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On the Computation of High Order Rys Quadrature Weights and Nodes

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Since its introduction in 1976,[1] the Rys Quadrature method has proven a very attractive method for evaluating electron repulsion integrals for calculations using Gaussian type orbitals. Since then, there have been considerable refinements of the method,[2,3] but at it's core, Gaussian weights and nodes are used to exactly evaluate using a numerical approach the transform integral. One of the powers of the Rys Quadrature method is the relative ease in evaluating integrals involving functions of high angular momentum, and Seward[2] can handle up to i functions ($\ell = 6$). This requires Rys quadrature of order $2\ell + 1 = 13$, yet when we tried to compute weights and nodes for higher order quadratures, we ran into numerical difficulties. In this work we report on the complete resolution of these numerical difficulties, and we have easily computed accurate quadrature weights and nodes up to order 101, thus now functions up to $\ell = 50$ can be handled, if desired. All calculations were carried out using 128-bit precision.

King and Dupuis very nicely described the calculation of Rys quadrature weights and nodes,[4] and we initially followed many of their procedures. However we used more sophisticated algorithms for computing the weights and nodes. In our first attempt, we computed the moments

$$\int_0^1 \exp(-Xt^2)t^{2n}dt = M_n(X) \qquad \text{Eq 1}$$

for the fixed parameter X in terms of the incomplete gamma function via the algorithm given by Press *et al.*[5] and then used them with the algorithm of Wheeler,[6] an efficient reformulation of the Sack and Donovan[7] method, to compute the weights and nodes. In order to compute a N point quadrature, the moments for $n = 0,1,\ldots,2N-1$ are required. However, even though we used 128-bit precision, we had difficulties in obtaining all positive nodes for the higher order quadratures.

In our second attempt, we computed the modified moments

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$$\int_{-1}^{1} \exp(-Xt^2)\pi_n^a(t)dt = M_n^a(X)$$

Eq 2

where π_n^a is an orthogonal polynomial. Note that now the integration interval has changed to be symmetric about the origin – this means that all odd n lead to zero modified moments, so for a N point quadrature, the moments for $n = 0,1, \ldots, 4N$ are required. In the limit $X \to 0$, the Rys polynomials become Legendre polynomials, and so for "small" X we used $a=L$, *i.e.,* the π_n^a are Legendre polynomials. In the limit $X \to \infty$, the Rys polynomials are proportional to Hermite polynomials of argument $t/\sqrt{X}$, and so for "large" X we used $a=H$, *i.e.,* the π_n^a are Hermite polynomials of argument $t/\sqrt{X}$. By means of these choices, rather than increasing in magnitude as n increases, the modified moments rapidly decrease as n increases. But the trade off is the modified moments must be evaluated numerically. Initially we tried Romberg integration,[5] whereby the integral was evaluated by the trapezoidal rule for step sizes $h, \frac{h}{2}, \frac{h}{3}, \frac{h}{5}, \ldots$ and then extrapolated to zero step size. This eliminated the non-positive node problem seen in the first attempt, and we moved onto the next stage of the development, namely the interpolation of the weights and nodes with respect to X.

We follow King and Dupuis[4] and interpolate using a Chebyshev expansion of the dependence of the weights and nodes on X. This turned out to be a critical factor in obtaining accurate high order weights and nodes. This is because the Chebyshev expansion coefficients are a very good indicator of numerical noise in the calculations, and we found that although our weights and nodes looked reasonable for individual X, they clearly showed unacceptable noise levels when looked at as a function of X. This lead to our next level of refinement. We experimented with several ways of carrying out the Chebyshev expansion and ended up dividing X into evenly space intervals of width unity.

In order to reduce the numerical noise, we tried increasing the accuracy of the computation of the modified moments, but found that the Romberg integration simply could not provide the required accuracy. The first step in improving the process was to switch from the trapezoidal rule to repeated 10 point Gauss-Legendre quadrature. We evaluated the integrals by dividing the range into $1,2,3,5, \ldots$ equal segments, integrating each segment by the 10 point quadrature rule, then stopped when two successive number of segments gave the same results to within an input error tolerance, typically 10^{-24}. This turned out to be much more efficient than the Romberg integration, but still was not able to deliver the required accuracy. The solution to this problem was to look at the integrand: the reason the desired accuracy was hard to obtain was that the integrand was highly oscillatory and thus there was significant cancellation between various regions. Thus, we then determined the nodes in the integrand and split up the integration range so that each range started and ended on a node, and included a node between the starting and ending range, if possible. This procedure worked very well. We determined the

nodes via bisection,[5] with the bisection search stopping when the node was determined to nearly machine precision (10^{-31}).

By means of this procedure, we could generate accurate weights and nodes for quadrature's up to $N = 18$ before unacceptable numerical noise again crept into the calculations. This time we attribute the problem to the fact that the modified moments for high order become so small that numerically they were similar to the odd modified moments that are all identically zero.

This then led to the final procedure. If one reads the discussion of algorithms in Ref. 5, a primary driver is numerical efficiency, with numerical stability being an important, but secondary concern. In the present application, numerical efficiency is not an important concern, since the quadrature weights will be computed only once. Thus, we will proceed as follows: we will directly determine the coefficients a_n and b_n in the recursion relation

$$R_{n+1}(t^2) = (t^2 - a_n)R_n(t^2) - b_n R_{n-1}(t^2)$$

Eq 3

by requiring

$$\int_0^\infty \exp(-Xt^2)\, R_{n+1}(t^2) R_m(t^2) dt = \langle R_{n+1} R_m \rangle = 0$$

Eq 4

for $m = n$ and $n - 1$ subject to the boundary conditions $R_{-1} = 0$ and $R_0 = 1$, where we imply the dependence of a_n and b_n on X. This is the procedure of Stieltjes,[5] and requires the evaluation of the integrals $\langle R_n t^2 R_{n-1} \rangle$, $\langle R_n t^2 R_n \rangle$, $\langle R_n R_n \rangle$, and $\langle R_{n-1} R_{n-1} \rangle$. These are evaluated using the repeated 10 point quadrature described above. Once the recursion coefficients are determined, we determine the nodes by root finding, using the intervals from the roots of the previous order polynomials as initial guesses to a several step bisection search followed by Newton-Raphson refinement. Since the functions are evaluated by recursion, the derivative required for the Newton-Raphson procedure is easily computed and thus we have all the required information for evaluating the quadrature weights via[5]

$$w_i = \frac{\langle R_{N-1} R_{N-1} \rangle}{R_{N-1}(t_i^2) R_N'(t_i^2)}$$

Eq 5

where t_i is one of the roots of R_N.

This method requires about $3N$ integrals for a N point quadrature, whereas the previous algorithm requires about $2N$ integrals, so is clearly less efficient, but it gives very good results, for the recursion coefficients are given as a simple ratio of integrals: $a_n = \langle R_n t^2 R_n \rangle / \langle R_n R_n \rangle$ and $b_n = \langle R_n t^2 R_{n-1} \rangle / \langle R_{n-1} R_{n-1} \rangle$. We have used

this method up to $N = 101$ with absolutely no sign of numerical noise at the 10^{-16} level.

It is instructive to compare the present method with that used by King and Dupuis.[4] The principle difference is they based their calculations on the moments of Eq 1, and used Schmidt orthogonalization to determine the Rys polynomials. Our procedure, in contrast, explicitly evaluated the integrals $\langle R_n t^2 R_{n-1} \rangle$, $\langle R_n t^2 R_n \rangle$, and $\langle R_n R_n \rangle$ at each step once R_n had been determined. This is exactly the difference between the Gram-Schmidt orthogonalization and Modified Gram-Schmidt orthogonalization,[8] and is the reason Modified Graham-Schmidt orthogonalization has such superior numerical stability compared to the original version.

We now address the issue of evaluating the quadrature weights and nodes in the large X limit. As mentioned previously, as $X \rightarrow \infty$, the Rys polynomials become scaled Hermite polynomials, thus the Rys quadrature weights and nodes can be computed from Gauss-Hermite quadrature weights and nodes. King and Dupuis[4] examined this transition carefully, and came up with a fitting procedure which enabled them to interpolate between the asymptotic limit and the X values used in the Chebyshev expansion. We have found that this smooth transition was present for low weights and nodes, w_i and t_i for $i \ll N$, but not for high weights and nodes, w_i and t_i for $i \approx N$. Thus for simplicity, we carried out the Chebyshev expansion until the asymptotic region where the Rys quadrature weights and nodes can be computed accurately from Gauss-Hermite quadrature weights and nodes. Compared to the algorithm of King and Dupuis,[4] our method requires more memory, but this is not an issue for modern computers.

We have every expectation that the developments reported herein will enable some very exciting new calculations in molecular electronic structure theory.

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