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A Quadrature Scheme for Matrix Elements between Numerical Wavefunctions

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A Gaussian-like quadrature scheme for evaluating matrix elements between one-dimensional numerical wavefunctions is developed. The abscissae are the zeroes of a high vibrational wavefunction for the potential curve concerned, and the weights are defined so that integrals over low-order wavefunctions are evaluated exactly. The method gives results sufficiently accurate for most purposes with only a few quadrature points, and is significantly more accurate than Gauss–Hermite quadrature. It should be particularly valuable in reactive and inelastic scattering problems.

There are many problems in molecular scattering and spectroscopy which require matrix elements of operators between numerically calculated vibrational wavefunctions. In the one-dimensional case, the wavefunctions themselves are usually calculated on an equally spaced radial mesh using Numerov integration and the Cooley method [1]. Traditionally, matrix elements are then calculated using Simpson's rule or the trapezoidal rule on the same radial mesh.

The traditional methods are quite expensive to apply, but present no difficulty when only a few matrix elements are required. However, this is not always the case. For example, in reactive and vibrationally inelastic scattering problems using realistic potentials, matrix elements of potential energy functions must be calculated many thousands of times, and it is not feasible to store all the vibrational wavefunctions on a sufficiently fine mesh to evaluate the integrals accurately using the traditional methods. It would also be computationally intractable to recalculate each vibrational wavefunction every time it is required. It is thus desirable to devise a quadrature scheme which allows matrix elements of an arbitrary function to be calculated using a small number of quadrature points. To this end, we wish to find optimum sets of points x_i and weights w_i such that a matrix element may be approximated

$$\int_0^\infty \psi_m(r)\, f(r)\, \psi_n(r)\, dr = \sum_{i=1}^{N} \psi_m(x_i)\, f(x_i)\, \psi_n(x_i)\, w_i. \tag{1}$$

The family of Gaussian quadratures enables a wide a range of integrals to be calculated accurately with very few integration points, but none of them is

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particularly suitable for integrands of the type found in vibrational matrix elements. If Gauss–Legendre quadrature is used the integrand must be arbitrarily assumed to be negligible beyond a specified range of r, while for Gauss–Laguerre and Gauss–Hermite quadrature an appropriate exponent parameter must be chosen. In neither case is the appropriate choice immediately obvious, although Gaussian quadratures have been used for such problems [2]. For the special case of matrix elements between orthogonal functions, Harris *et al.* [3] have introduced a useful quadrature scheme, and this has been shown to be related to generalised Gaussian quadrature [4]; however, the restriction to orthogonal functions prevents the application of this scheme to matrix elements between states of different angular momenta.

Although the usual Gaussian quadratures are not themselves appropriate for calculating vibrational matrix elements, the methods used in deriving them [5] suggest a useful approach to the development of a quadrature scheme with the required properties. Gaussian quadratures choose as abscissae for an N-point quadrature the zeroes of an Nth-order orthogonal polynomial. Vibrational wavefunctions are not actually orthogonal polynomials, but they share some of their important properties (notably orthogonality!). It therefore seems reasonable that the zeroes of a vibrational wavefunction $\psi_N(r)$ would be a suitable set of points for evaluating integrals over wavefunctions of the same potential with less than N nodes.

At first sight, one drawback of choosing the zeroes of $\psi_N(r)$ as abscissae appears to be that the number of points cannot be increased without increasing the range they span: the abscissae lie between the classical turning points at the energy E_N of $\psi_N(r)$. However, this is not an insuperable problem. A denser set of points may be obtained by using the zeroes of a wavefunction $\phi_M(r)$ corresponding to a reduced mass η different from the real reduced mass μ but using the same potential curve; the $\phi_m(r)$ will be referred to below as the *artificial* wavefunctions. Within the WKB approximation, multiplying the reduced mass by a factor f^2 gives a wavefunction $\phi_M(r)$ with $M = fN$ nodes at an energy ε_M which is approximately (neglecting zero-point corrections) the same as E_N. The zeroes of the artificial wavefunction may then be used to obtain abscissae for an M-point quadrature.

Once the quadrature points have been chosen, it is necessary to establish the optimum values for the weights w_i. If there are M such weights, we require M equations to determine them. Again by analogy with the Gaussian quadratures, which choose the weights such that integrals over the appropriate orthogonal polynomials are exact for order $n < 2N$, we define the weights by the requirement that all integrals over the artificial wavefunctions be exact for $m < M$. The M equations defining w_i are then

$$\sum_{i=1}^{M} \phi_m(x_i)\, w_i = \int \phi_m(r)\, dr, \qquad m = 0, \qquad M-1. \tag{2}$$

This is a matrix equation for the weights, which must be solved numerically in the present case. In our implementation, the $\phi_m(r)$ are first calculated on an equally

spaced mesh using the Cooley method, and the integrals on the right-hand side are calculated (once) by the trapezoidal rule. The abscissae x_i are determined by inverse linear interpolation to find the zeroes of $\phi_M(r)$; the linear approximation is adequate because the second derivative of a wavefunction is exactly zero at a node. Finally, the $\phi_m(x_i)$ are determined using 4-point Lagrangian interpolation on the mesh used to solve the eigenvalue problem, and the matrix equation is solved using standard techniques.

The most accurate quadrature is obtained using artificial wavefunctions calculated with reduced mass $\eta = 4\mu$. This is because all the quadrature points necessarily lie between the classical turning points at energy ε_M, and the quadrature implicitly assumes that outside this region the integrands behave in the same way as the functions used to optimise the weights. The artificial wavefunctions should therefore be chosen to have the same behaviour in the classically forbidden regions as the integrands of matrix elements. In a classically forbidden region, a wavefunction behaves approximately according to the WKB approximation [6]

$$\psi(r) \approx [p(r)]^{-1/2} \exp\left[-\int_a^r p(r)\, dr\right] \tag{3}$$

where

$$p(r) = [(2\mu/\hbar^2)[V(r) - E]]^{1/2} \tag{4}$$

and a is the classical turning point. Since the integrands of matrix elements involve a product of *two* wavefunctions corresponding to reduced mass μ, the artificial functions $\phi_m(r)$ at a given energy should ideally decay with an exponent twice that of the real wavefunctions. This is achieved if the artificial reduced mass is taken to be $\eta = 4\mu$, giving $M \approx 2N$ quadrature points between the classical turning points at energy $\varepsilon_M \approx E_N$. It was found empirically that an attempt to use more quadrature points than this did indeed give lower accuracy, and all calculations reported below used $\eta = 4\mu$.

Higher-order quadratures may be obtained by using the zeroes of higher-order artificial wavefunctions. This has the side effect of moving quadrature points into a region that was previously classically inaccessible, and thus results in a better representation of the exponential tails of integrands as well as of the oscillatory region. However, the order of quadrature available is limited by the fact that the artificial problem has a finite number of bound states.

Numerical Tests

This section presents three illustrative examples of the numerical results obtainable with the present method. The first is a numerically simple example designed to show the accuracy obtainable when the true results are known exactly, and the second demonstrates the generality of the method. The third is a test case taken from the

TABLE I

Errors in Overlap Integrals of Lennard–Jones Wavefunctions for a 33-Point Quadrature
(Quantities in Parentheses are Exponents)

v	0	1	2	3	4	5	6	7	8	9
0	5.0(−9)									
1	−1.9(−9)	1.4(−8)								
2	−6.5(−9)	−1.6(−8)	5.4(−8)							
3	7.8(−9)	6.8(−9)	−5.6(−8)	1.1(−7)						
4	−1.0(−9)	−8.0(−9)	3.1(−8)	−1.4(−7)	3.3(−7)					
5	−7.0(−9)	1.5(−8)	−4.7(−8)	2.0(−7)	−5.8(−7)	1.2(−6)				
6	1.3(−8)	−2.7(−8)	1.1(−7)	−3.8(−7)	1.0(−6)	−2.2(−6)	4.2(−6)			
7	−1.9(−8)	5.4(−8)	−2.2(−7)	6.8(−7)	−1.7(−6)	3.7(−6)	−7.2(−6)	1.3(−5)		
8	2.5(−8)	−9.7(−8)	3.7(−7)	−1.1(−6)	2.7(−6)	−6.0(−6)	1.2(−5)	−2.1(−5)	3.4(−5)	
9	−3.3(−8)	1.5(−7)	−5.7(−7)	1.7(−6)	−4.1(−6)	8.9(−6)	−1.8(−5)	3.1(−5)	−5.2(−5)	8.1(−5)

literature, and demonstrates the superiority of the present method over Gauss–Hermite quadrature.

For the first example, we take a Lennard–Jones 12-6 potential with the reduced depth parameter $B_z = 10{,}000$ [7]. This potential supports 24 bound levels. We seek a quadrature which is accurate for matrix elements between the lowest 10 or so levels, and choose a 33-point quadrature based on the wavefunctions $\phi_m(r)$ of an artificial problem with $\eta = 4\mu$ and $m \leqslant 33$. The quadrature points and weights were calculated using a radial mesh of 8000 points between $r/r_m = 0.65$ and 6. These quadrature points were then used to calculate overlap integrals between the true wavefunctions $\psi_n(r)$ for $n < 10$; these wavefunctions should of course be orthonormal. The errors in the calculated overlap integrals are given in Table I; the quadrature is accurate to one part in 10^8 for low vibrational quantum numbers and decreases to one part in 10^4 for the highest considered. It should be noted that the integrand for the off-diagonal element between $m = 8$ and $m = 9$ has 19 lobes, so that the accuracy achieved is quite impressive for a 33-point quadrature.

The second test case is taken from vibrationally inelastic scattering of H_2 molecules from rare gases, where the intermolecular potential can be expanded in powers of the diatom stretching coordinate $\xi = (r - r_0)/r_0$, with $r_0 = 0.7666438$ Å [8]; matrix elements of powers of ξ are thus required between all vibration–rotation

TABLE II

Points and Weights for 19-Point Quadrature in H_2 Model Problem (the Points Are the Zeroes of the $v = 19, j = 0$ Wavefunction)

x_i (Å)	w_i
0.5044269369	0.0877984211
0.5662262160	0.0459524097
0.6212003658	0.0619016068
0.6734756650	0.0442067301
0.7246506765	0.0575426752
0.7755982590	0.0448819010
0.8269023352	0.0575604055
0.8790200495	0.0468415126
0.9323562055	0.0599145585
0.9873104365	0.0499359387
1.0443114140	0.0643950022
1.1038542386	0.0544033097
1.1665463922	0.0716808388
1.2331783376	0.0609327971
1.3048430638	0.0838904589
1.3831658691	0.0712592550
1.4708127594	0.1081137890
1.5728782184	0.0911475502
1.7024620890	0.1955244456

levels of H_2. We consider matrix elements $\langle v, j|\xi^2|4, 0\rangle$, evaluated between wavefunctions calculated for the H_2 potential of Bishop and Shih [9]. The eigenfunctions were computed on a mesh of 8000 points between $r = 0.05$ and 8.0 Å. The points and weights for a 19-point quadrature are given in Table II, and the results of this quadrature scheme are compared with those of (essentially exact) trapezoidal integration on the 8000-point mesh in Table III for vibrational levels up to $v = 8$ and rotational levels up to $j = 8$. The quadrature is accurate to about one part in 10^4 for the lower vibrational levels and decreases to a few parts in 10^3 for the highest.

Another useful test case has been given by Truhlar and Onda [2] in demonstrating the efficiency of Gauss–Hermite quadrature for vibrational matrix elements. They considered off-diagonal matrix elements of the quadrupole moment function for N_2

$$Q(r) = -1.8919 + 2.7137(r - r_m) + 0.60733(r - r_m)^2 \text{ a.u.} \tag{5}$$

for a Morse potential chosen to model the lowest vibrational levels of N_2

$$V(r) = D[1 - \exp(-a(r - r_m))]^2 \tag{6}$$

TABLE III

Comparison of Matrix Elements $\langle v, j|\xi^2|4, 0\rangle$ for the H_2 Model Problem (the Upper Entry of Each Pair Is the Result of Trapezoidal Integration on an 8000-Point Mesh and the Lower Entry Is the 19-Point Quadrature Result)

v \ j	0	2	4	6	8
0	0.0020175	0.0017206	0.0010816	0.0002316	−0.0006107
	0.0020176	0.0017207	0.0010818	0.0002317	−0.0006107
1	−0.0107875	−0.0100482	−0.0082061	−0.0049263	0.0004687
	−0.0107876	−0.0100486	−0.0082067	−0.0049267	0.0004685
2	0.0370938	0.0391295	0.0443424	0.0538170	0.0690897
	0.0370940	0.0391304	0.0443441	0.0538185	0.0690902
3	0.0958679	0.1013887	0.1142172	0.1338712	0.1586262
	0.0958678	0.1013868	0.1142131	0.1338674	0.1586249
4	0.2169965	0.2187201	0.2213326	0.2214234	0.2138122
	0.2169961	0.2187238	0.2213412	0.2214319	0.2138155
5	0.1445831	0.1391126	0.1256051	0.1028711	0.0707376
	0.1445855	0.1391067	0.1255887	0.1028538	0.0707300
6	0.0473818	0.0417910	0.0297363	0.0138943	−0.0011420
	0.0473741	0.0417989	0.0297648	0.0139268	−0.0011264
7	−0.0274922	−0.0276111	−0.0269078	−0.0236360	−0.0167396
	−0.0274730	−0.0276189	−0.0269534	−0.0236925	−0.0167691
8	0.0142609	0.0153361	0.0172940	0.0187665	0.0178717
	0.0142199	0.0153391	0.0173615	0.0188582	0.0179234
9	−0.0078088	−0.0088080	−0.0109450	−0.0135306	−0.0151299
	−0.0077311	−0.0087978	−0.0110377	−0.0136690	−0.0152129

TABLE IV

Comparison of the Results of the Present Method with Those of Gauss–Hermite Quadrature

N	Q_{01}	Q_{02}	Q_{03}	Q_{06}	Q_{12}	Q_{16}	Q_{24}
(a) Present method							
3	1.6550233(−1)	−1.503714(−2)	−2.50737(−3)	1.565(−1)	2.2497608(−1)	1.224(−1)	5.10185(−1)
5	1.6542524(−1)	−6.990855(−3)	6.23781(−4)	1.920(−1)	2.3634992(−1)	−4.936(−1)	8.64232(−1)
7	1.6542419(−1)	−6.980964(−3)	5.45349(−4)	−3.172(−3)	2.3621218(−1)	−2.159(−3)	−3.26789(−2)
9	1.6542417(−1)	−6.980769(−3)	5.43844(−4)	−9.306(−6)	2.3620955(−1)	1.342(−4)	−1.76743(−2)
11	conv	−6.980764(−3)	5.43805(−4)	−1.369(−6)	2.3620948(−1)	2.236(−5)	−1.76421(−2)
13	conv	−6.980765(−3)	5.43803(−4)	−1.121(−6)	conv	1.898(−5)	−1.76410(−2)
15	conv	conv	5.43805(−4)	−1.112(−6)	conv	1.886(−5)	conv
17	conv	conv	conv	−1.111(−6)	conv	1.885(−5)	conv
19	conv	conv	conv	−1.108(−6)	conv	conv	conv
(b) Gauss–Hermite results of Truhlar and Onda							
3	1.6519(−1)	−7.7057(−3)	5.0479(−2)	−8.7704(−2)	3.3762(−1)	−1.0071	5.2347(−1)
5	1.6551(−1)	−6.9038(−3)	2.0919(−3)	1.5518(−2)	2.3922(−1)	1.7485(−2)	1.1343(−1)
7	1.6543(−1)	−6.9724(−3)	5.6752(−4)	8.7106(−4)	2.3626(−1)	8.0248(−3)	−1.0018(−2)
9	1.6542(−1)	−6.9805(−3)	5.4488(−4)	5.1481(−4)	2.3621(−1)	6.4198(−4)	−1.7220(−2)
11	conv	−6.9808(−3)	5.4385(−4)	2.3513(−6)	conv	5.7673(−5)	−1.7618(−2)
13	conv	conv	5.4381(−4)	−9.3914(−7)	conv	2.1145(−5)	−1.7640(−2)
15	conv	conv	5.4380(−4)	−1.1090(−6)	conv	1.8960(−5)	−1.7641(−2)
17	conv	conv	conv	−1.1122(−6)	conv	1.8851(−5)	conv
19	conv	conv	conv	−1.1174(−6)	conv	1.8848(−5)	conv
(c) Numerical integration on 8000-point mesh							
	1.6542417(−1)	−6.980765(−3)	5.43805(−4)	−1.110(−6)	2.3620948(−1)	1.885(−5)	−1.76410(−2)

Note. Quantities in parentheses are exponents. "Conv" indicates that the result is converged (i.e., the same as the previous entry). However, note that for most matrix elements more significant figures are quoted for the present method.

with $D = 0.363900$ a.u., $a = 1.422760$ a.u., and reduced mass $\mu = 12765.813$ a.u. Their results are compared with those of the present method in Table IV. It may be seen that the present method gives errors about an order of magnitude smaller than Gauss–Hermite quadrature for the same number of quadrature points.

The quadrature scheme presented here thus provides sufficient accuracy for most purposes, and involves very few multiplications for each matrix element evaluation. In normal use, the points and weights and the values of all wavefunctions at the quadrature points are stored in a look-up table, so that no recalculation of wavefunctions is necessary. The present scheme is expected to be particularly valuable in inelastic scattering problems, where matrix elements of complicated intermolecular potential functions are required. However, if the potential itself is expanded in terms of a series of polynomials, it may be simpler to store the matrix elements of the expansion functions than to apply the present quadrature scheme.

A Fortran program for evaluating points and weights for this quadrature scheme for an arbitrary potential curve is available from the author on request.

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