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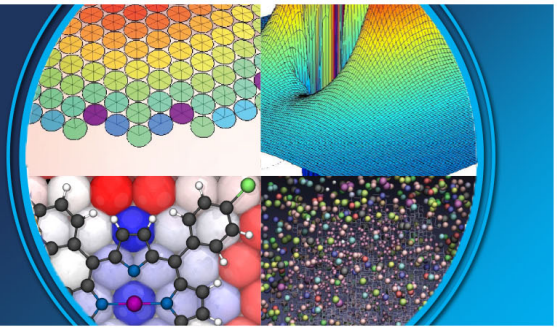

Again, one can apply the stripping mechanism. When the C^+ ion makes a head-on collision with an oxygen atom in O_2, it can impart most of its kinetic energy to the oxygen causing the O–O bond to rupture and the struck oxygen atom leaves the reaction scene. The C^+ ion has very little residual kinetic energy and remains in the region of the remaining oxygen long enough to form the product, CO^+. There will, of course, be a certain threshold for bond rupture, and there will also be an upper energy limit beyond which the product cannot form since the internal energy would exceed the bond energy. Another mechanism by which these high-energy reactions can possibly proceed is a multiple collision process suggested by Bates *et al.*[20]

The production of CO^+ by the ^4P state of the C^+ is illustrated in Fig. 10. This is a typical cross-section curve for an exothermic ion-molecule reaction and probably proceeds by the ion-induced-dipole mechanism. A small amount of CO^+ is also formed at high ion kinetic energies. This presumably arises as a direct process proceeding by a stripping mechanism or some other high-energy process.

[20] D. R. Bates, C. J. Cook, and F. J. Smith, Proc. Phys. Soc. (London) **83**, 49 (1964).

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Calculation of Matrix Elements for One-Dimensional Quantum-Mechanical Problems*

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A simple method proposed by Harris *et al.* using the techniques of transformation theory for the generation of the matrix elements of one-dimensional potential functions in a discrete, orthonormal basis is shown to be equivalent to Gaussian quadratures when the basis is constructed of orthogonal polynomials. The basis $\exp(in\theta)$ on $(-\pi, \pi)$ is also discussed.

I. INTRODUCTION

A method has been proposed by Harris *et al.*[1] and employed by several authors,[2] for the calculation of the matrix of a one-dimensional potential function $V(x)$ in a discrete, orthonormal basis $\phi_n(x)$, $n=0, 1, \cdots, N$, where the set ϕ_n is complete for $N\to\infty$. The variable x has the range (a, b). The implementation of the method requires the existence of a single-valued function $u(x)$ on the range (a, b), in which case their prescription for the evaluation of the matrix elements of V is

$$V_{nm}=\int_a^b \phi_n(x)\,V[x(u)]\phi_m(x)\,dx$$

$$=\sum_{j=0}^{N} T_{nj}T_{mj}V[x(\lambda_j)], \qquad 0\leq n, m\leq N, \quad (1)$$

where the T_{nj} and λ_j are determined by

$$\int_a^b \phi_n(x)\phi_m(x)\,dx=\delta_{nm}=\sum_{j=0}^{N} T_{nj}T_{mj}, \quad (2)$$

$$\int_a^b \phi_n(x)u(x)\phi_m(x)\,dx=u_{nm}=\sum_{j=0}^{N} T_{nj}T_{mj}\lambda_j, \quad (3)$$

i.e., the orthogonal matrix $\mathbf{T}=(T_{nm})$ diagonalizes $\mathbf{u}=(u_{nm})$.

For the case where the $\mathbf{u}$ is tridiagonal, Harris *et al.* have shown that V_{nm} is exact for V, a polynomial in u of precise degree $2N-n-m+1$ or less. For the general case where only $u_{n,n\pm i}$, $i\leq r$, is nonvanishing, it may be shown that V_{nm} is exact for V of precise degree $(2N-n-m)/r+1$ or less. Hence, it is desirable to employ a function u whose matrix is tridiagonal.

Since the formula (1) is very suggestive of an $(N+1)$-point mechanical quadrature, it may be compared with the Gaussian-type quadrature of the same order. In the present paper, the relationship of (1) to Gaussian quadratures is considered for: (i) the set ϕ_n constructed from orthogonal polynomials on (a, b) and; (ii) $\phi_n=(2\pi)^{-1/2}\exp(in\theta)$ on $(-\pi, \pi)$.

II. ORTHOGONAL POLYNOMIALS

If $u(x)=x$, and the basis ϕ_n is obtained from the first $N+1$ polynomials in x orthogonal with respect to

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[1] D. O. Harris, G. G. Engerholm, and W. D. Gwinn, J. Chem. Phys. **43**, 1515 (1965).

[2] (a) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, J. Chem. Phys. **44**, 3467 (1966); (b) D. F. Zetik and F. A. Matsen, J. Mol. Spectry. **24**, 122 (1967); (c) P. F. Endres, J. Chem. Phys. **47**, 798 (1967); (d) C. Schwartz, J. Comput. Phys. **3**, 90 (1967).

the positive weight function $w(x)$ on (a, b), i.e., if

$$\phi_n(x)=[w(x)/h_n]^{1/2}f_n(x), \qquad n=0, 1, \cdots, N, \quad (4)$$

where

$$\int_a^b f_n(x)f_m(x)w(x)\,dx=h_n\delta_{nm}$$

and

$$f_n(x)=k_nx^n+k_n'x^{n-1}+\cdots, \quad (5)$$

then the equivalence of (1) and a Gaussian quadrature may be explicitly demonstrated.

Using the Gaussian quadrature defined by $w(x)$ on (a, b), the formula for V_{nm} is[3]

$$V_{nm}=\sum_{j=0}^{N}(h_nh_m)^{-1/2}W_j^{(N)}f_n(a_j^{(N)})f_m(a_j^{(N)})V(a_j^{(N)}), \quad (6)$$

where the $a_j^{(N)}$ are the zeros of f_{N+1},

$$f_{N+1}(a_j^{(N)})=0, \qquad j=0, 1, \cdots, N \quad (7)$$

and

$$W_j^{(N)}=-k_{N+2}h_{N+1}/k_{N+1}f_{N+1}'(a_j^{(N)})f_{N+2}(a_j^{(N)}), \quad (8)$$

where $f'(x)=df/dx$. In the following the explicit dependence of the $a_j^{(N)}$ and $W_j^{(N)}$ upon N will be suppressed.

To establish the identity of (1) and (6) it is necessary to prove the following relations:

(i) λ_j[Eq. (3)]$=a_j$[Eq. (7)], where both are arranged monotonically;
(ii) $T_{nj}=(W_j/h_n)^{1/2}f_n(a_j)$.

The statement (i) follows from the recursion relation[4] among the f_n

$$f_{n+1}=(A_n+B_nx)f_n-C_nf_{n-1}, \quad (9)$$

where

$$A_n=B_n[(k_{n+1}'/k_{n+1})-(k_n'/k_n)],$$
$$B_n=k_{n+1}/k_n,$$
$$C_n=B_nh_n/B_{n-1}h_{n-1}. \quad (10)$$

This greatly simplifies the construction of the secular equation to determine the λ_j,

$$D_{N+1}(\lambda_j)=0, \qquad j=0, 1, \cdots, N, \quad (11)$$

where

$$D_N(\lambda)=(-)^Nk_N\det(\mathbf{u}-\lambda\mathbf{1}), \quad (12)$$

and $\mathbf{u}$ and $\mathbf{1}$ are of dimension $N\times N$.

Expanding along the last row of (12), we see that the D_N satisfy the recursion relation

$$D_{N+1}(\lambda)=(A_N+B_N\lambda)D_N(\lambda)-C_ND_{N-1}(\lambda). \quad (13)$$

It is easy to check that $D_1(\lambda)=f_1(\lambda)$ and $D_2(\lambda)=f_2(\lambda)$ so that by (13), $D_N(\lambda)=f_N(\lambda)$ for all $N>0$, and hence (11) is the same as (7). This demonstrates statement (i).

To show the validity of (ii) we make use of two identities which are easily derived from Eq. (9). The first is a special case of the Christoffel–Darboux identity,[4]

$$\sum_{n=0}^{N}h_n^{-1}f_n(a_i)f_n(a_j)=\delta_{ij}W_j^{-1}, \quad (14)$$

and the second is

$$\sum_{n=0}^{N}h_n^{-1}f_n(a_i)f_n(a_j)A_nB_n^{-1}=-\delta_{ij}a_jW_j^{-1}+\sum_{n=0}^{N}\frac{f_{n+1}(a_i)f_n(a_j)+f_n(a_i)f_{n+1}(a_j)}{h_nB_n}, \quad (15)$$

where a_i, a_j are zeros of f_{N+1}.

Let $S_{nj}=(W_j/h_n)^{1/2}f_n(a_j)$. Then (14) implies that

$$\sum_{n=0}^{N}S_{nj}S_{nk}=\delta_{jk}, \quad (16)$$

and (15) implies that

$$\sum_{n=0}^{N}\sum_{m=0}^{N}S_{nj}S_{mk}x_{nm}=a_j\delta_{jk}=\lambda_j\delta_{jk}. \quad (17)$$

Hence, the S_{nj} are the elements of an orthogonal matrix which diagonalizes $\mathbf{x}$. Since the eigenvalues of the latter matrix are nondegenerate,[3] the elements S_{nj} are unique and thus equal to the T_{nj}.

Thus, since (1) is a Gaussian quadrature when the ϕ_n are obtained from (4) and (5), V_{nm} will be exact for V, a polynomial of precise degree p, where $p\leq(2N+1-n-m)$, as was shown by Harris *et al.*

For many of the basis sets satisfying (4) and (5) likely to be employed in problems of physical interest there exist corresponding quadratures with published values[5] of the a_j, which substantially reduces the effort required to diagonalize $\mathbf{x}$.

III. THE BASIS $\exp(in\theta)$

Where the basis functions ϕ_n do not satisfy (4) and (5), the transformation method may again be equivalent to a Gaussian quadrature, but not necessarily to the most efficient choice of weight function $w(x)$. The

[3] A. Ralston, *A First Course in Numerical Analysis* (McGraw-Hill Book Co., New York, 1965), pp. 85–111.
[4] G. Szegö, *Orthogonal Polynomials* (American Mathematical Society Colloquium Publications, New York, 1959), Vol. 23, Sec. 3.2.
[5] A. H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1966).

basis $\exp[i(n-N)\theta]$, $-\pi\leq\theta\leq\pi$, $n=0, 1, \cdots, 2N$, discussed by Harris *et al.* may be taken as an example.

It is assumed that V is a polynomial of precise degree p in $u=\cos\theta$. Since $\mathbf{u}$ is tridiagonal in this basis, the characteristic polynomials D_N, defined by (12), satisfy a three-term recursion relation. This is easily identified as that satisfied by the Chebyshev polynomials of the second kind,[6] $U_n(x)$. It should be noted that the zeros of U_n can be written in closed form, and $\mathbf{T}$ can be obtained from statement (ii) above. Therefore, by (6) the matrix transformation technique evaluates the $(2N+1)$-point Gauss–Chebyshev quadrature (of the second kind) of the integral

$$\frac{2}{\pi}\int_0^\pi V(\cos\theta)\,U_n(\cos\theta)\,U_m(\cos\theta)\sin^2\theta d\theta, \quad 0\leq n,m\leq 2N,$$

which is exact for $p\leq 4N+1-n-m$. On the other hand, using the relations between the U_n and the Chebyshev polynomials of the first kind T_n, V_{nm} may be written

$$V_{nm}=\frac{2}{\pi}\int_0^\pi V(\cos\theta)\,U_n(\cos\theta)\,U_m(\cos\theta)\,\sin^2\theta d\theta + \pi^{-1}\int_0^\pi V(\cos\theta)\,T_{n+m+2}(\cos\theta)\,d\theta.$$

The second integral on the right vanishes for $p<n+m+2$ by orthogonality. The two conditions on p for V_{nm} to be exact may be combined to $p\leq 2N+1-|2N-n-m|$, for a basis consisting of $2N+1$ functions.

The connection between the transformation method and Gaussian quadratures for this case may be clarified by applying the Wang transformation.[7] This is equivalent to choosing as a $(2N+1)$-term basis, the functions

$$T_n(\cos\theta), \quad 0\leq n\leq N$$

and

$$\sin\theta U_n(\cos\theta), \quad 0\leq n\leq N-1.$$

These are, respectively, symmetric and antisymmetric with respect to $\theta\rightarrow-\theta$ and hence, the matrix $\mathbf{V}$ factors into an $(N+1)\times(N+1)$ block and an $N\times N$ block. Since the basis now consists of orthogonal polynomials, the analysis of the preceding section may be applied separately to each block. This leads to the same conditions on p for V_{nm} to be exact as given in the previous paragraph.

IV. CONCLUSIONS

The matrix transformation method provides a convenient technique for generating integrals for a one-dimensional variational problem using standard matrix manipulations. As Harris *et al.* point out, the diagonalization of $\mathbf{u}$ need only be performed once for a given N, if the λ_j and $\mathbf{T}$ are retained from problem to problem. In addition, for many cases of physical interest, a scaling parameter may be introduced into the basis, enabling several different basis sets to employ the same λ_j and $\mathbf{T}$. For example, in the work of Zetik and Matsen[2b] on the computation of vibrational–rotational energy levels, if the matrix of $u=(R-R_0)(\mu k/\hbar^2)^{-1/4}$, where the parameters have their usual significance, is computed, then the values of the independent variable R may be obtained by a suitable choice of R_0 and k.

The method does, however, add an unnecessary inflexibility to the energy eigenvalue problem in that evaluation of the matrix elements and the convergence of the eigenvalues with increasing N need not be considered simultaneously. The minimum number of values of V required for the accurate evaluation of V_{nm} is not independent of n and m and need not equal the number of basis functions required for a satisfactory representation of the wavefunction.

Note added in proof: The properties of the matrix $\mathbf{u}$ of Sec. II are also discussed by Wilf.[8] See also Golub and Welsh.[9]

[6] *Handbook of Mathematical Functions*, M. Abramowitz and I. A. Stegun, Eds. (National Bureau of Standards, Washington, D.C., 1964), Chaps. 22 and 25. The D_2 distinguishes between the Chebyshev polynomials of the first kind, $T_n(\cos\theta)=\cos n\theta$, and of the second kind, $U_{n-1}(\cos\theta)=(\sin n\theta)/\sin\theta$, which otherwise satisfy the same recurrence relation.

[7] J. E. Wollrab, *Rotational Spectra and Molecular Structure* (Academic Press Inc., New York, 1967), p. 26. We are indebted to the referee for bringing this to our attention.

[8] H. S. Wilf, *Mathematics for the Physical Sciences* (John Wiley & Sons, Inc., New York, 1962), p. 55.

[9] G. H. Golub and J. H. Welsch, Calculation of Gauss Quadrature Rules, Computer Science Department Technical Reference CS81, Stanford University, Stanford, Calif., 1967 (unpublished).