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Calculation of Matrix Elements for One-Dimensional Quantum-Mechanical Problems and the Application to Anharmonic Oscillators

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A simple method using the techniques of transformation theory for the generation of the matrix elements of unusual potential functions for one-dimensional quantum-mechanical problems is described. It is applicable both to functions which exist as a set of points, for example, a curve or table, as well as to those in explicit form. Some representative calculations have been made for anharmonic oscillators.

OF the various methods available for the practical solution of quantum-mechanical problems having unusual potential functions, the one we have found to be most convenient uses the matrix formulation of quantum mechanics. The energy levels are obtained by setting up the Hamiltonian in some convenient representation and diagonalizing the resultant matrix. The expectation values of various dynamical variables and transition dipole moments are then obtained by transforming the matrices of the appropriate operators to the energy representation. Systems having infinite basis sets can be easily handled simply by truncating the matrices to some convenient size. This procedure has given, for example, the first 20 quartic oscillator energy levels and associated eigenvectors very accurately by starting with 100 harmonic-oscillator basis functions.[1]

The matrix formulation requires a set of matrices which satisfy the basic commutation rules for the coordinates and momenta; it also requires being able to generate the appropriate matrix to represent the potential function. These matrices may be computed by direct integration, or by the use of generating functions, or, as Chan has done, by combining generating functions and commutation relations.[2] Often, however, the generation of these matrices can be the most difficult and tedious part of the problem. A well-known method which makes use of transformation theory can be used to greatly facilitate the computation.[3] An analysis of residual errors due to the truncation has been made and is described in the last section of this paper.

The method is applicable to almost any system; for example, the computation of $\exp(-\beta x^2)$ in the representation of the harmonic oscillator or of

$$\exp-(\alpha \sin^2\theta+\beta \sin^4\theta)$$

for a torsional oscillator in the $\exp(\pm im\theta)$ representation. In addition, the function need not be expressed in explicit form; all that is needed is to be able to supply the value of the function for a series of values of the variable. This makes the method quite attractive, since, in many cases, the function may exist only as a curve, graph, or table over the range spanned by the problem. The only limitation on the method is that the function be capable of being expressed as a convergent power series in the variable.

The method is as follows:

(I) Diagonalize X by a similarity transformation, i.e.,

$$\lambda = T^{-1}XT. \tag{1}$$

(II) Compute $V(\lambda_{ii})$.

(III) Transform back to the original representation,

$$V(X) = TV(\lambda)\,T^{-1}. \tag{2}$$

Step (I) above involves the diagonalization of X. This step finds the eigenvalues of $(X-\lambda)\Psi=0$ and would give a continuum if the matrix is of an order which is large without limit; however, since we are dealing with matrices of finite order there will be only a finite number of eigenvalues of X. For example, there would only be 50 if we are dealing with matrices of dimension 50×50. These discrete eigenvalues would be spread symmetrically about zero through the region of space spanned by the problem. It should be pointed out that Step (I) need be carried out only once, if the transformation and the eigenvalues are saved from problem to problem. Step (II) may be accomplished by generating $V(\lambda_{ii})$ by the use of an explicit expression, or alternately, the values of $V(\lambda_{ii})$ may be obtained by interpolation from a graph or table and entered into the program as a table. Step (III) in practice would probably not be carried out; what would be done is to transform the remaining operators of interest to the representation where X is diagonal and proceed from there in setting up the Hamiltonian matrix, finding expectation values, and so on. In this case, the final transformation to the energy representation is the product of two transformations; one is the inverse of the transformation which diagonalized X, and the other is the transformation which would diagonalize the Hamiltonian if it were set up in the original representation.

[1] S. I. Chan and D. Stelman, J. Mol. Spectry. **10**, 278 (1963).
[2] S. I. Chan and D. Stelman, J. Chem. Phys. **39**, 545 (1963).
[3] See, for example, B. Friedman, *Principles and Techniques of Applied Mathematics* (John Wiley & Sons, Inc., New York, 1956), Chap. 2.

TABLE I. The convergence of the elements of $\exp(-X^2)$ and $\sin X/X$ with the increase in the dimension of X.

Element	10	20	30	40	50	Exact
						[a]
$\langle 1 \mid \exp(-X^2) \mid 1\rangle$	0.99997762	0.99999999	0.99999999	1.00000000	1.00000000	1.00000000
$\langle 1 \mid \exp(-X^2) \mid 19\rangle$	···	−0.00063911	−0.00084106	−0.00084113	−0.00084113	−0.00084114
$\langle 10 \mid \exp(-X^2) \mid 10\rangle$	0.36142982	0.18839847	0.18547310	0.18547051	0.18547057	0.18547058
$\langle 20 \mid \exp(-X^2) \mid 20\rangle$	···	0.25391532	0.13953067	0.12866183	0.12858544	0.12858532
						[b]
$\langle 1 \mid \sin X/X \mid 1\rangle$	0.85562439	0.85562439	0.85562439	0.85562439	0.85562439	
$\langle 1 \mid \sin X/X \mid 19\rangle$	···	0.00000000	0.00000000	0.00000000	0.00000000	
$\langle 10 \mid \sin X/X \mid 10\rangle$	0.31260822	0.11767075	0.11767075	0.11767075	0.11767075	
$\langle 20 \mid \sin X/X \mid 20\rangle$	···	0.22671907	0.14343203	0.14343200	0.14343200	

[a] From Ref. 2. [b] Not available from other sources.

APPLICATION TO ANHARMONIC OSCILLATORS

We have used this method to compute the eigenvalues of the Hamiltonian $H=P^2+X^2+aX^4+\alpha\exp(-\beta X^2)$ for several values of a, α, and β using a 50×50 matrix for X in the harmonic oscillator representation. Comparison of the eigenvalues obtained by this method and those obtained by Chan *et al.* show that they are identical to ±1 in the sixth significant figure which is the limit of accuracy to which they are reported.[2,4] In addition, we have used this method to obtain the eigenvalues of the Hamiltonian

$$H=P^2+V/2(1-\cos2\theta)+\alpha\exp-\beta(1-\cos2\theta)$$

in the $\exp(\pm im\theta)$ representation. In this case, the evaluation of the matrix elements of the potential-energy function in the original representation is quite difficult and the solution of the Hamiltonian was greatly facilitated by the use of this method. As can be seen in the next section, the method works best if the function can be expanded in terms of small powers of X. As an extreme test, we have carried out the calculation of the energy levels of a particle in a box using 50 harmonic oscillator basis functions. The potential function that was used was defined by the relations $V=10^{10}$ for $|\lambda_i|>2$ and $V=0$ for $|\lambda_i|\leq2$, where λ_i is the ith eigenvalue of X. With this particular box width there are 10 eigenvalues of X which fall in the region where $V=0$; when the kinetic energy is added to form the Hamiltonian these 10 eigenvalues yield the first 10 energy levels of the particle in a box with the remaining eigenvalues of the Hamiltonian being of the order of 10^{10}. The first nine of these energy levels were accurate to $\pm0.1\%$; the tenth was good to 5%. The square well of width a can be represented as the limit of aX^m as m approaches infinity; since this involves high powers of X, it is unreasonable to expect the same high accuracy for this calculation as was obtained for the more conventional functions. It should also be noted that since the eigenvalues of X are discrete, all boxes with widths falling between the same two eigenvalues are defined exactly the same. In the above calculation where $a/2$ was nominally 2.0, the two eigenvalues of X which bracket this value are 1.995904 and 2.443489; the energies that were obtained correspond to $a/2$ equal to 2.389785.

ERROR ANALYSIS

Since a finite number of basis functions are employed instead of the complete infinite set, errors may be introduced into the matrices calculated in this way. However, the error may be eliminated in all the elements of interest by increasing the size of the basis set until the desired elements no longer change significantly. An example of this procedure is shown in Table I. Alternatively, in many cases it is possible to estimate the maximum error in a particular element arising from the truncation of the basis set. For example, suppose the function may be expanded in a Taylor's series in X as

$$V(X)=a_0+a_1X+a_2X^2+\cdots a_mX^m+R_m, \qquad (3)$$

where R_m is the remainder if the series is truncated after m terms. X is the X matrix in the harmonic oscillator representation and X^m is evaluated from X by matrix multiplication. In this representation, X has elements only of the type $\langle n \mid X \mid n\pm1\rangle$; that is, it has elements only one off the principal diagonal. Consequently, the $\langle n \mid X \mid n+1\rangle$ element will contribute to the (i,j)th element of X^m only if $(i+j)>2n-m$ for m even and $(i+j)>2n-m+1$ for m odd. As a result, there will be no error introduced into $\langle i \mid X^m \mid j\rangle$ by truncation of the basis set at the nth basis function so long as $(i+j)\leq2n+1-m$. It should be pointed out that the eigenvalues and associated eigenvectors of X are a function of the dimension of the X matrix,

[4] S. I. Chan, D. Stelman, and L. E. Thompson, J. Chem. Phys. 41, 2828 (1964).

and hence are incorrect in the sense that they differ from those that would be obtained if X were an infinite matrix. In particular, the eigenvectors are not the delta functions they would be if the set of basis functions were infinite. The eigenvectors which are obtained simply constitute a transformation that brings the finite X matrix to a diagonal form. Any effects that the difference in this transformation and that for the infinite basis might have on the calculation of each term in Eq. (3) are exactly cancelled by the inverse transformation of Step (III).

It may then be noted that in the Taylor's series expansion of the function in terms of an $n\times n$ X matrix, the X matrix is exact, the X^2 is exact except for the (n, n)th element, the X^3 except for the $(n-1, n)$th element, and so on. In general, the (i, j)th element of $V(X)$ is exact up to and including the $X^{2n+1-i-j}$ term; thus any error in the (i, j)th element must arise from terms higher than this. For example, starting with a 50×50 matrix for X, the $\langle 1 \mid V(X) \mid 1\rangle$ is exact up to and including the X^{99} term in the expansion, and the $\langle 30 \mid V(X) \mid 30\rangle$ is exact through the term X^{41}, etc.

Through the use of remainder theorems for series expansions, the contribution to the (i, j)th element of $V(X)$ due to truncation of the series at X^m can be estimated. A useful form of the remainder is given by

$$R_m \leq AX^{m+1}/(m+1)!, \tag{4}$$

where A is some number characteristic of the function in question. In our case, where we are concerned with the error in the (i, j)th element of the matrix expansion, the remainder is given by

$$(R)_{ij} \leq A(X^{2n+2-i-j})_{ij}/(2n+2-i-j)!. \tag{5}$$

It is possible to estimate the magnitude of the (i, j)th element of $X^{2n+2-i-j}$ as follows:

$$(X^{2n+2-i-j})_{ij} = \sum_{\cdots k,l\cdots} X_{ia}X_{ab}\cdots X_{kl}\cdots X_{zj}. \tag{6}$$

Since X has elements only one off the main diagonal, the number of nonzero terms in the sum is given by the binominal coefficient[5]

$$\binom{2n+2-i-j}{n+1-i} = \frac{(2n+2-i-j)!}{(n+1-i)!(n+1-j)!}. \tag{7}$$

Therefore,

$$(X^{2n+2-i-j})_{ij} \leq \frac{(2n+2-i-j)!}{(n+1-i)!(n+1-j)!}(\max X_{kl}) \tag{8}$$

where $\max X_{kl}$ is the largest X in the product and is the one having the largest index; this index is given by the expression

$$\tfrac{1}{2}[(i+j)+\text{power of } X] = \tfrac{1}{2}[(i+j)+2n+2-i-j] = n+1.$$

Hence the maximum X_{kl} is $X_{n,n+1}$. The matrix element of $X_{n,n+1}$ in the harmonic oscillator representation is given by $(n+1)^{\frac{1}{2}}$, so the remainder can be written

$$(R)_{ij} \leq \frac{A(n+1)^{(2n+2-i-j)/2}}{(n+1-i)!(n+1-j)!}. \tag{9}$$

Therefore, given a particular function, the maximum error in the (i, j)th element can be estimated.

For the case where the function of interest is of the form $V(\cos\theta)$ and the calculations are made in the $\exp(\pm im\theta)$ basis, the errors are much smaller. Since $\langle n \mid \cos\theta \mid n\pm 1\rangle = \frac{1}{2}$, and since these are the only nonzero elements of $\cos\theta$, the error expression for this case reduces to

$$(R)_{ij} \leq \frac{A(\frac{1}{2})^{2n+2-i-j}}{(n+1-i)!(n+1-j)!}. \tag{10}$$

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[5] *Note added in proof*: A more extensive and general theory of the X^n matrices in the harmonic oscillator basis is now available in a paper by J. F. Kilpatrick and R. L. Sass, J. Chem. Phys. **42**, 2581 (1965).