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ON THE CALCULATION OF MATRIX ELEMENTS BETWEEN POLYNOMIAL BASIS FUNCTIONS

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A method of evaluating matrix elements between polynomial basis functions is proposed involving the explicit expansion of the operator in terms of the polynomial. The method is shown to have several advantages over the direct evaluation of these matrix elements by Gaussian quadrature, including savings of up to a factor of 6^N for an N-dimensional integral. Application to the calculation of polyatomic rotation–vibration spectra is discussed.

In the calculation of molecular rotation–vibration spectra the nuclear motions are commonly carried by a basis of appropriate polynomial functions [1–11]. Matrix elements of these functions which cannot be evaluated analytically are computed using numerical quadrature:

$$\langle \boldsymbol{m}|V(\boldsymbol{x})|\boldsymbol{m}'\rangle \approx \sum_i V(\boldsymbol{x}_i)\prod_j \omega_{ij}P_{m_j}(q_{ij})P_{m'_j}(q_{ij}), \tag{1}$$

where q_{ij} and ω_{ij} are the ith point and weight for integration of the jth coordinate; P_{m_j} is a polynomial of order m_j, and V is some generalised potential, for example including a Watson term [1]. The N internal coordinates $\boldsymbol{x}$ are related to vibrational, e.g. normal, coordinates $\boldsymbol{q}$ by a transformation.

Usual practice [2–11] is to evaluate matrix element (1) using N one-dimensional Gaussian quadrature schemes [12], each based on the polynomial used as a basis in that coordinate. This method requires $\frac{1}{2}(K_j + m_j + m'_j + 1)$ quadrature points in each coordinate, where K_j is the highest order polynomial in q_j needed to give an accurate representation of V in the jth coordinate.

The expense of this procedure as the number of coordinates increases has led to severe compromises in the accuracy of the matrix elements used in calculating the vibrational levels of tetra-atomic, $N = 6$, molecules [9,10] and pessimism about the possibility of performing accurate ro-vibrational calculations on molecules larger than triatomic, $N = 3$ [1]. A way round this bottleneck is thus highly desirable.

In this note I propose an alternative method of evaluating matrix elements between polynomials basis functions. The method has several advantages while retaining the use of Gaussian quadrature. Only $K_j + 1$ integration points are required in each coordinate, independent of the size of the basis. This is the number of integration points proposed recently for the optimized quadrature scheme of Schwenke and Truhlar [13]. Furthermore, because the matrix elements can be constructed as products of simple one-dimensional integrals, the numerical integration can be performed outside the matrix element evaluation loops. Analysis of these integrals shows that they have the desired properties of (a) placing a bound on K_j for the exact evaluation of a matrix element between given basis functions and (b) leading to a substantial reduction in the number of terms that need to be computed compared to the direct evaluation of eq. (1).

Implicit in the choice of polynomial basis functions and Gaussian quadrature is the belief that the generalised potential can be represented as a

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polynomial expansion. Doing this explicitly gives

$$V(\boldsymbol{x}) = \sum_{\lambda} V_{\lambda} \prod_{j} P_{\lambda_j}(q_j). \tag{2}$$

The coefficients of the expansion, V_λ, can be obtained by multiplying by $\prod_j P_{l_j}(q_j) W(q_j)$, where W is the weighting function associated with polynomial P [14], and integrating over all $\boldsymbol{q}$. Using the orthonormality of the polynomials gives

$$\begin{aligned} V_l &= \int V(\boldsymbol{x}) \prod_j P_{l_j}(q_j) W(q_j) \mathrm{d}q, \\ &\approx \sum_i V(\boldsymbol{x}_i) \prod_j P_{l_j}(q_{ij}) \omega_{ij}. \end{aligned} \tag{3}$$

The second equality in (3) is exact if the number of Gaussian integration points in the jth coordinate is greater than l_j.

This method of expanding the potential function is standard and has even been used to represent directly ab initio data [11]. However, the advantage it yields in evaluating the matrix elements has not been exploited. With the generalised potential expanded in the form of eq. (2), the matrix elements are given by:

$$\langle \boldsymbol{m} | V(\boldsymbol{x}) | \boldsymbol{m}' \rangle = \sum_{\lambda} V_{\lambda} \prod_{j} \langle m_j \lambda_j m_j' \rangle, \tag{4}$$

where $\langle m\ \lambda\ m' \rangle$ is a one-dimensional integral over polynomial functions. For commonly occurring polynomials analytic solutions of this integral are available. For example, for Hermite polynomials of degree m and m' [15]:

$$\langle m\ \lambda\ m' \rangle = 2^2 \pi^{1/2} \frac{m!\ \lambda!\ m'!}{(s-m)!(s-\lambda)!(s-m')!}, \tag{5}$$
$$2s = m + \lambda + m',$$

and for Legendre polynomials of degree m and m' [3,16]:

$$\langle m\ \lambda\ m' \rangle = (-1)^k\, \delta_{kk'} [(2m+1)(2m'+1)]^{1/2} \times \begin{pmatrix} m & \lambda & m' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m & \lambda & m' \\ -k & 0 & k \end{pmatrix}, \tag{6}$$

where $k \neq 0$ generalises this integral to a basis of associated Legendre functions [3–8].

Integrals (5) and (6), in common with other polynomials whose range is symmetric about the origin, are only non-zero if:

(a) $2s = m + \lambda + m'$ is even,

(b) m, λ, m' obey the usual triangulate conditions such that $|m - m'| \leqslant \lambda \leqslant m + m'$.

This means that only alternate terms in each sum on the right of eq. (4) need be evaluated and only limited values of λ need to be included to obtain exact integrals. Thus, if M_j is the highest order basis function in coordinate j, it is only necessary to take $K_j = 2M_j$ terms in the potential expansion for that coordinate. This leads to the requirement of only $\frac{1}{6}(M_j+1)(M_j+2)(M_j+3)$ terms for the exact evaluation of all matrix elements in the jth coordinate. The same accuracy is achieved in the conventional procedure using $\frac{1}{4}M_j(M_j+1)(4M_j+1)$ terms in (1), for large M_j this requires 6 times as many terms in each coordinate. Of course in both procedures computational savings can be made by truncating expansion (2) and using $K_j < 2M_j$.

Laguerre polynomials are the only polynomials which have commonly been used in numerical ro-vibrational calculations [3–6,17] whose range is not symmetric about the origin. For associated Laguerre polynomials of degree m and m', and common index α, the integral in eq. (4) can be written [18]:

$$\langle m\ \lambda\ m' \rangle = \sum_k 2^{(2s-2k)} \times \frac{\Gamma(k+\alpha+1)}{(2s-2k)!(k-m)!(k-\lambda)!(k-m')!}, \tag{7}$$
$$2s = m + \lambda + m',$$

where the sum over k runs from the minimum of (m, λ, m') to the highest integer value of s and is zero unless condition (b) above is satisfied. In this case $\frac{1}{2}(M_j+1)(M_j+2)(M_j+3)$ terms in eq. (4) need to be evaluated for the exact evaluation of all matrix elements in the jth coordinate.

In summary, expanding the operator acting on polynomial basis functions in terms of those basis functions leads not only to exact limits on the number of Gaussian quadrature points required to evaluate matrix elements, but also to greatly truncated series to be evaluated. For exact N-dimensional integrals, the number of terms requiring evaluation can be reduced by a factor as great as 6^N. It is thus hoped that the improved speed and accuracy thus achieved will enhance the prospects of tractable ro-vibrational calculations on polyatomic molecules. A hybrid scheme for triatomic molecules, which uses a potential expansion in one coordinate, has already been shown to give satisfactory results [5,6,19].

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