomic oscillator. D = 6.0146 × 10<sup>-12</sup> erg (energy × 10<sup>12</sup> erg).

Harmonic potentials			Morse potentials	
Exact	Product function basis		Product function	
	25 terms	36 terms	25 terms	36 terms
0.54375	0.54375	0.54375	0.53761	0.53761
1.06640	1.06640	1.06640	1.03706	1.03706
1.10860	1.10860	1.10860	1.07644	1.07644
1.58905	1.58905	1.58905	1.52313	1.52313
1.63125	1.63125	1.63125	1.55214	1.55214
1.67346	1.67346	1.67346	1.60318	1.60318
2.11170	2.11170	2.11170	1.99400	1.99391
2.15390	2.15390	2.15390	2.01188	2.01176
2.19610	2.19610	2.19610	2.06109	2.06103
2.23831	2.23831	2.23831	2.11654	2.11653
2.63434	2.63466	2.63435	2.44656	2.44535
2.67655	2.67768	2.67656	2.45488	2.45336
2.71875	2.72028	2.71876	2.50848	2.50766
2.76096	2.76188	2.76096	2.55681	2.55620
2.80316	2.80337	2.80316	2.61670	2.61655
3.15699	3.16457	3.15720	2.93602	2.87331
3.19920	3.22977	3.20009	2.97258	2.87583
3.24140	3.30123	3.24300	3.03793	2.94634
3.28361	3.36265	3.28504	3.10324	2.98297
3.32581	3.70637	3.32646	3.41360	3.04020
3.36802	3.81238	3.36813	3.49062	3.01314
3.67964	3.91225	3.68409	3.57330	3.36556
3.72185	4.27393	3.74223	3.89596	3.38569
3.76405	4.44243	3.80968	4.01961	3.45025

Calculations were performed for linear triatomic systems with parameters chosen to represent linear CH<sub>2</sub> and HCN systems. Following Baetzold, Tahk, and Wilson,<sup>1</sup> the Hamiltonian, in terms of the coordinates x<sub>1</sub> and x<sub>2</sub> representing the extensions of the two bonds, is taken to be

$$\mathcal{H} = -\frac{1}{2}\hbar^2 \left( \frac{1}{\mu_{12}} \frac{\partial^2}{\partial x_1^2} - \frac{2}{M_2} \frac{\partial^2}{\partial x_1 \partial x_2} + \frac{1}{\mu_{23}} \frac{\partial^2}{\partial x_2^2} \right) + V(x_1) + V(x_2).$$

Either harmonic or Morse potential functions were employed for the two coordinates. A basis set for this problem was formed from basic product functions of the form

$$\Phi_i(1, 2) = \phi_j(1)\phi_k'(2).$$

Here, φ<sub>j</sub> and φ<sub>k</sub>' are chosen from the sets of eigenfunctions for the diatomic oscillator problems for coordinates x<sub>1</sub> and x<sub>2</sub>, respectively. These diatomic functions were obtained in turn from the original Gaussian basis sets. The diatomic eigenfunctions are members of the same set for the symmetrical CH<sub>2</sub> case and are from the two different sets of solutions for the CH and CN species when considering HCN. Basic-product basis sets of 25 and 36 terms were tried for CH<sub>2</sub> using combinations of the first five or six diatomic eigenfunctions. Solutions of the eigenvalue problem in this orthonormal basic-product basis presented no numerical difficulties for the triatomic case once the diatomic eigenfunctions had been obtained in terms of the Gaussian basis set.

TABLE III. Energy levels for linear HCN system. Potential parameters for CH coordinate are same as for Table I. For CN coordinate,  $h\nu_0=0.410749\times 10^{-12}$  erg;  $D=1.22232\times 10^{-11}$  erg. 30-Term product function basis (energy  $\times 10^{-12}$  erg).

Harmonic potentials		Morse potentials Product function
Exact	Product function	
0.47498	0.47498	0.47109
0.86745	0.86745	0.85615
1.03246	1.03246	1.00453
1.25992	1.25992	1.23610
1.42494	1.42494	1.38434
1.59005	1.58995	1.51694
1.65240	1.65240	1.61090
1.81741	1.81742	1.75950
1.98242	1.98250	1.89021
2.04487	2.04520	1.98110
2.14754	2.14759	2.01011
2.20988	2.21011	2.13055
2.37490	2.37608	2.26167
2.43734	2.44861	2.35584
2.53992	2.54434	2.37946
2.60236	2.60693	2.48778
2.70502	2.71185	2.50182
2.76737	2.77410	2.63986
2.82982	2.94784	2.78218
2.93238	2.95812	2.82746
2.99483	3.16089	2.92584
3.09739	3.16835	3.00696
3.15984	3.37409	3.17560
3.22229	3.46781	3.29893

The results are given in Table II for the two product basis set sizes for  $\text{CH}_2$  using both harmonic and Morse potentials as well as the exact eigenvalues expected for the harmonic case. Twenty-term Gaussian basis sets were used in obtaining the solutions for the harmonic and Morse diatomic CH problems.

Table III summarizes results obtained for the linear model HCN system using both harmonic and Morse potentials for the two bond coordinates and product

basis sets obtained from the diatomic problems. The previously mentioned parameters were used for the CH potential, and the values employed for CN are given in Table III for  $D$  and  $h\nu_0$ . The exponent for the Gaussian basis for the CN diatomic problem was chosen to be  $\mu(h\nu_0)/(2\hbar^2)$  as was done for the CH system, and the Gaussian basis spacing was adjusted to obtain the same overlap for adjacent functions as was used for the CH calculations. Twenty-term Gaussian basis sets were again used for the diatomic eigenvector calculations; the first five CH diatomic eigenfunctions were combined with the first six CN eigenfunctions to give a 30-term product basis set for the triatomic problem. Harmonic or Morse potentials were again used for the diatomic problems to obtain basis sets for use with harmonic or Morse potentials for the triatomic case.

### CONCLUSIONS

It is seen that the distributed Gaussian basis sets are more effective than the harmonic oscillator basis employed by Endres and Wilson<sup>2</sup> for the CH Morse oscillator. Anharmonic potential problems in model oscillator systems of more than one coordinate seem to be approachable with the Gaussian basis sets. It is found that the 36-term product set gives energy values to better than 1% for  $E/D$  up to 0.62 for triatomic systems with two internal coordinates. The basic-product basis set could be enlarged without orthogonality problems by using more terms from the diatomic function sets. Improved numerical methods such as double precision calculations, or use of a technique for solving the  $\mathbf{H}-ES$  eigenvalue problem for the diatomic levels in the Gaussian basis which requires only one matrix diagonalization should eliminate the difficulties encountered here.

Although the Morse diatomic problem is soluble by other techniques, more general potential functions should be tractable with the Gaussian basis due to general ease of integral evaluation, and Gaussian basis sets would seem to have some utility in other than electronic energy-state calculations.